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Dynamic Polymers

Metallodynamers: Neutral Dynamic Metallosupramolecular Polymers Displaying Transformation of Mechanical and Optical Properties on Constitutional Exchange**

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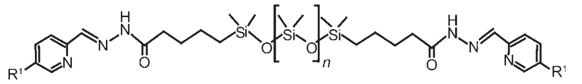
Supramolecular polymers,[1–5] which result from the connection of monomers through noncovalent interactions, are the subject of intense investigation. The lability of these connections means they are constitutional dynamic materials capable of constitutional variation through exchange and reshuffling of their components. A special class is formed by coordination polymers,[4,5] where the monomers are linked through metal-ion coordination. Dynamic polymers (dynamers)[3] are polymeric entities based on monomeric components connected through either labile noncovalent interactions or reversible covalent bonds.

Constitutional dynamics in supramolecular polymer chemistry offer possibilities to develop new functional materials.[3] Kinetically labile metal–ligand interactions are by nature dynamic, as the coordinative bonding may in principle dissociate and associate under the influence of the chemical and physical conditions of the environment. Most importantly, the dynamic metallosites in a coordination polymer may modify their constitution by exchanging and reshuffling their ligand components with another dynamic polymer, thereby resulting in new materials. Dynamic polymers based on reversible covalent bonds[3,6–8] or on hydrogen bonding[1–3] exhibit such exchange reactions in solution with or without a catalyst,[3,6–8] as well as in the neat polymer film state.[7b] Coordination polymers[4,5] are a special class of dynamers, they are dynamic metallosupramolecular entities (metallodynamers). While most of them are either cationic or anionic,[4,5] it would be of great interest to assemble monomeric ligands and metal ions in such a way that they generate neutral coordination polymers that present functional properties such as luminescence, magnetism, and diverse morphology which could ultimately be used to blend into conventional neutral polymers.

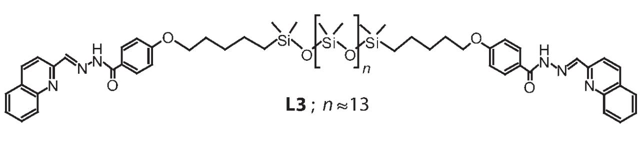
The present coordination polymers combine a particularly broad range of features: 1) a metallosupramolecular linkage through metal-ion coordination; 2) self-assembly of the connection sites from ligand subunits; 3) neutral/charged interchange through NH ionization or NR substitution with concomitant organophilic/hydrophilic behavior; 4) constitutional dynamics modulated by the nature of the coordination center, thus allowing reshuffling of the coordination site by exchange of either the ligand or metal ion; 5) orthogonal double dynamics involving both reversible coordination and reversible covalent bond (imine) formation; 6) control of the initiation and polymerization through either metal-ion coordination or imine condensation or both; and 7) dynamic modulation of functional features such as optical or mechanical properties through component recombination.

Neutral coordination centers may be obtained by using coordination subunits presenting ionizable sites. This is the case for the ionizable analogues of the tridentate terpyridine group[9] based on pyridyl hydrazone[10] and acylhydrazone[11] units that incorporate an NH site that undergoes acidification and facile ionization upon binding of a metal ion.[12] The coordination polymers **P1**–**P4**, which are connected through neutral coordination centers, have been obtained by a one-pot reaction of a bis-hydrazide **BH1** or **BH2** with a carboxaldehyde **Py2al**, **Py2alC$_{10}$**, or **Qui2al** and a Zn^{II} or Ni^{II} salt in 1:2:1 molar ratio in the presence of a mild base in MeOH/CH$_2$Cl$_2$ (1:1 v/v; Scheme 1).[13,14] The generation of **P1**–**P4** results from a self-assembly polymerization involving three processes: 1) subunit condensation to form the tridentate coordination moiety; 2) multiple metal–ligand coordination to connect the ligand monomers; and 3) simultaneous deprotonation to form neutral coordination centers.

The free ligands **L1**–**L3**[14] incorporated in polymers **P1**–**P4** were prepared independently and obtained as oily materials. The polymer **P2** was a gum, while **P1**, **P3**, and **P4** formed transparent free-standing films after evaporation of a solution in CH$_2$Cl$_2$ (Figure 1). Polymers **P1**–**P4** are highly soluble in common organic solvents—the polymeric dime-



L1: R^1=H; **L2**: R^1=CH$_3$(CH$_2$)$_9$O; $n\approx13$



L3; $n\approx13$

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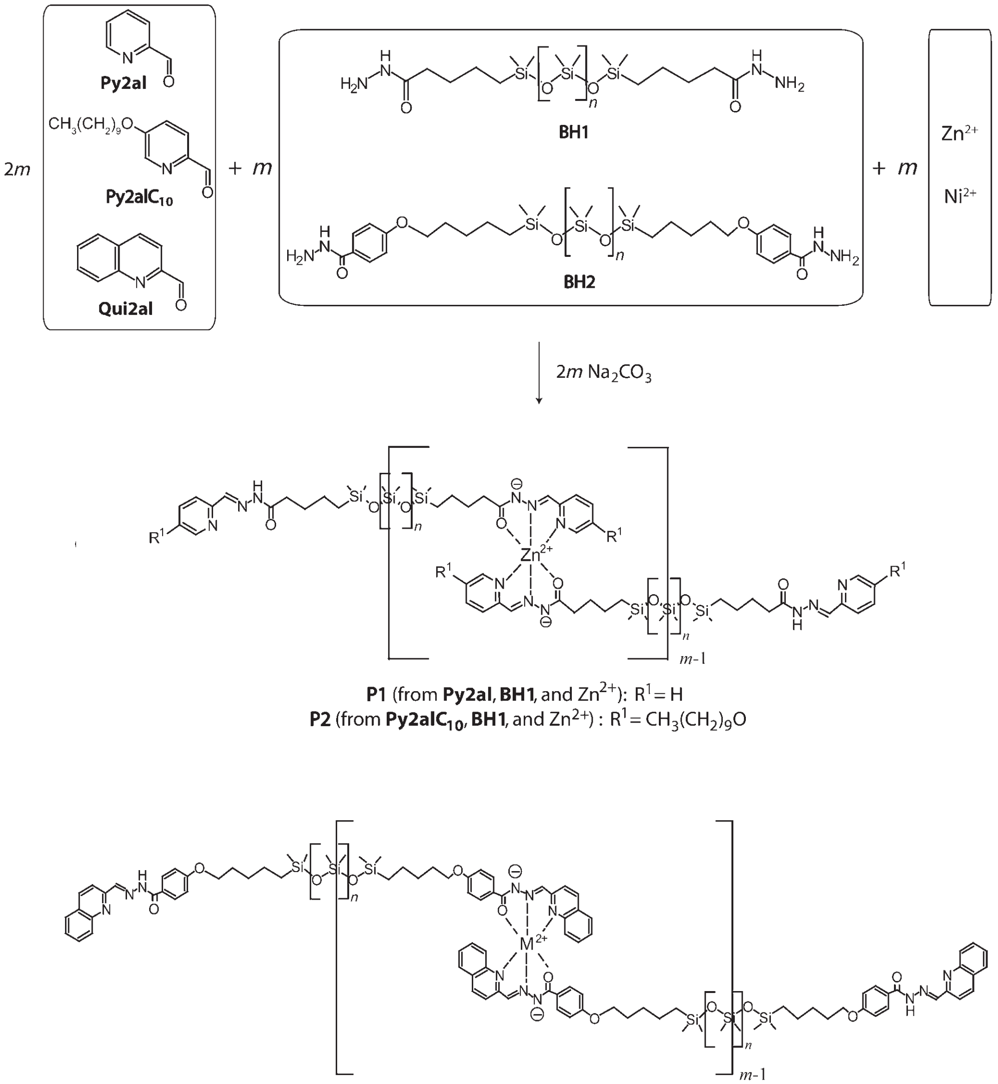


P1 (from **Py2al**, **BH1**, and Zn^{2+}): $R^1 = H$
P2 (from **Py2alC$_{10}$**, **BH1**, and Zn^{2+}) : $R^1 = CH_3(CH_2)_9O$

P3 (from **Qui2al**, **BH2**, and Zn^{2+})
P4 (from **Qui2al**, **BH2**, and Ni^{2+})

Scheme 1. Synthesis of the neutral zinc(II) (**P1**–**P3**) and nickel(II) (**P4**) metallosupramolecular polymers by self-assembly through multiple condensation-coordination-deprotonation reactions between a bishydrazide **BH1** or **BH2** (0.15 mmol), an aldehyde **Py2al**, **Py2alC$_{10}$**, or **Qui2al** (0.3 mmol), and $Zn(SO_4)\cdot 7H_2O$ or $Ni(BF_4)_2\cdot 6H_2O$ (0.15 mmol) in the presence of Na_2CO_3 (0.33 mmol) and anhydrous Na_2SO_4 (3 mmol) in $MeOH/CH_2Cl_2$ (1:1 v/v, 15.0 mL) at room temperature; $n \approx 13$ in **BH1** and **BH2**.

thylsiloxanes spacer was expected to offer sufficient solubility properties.

^{1}H NMR spectroscopy confirms the formation of the supramolecular polymers. The ^{1}H NMR signal of the non-coordinated imine protons in free ligands **L1**–**L3** were found at $\delta = 7.98$, 7.88, and 8.46 ppm, respectively, while the corresponding signals of the zinc-coordinated imine protons in **P1**, **P2**, and **P3** were at $\delta = 8.31$, 8.27, and 8.80 ppm. As expected, the ^{1}H NMR features of **P4** showed that it was a paramagnetic material as a result of the nickel(II) centers. The supramolecular polymers **P1**–**P4** become neutral after deprotonation of the two NH sites of the coordination centers, thus conferring also solubility in organic solvents of low polarity. The linear supramolecular polymer structures were confirmed by the observation of ^{1}H NMR signals of uncomplexed acylhydrazone end-groups. However, large macrocyclic complexes may in principle also form. Integration of the ^{1}H NMR signals for the imine CH or OCH_2 protons on free and complexed coordination sites gave an average molecular weight of 33000 g mol^{-1} (ca. 20 repeating units) for **P1**, 39000 g mol^{-1} (ca. 20 repeating units) for **P2**, and 45000 g mol^{-1} (ca. 23 repeating units) for **P3** (all at 25 mM in $CDCl_3$). ^{1}H NMR spectroscopy also revealed the dynamic behavior of the metallodynamers. By progressively increasing the concentration of **P1** from 3.125 mM to 12.5 mM in $CDCl_3$, its average molecular weight increased from 15000 to 25000 g mol^{-1}; further increasing the concentration to 50 mM gave an average molecular weight of 41000 g mol^{-1}. The optical spectrum of **P3** shows an emission band at 512 nm under excitation at 478 nm, as a result of the zinc(II) coordination center containing quinoline residues. On the other hand, **P1** and **P2** give only weakly fluorescence at 450 nm under excitation at 390 nm as they only contain pyridine groups, while **P4** is nonluminescent, probably because of a quenching of the emission by the nickel(II) ion.

The dynamic behavior of the present neutral metallosupramolecular polymers, as a result of the reversibility of the coordination bonds[15] (Scheme 2), was demonstrated by the occurrence of ligand exchange and recombination, as shown by ^{1}H NMR studies of polymer blends. Polymer blend **B1** was prepared by just stacking two neat films of the homopolymers **P2** and **P3** on top of one other at 50 °C for 24 h without solvent or catalyst. ^{1}H NMR analyses of the resulting material **B1** in $CDCl_3$ (ca. 50 mM) allowed identification of the various kinds of connections between the zinc ion and acylhydrazone ligands from the signals of the CH protons of the imine and aromatic groups between $\delta = 6.6$–8.9 ppm (Figure 2). Three

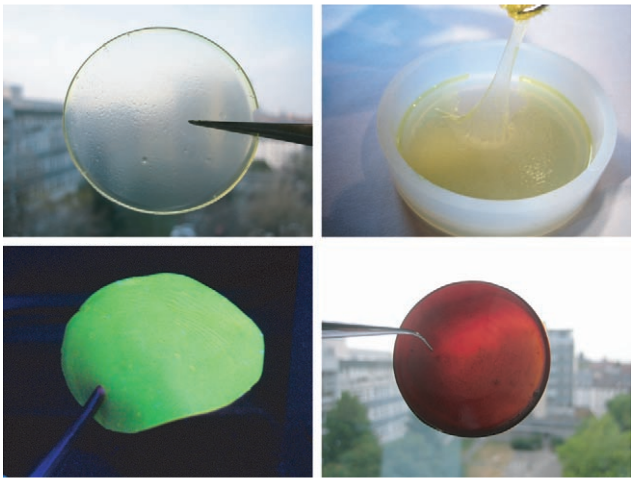


Figure 1. Photographs of neutral metallosupramolecular polymers: top left: zinc-based polymer film **P1**, top right: polymer gum **P2**, bottom left: luminescence property of **P3** under excitation at 365 nm, and bottom right: nickel-based polymer film **P4**.

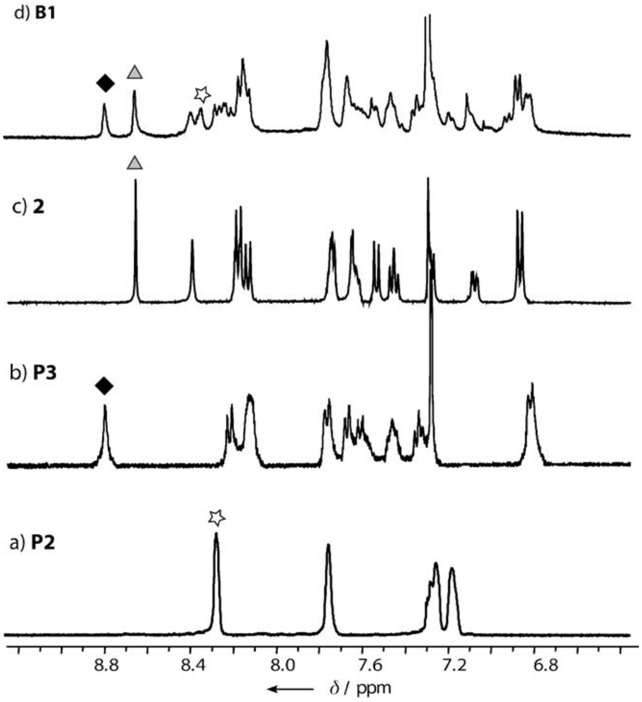
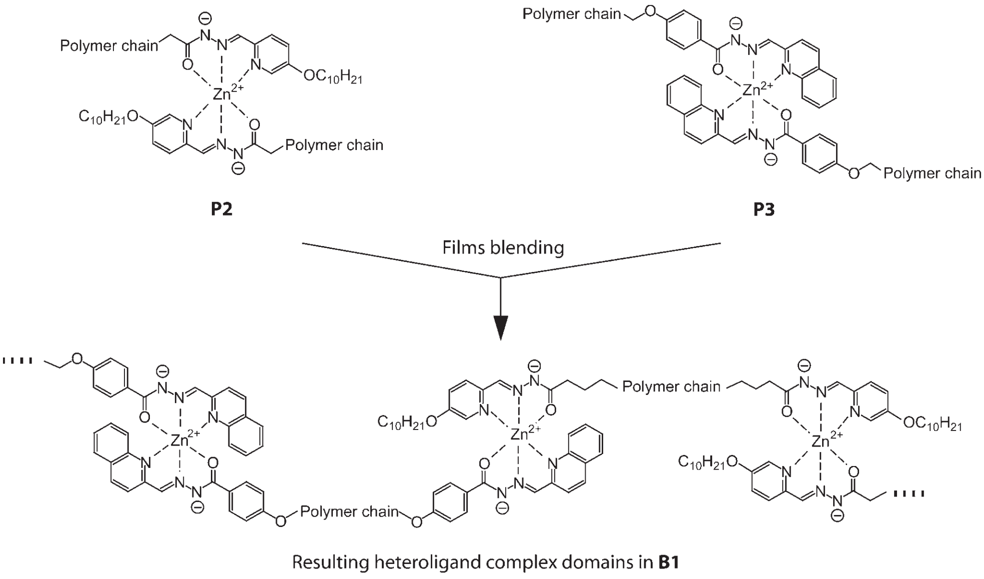


Figure 2. Part of the ^{1}H NMR spectra of polymers a) **P2**, b) **P3**, c) reference heteroligand complex **2**,[12] and d) blend **B1** in CDCl$_3$ (ca. 50 mM) showing the CH proton signals of the imine or aromatic entities. The symbols indicate the corresponding characteristic proton signals in the spectra of **B1** of the reference polymers and heterocomplex **2**.

characteristic imine proton signals were found, which were assigned to 1) **P2** (at 8.27 ppm); 2) **P3** (at $\delta = 8.80$ ppm); and most importantly, 3) a new imine signal (at $\delta = 8.60$ ppm), which corresponds to the formation of a heteroligand coordination center containing both a **Py2alC$_{10}$**- and a **Qui2al**-derived acylhydrazone unit. Confirmation of the latter was obtained by synthesizing such a heteroligand monomeric Zn$^{\text{II}}$ complex **2**[12] as a reference compound. These results indicated that blending of two different metallodynamers generated a new heteroligand metallosupramolecular polymer by ligand exchange even in the neat phase without a catalyst. The same random copolymer **P5** was also prepared as a reference material by treating the free ligands **L2** and **L3** with a Zn$^{\text{II}}$ salt in a 1:1:2 molar ratio. The proton signals found in **P5** were exactly the same as those in **B1**. Integration of the ^{1}H NMR signals for the CH$_2$(C=O) and CH(imine) protons of the free and complexed coordination sites gave an average molecular weight of approximately 28000 g mol^{-1} for **B1**, which is of the same order as the parent polymers **P2** and **P3**.



Scheme 2. Constitutional metal–ligand exchange reaction between metallodynamers (**P2** and **P3**)—evolution of the metallodynamers containing only the homoligand domains to the polymer blend **B1** containing the heteroligand domains.

Metal–ligand exchange in dynamers may be applied to the introduction of new functional properties. For example, mechanical properties can be easily transformed by component incorporation[7a] and polymer blends can be obtained by just stacking two different dynamers.[7b] Polymer blend **B2** was prepared from two stacked homopolymers **P2** and **P4** at 50 °C after 24 h in the absence of solvent or catalyst. **P2**, which contains two acylhydrazone-pyridine units, is a very weakly emissive gum while **P4** is a nonemissive film because of the presence of the paramagnetic Ni^{II} metal center. Spectrofluorimetric analyses of the exchanged polymer blend **B2** in $CHCl_3$ allowed identification of the dynamic exchange between the metal ions and acylhydrazone ligands by following its optical properties (Figure 3a). **B2** showed an excitation maximum at 478 nm and an emission maximum at 512 nm, which were fully matched to the excitation and emission spectra of homopolymer **P3**, thus indicating that crossover metal cation exchange had occurred during the preparation of the film of polymer blend. Figure 3b shows the optical features of **P2**, **P4**, **B2** (before exchange reaction), and **B2** (after exchange). Evolution of the mechanical properties of **B2** was also observed: the mechanical properties of polymer blend **B2**, which forms a soft film strong enough to stand by itself, lie between those of the parent gum **P2** and the hard film **P4** (Figure 3c).

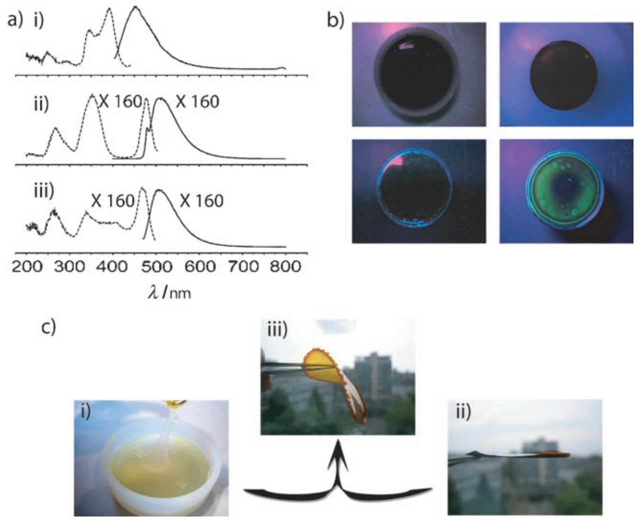


Figure 3. Evolution of the optical properties of the metallodynamers: a) Excitation (dashed line) and emission (solid line) spectra of: i) **P2**, ii) **P3**, and iii) polymer blend **B2** in $CHCl_3$ (0.2 mM). b) Photographs of the metallodynamer films taken under excitation at 365 nm: nonfluorescent films **P2** (top left), **P4** (top right), **B2** before the exchange reaction (bottom left); fluorescent film **B2** after exchange (bottom right). c) Evolution of the mechanical properties of the metallodynamers: i) **P2** (gum), ii) **P4** (hard film), and iii) blend **B2** (soft film).

The present results demonstrate that neutral metallosupramolecular polymers can be rationally designed and synthesized in a selective self-assembly manner. They also revealed that these coordination polymers are indeed dynamic (metallodynamers) capable of interchanging the elements (ligand components and metal ions) of their coordination centers as neat polymers even in the absence of solvent or catalyst. Thus, this allows the introduction of novel properties, a particularly attractive feature of such functional dynamic materials.

At the triple meeting point of metallosupramolecular chemistry, coordination chemistry, and polymer chemistry, coordination polymers are constitutional dynamic materials (metallodynamers) that offer a rich palette of entities and properties resulting from the blending of constitutional dynamic chemistry with pure and applied materials science.

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