



## Ferrocene-driven single-chain polymer compaction†

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**We introduce single-chain nanoparticles (SCNPs) exclusively folded by covalently bonded ferrocene units. Specifically, we demonstrate the ability of 2-ferrocenyl-1,10-phenanthroline to fuse single-chain collapse with the concomitant introduction of a donor functionality allowing the installation of a Pd-catalytic site, affording the first heterobimetallic ferrocene-functionalized SCNP.**

Over generations, nature has optimized the constitution and shape of macromolecular structures for catalytic applications.<sup>1</sup> One way of mimicking natural enzymes is the synthesis of so called single-chain nanoparticles (SCNPs), which are constructed from single polymer chains folded into compact nanoparticles *via* intramolecular linkages.<sup>2</sup> While nature's perfection regarding sequence, conformation and configuration has never been reached for synthetic polymers,<sup>2a,3</sup> controlled polymerization techniques<sup>4</sup> allow for the synthesis of functional polymers with low dispersity. SCNP folding can principally be achieved by covalent or non-covalent interactions. Covalent folding can, for instance, be induced by (photo)cyclo-additions,<sup>5</sup> alkene metatheses<sup>6</sup> or reactions of nucleophilic and electrophilic centers.<sup>7</sup> Non-covalent crosslinking is often based on the formation of intramolecular hydrogen bonds<sup>8</sup> or solvophobic interactions.<sup>9</sup> The folding units can either be randomly distributed along the polymer chain (repeat unit folding) or be located at predefined positions (selective point folding).<sup>2c</sup>

In recent years, our teams have focused on the incorporation of rare-earth and transition metal ions into SCNPs, leading to artificial metalloenzymes.<sup>10</sup> Thus, the adjustable characteristics of polymeric materials can be synergistically combined with the properties of metals.<sup>10,11</sup> Another intriguing feature of metals is their potential function as a redox switch when more than one stable oxidation state is accessible, although this is as yet largely unexplored in SCNP chemistry. One of the most famous redox switches is the organometallic sandwich complex ferrocene.<sup>12</sup> To the best of our knowledge, there are, up to now, only three examples of ferrocene-containing SCNPs reported in the literature.<sup>13</sup> However, all of them make use of non-covalent folding approaches, and single-chain collapse was either induced by the formation of hydrogen bonds or  $\beta$ -cyclodextrin insertion complexes.<sup>13</sup>

Herein, we close a critical gap in the literature, introducing ferrocene as a covalently bonded SCNP crosslinker. The direct polymerization of a ferrocene-containing monomer is however challenging, typically leading to polymers featuring low molar masses or high dispersities and often poor solubility.<sup>14</sup> Thus, we made use of a post-polymerization modification approach to incorporate ferrocene moieties into a polymer (Scheme 1). Specifically, a copolymer of styrene and chloromethyl styrene (Polymer **P1**) was synthesized using nitroxide-mediated polymerization (NMP).<sup>15</sup> While styrene constitutes the inert polymer backbone, the chlorobenzyl groups allow for simple and efficient post-polymerization modification by nucleophilic substitution. Size exclusion chromatography (SEC) in *N,N*-dimethylacetamide (DMAc) gave an indication of the number-averaged molar mass

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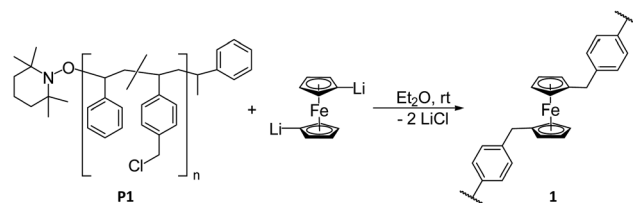
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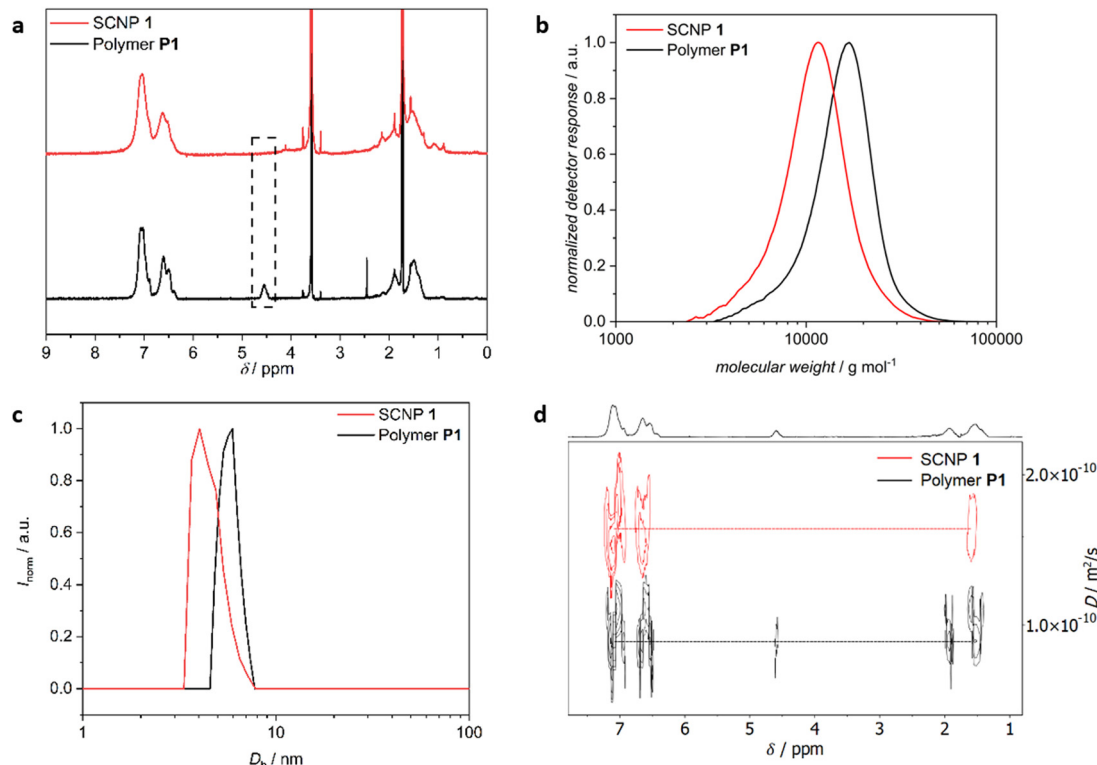
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Scheme 1 Synthesis of the ferrocene folded single chain nanoparticle **1**.





**Fig. 1** Stacked  $^1\text{H}$  NMR spectra (400 MHz, THF- $d_8$ , (a), the dashed box highlights the consumption of the chlorobenzyl functionality), number-averaged size distributions (SEC, DMAc, RI, PS cal., (b)), DLS data (mean diameter by number, THF, (c)) and stacked DOSY NMR spectra (400 MHz, THF- $d_8$ , (d)) of polymer **P1** (black) and SCNP **1** (red).

( $M_n$ ) of  $16,300 \text{ g mol}^{-1}$  and dispersity ( $\bar{D}$ ) of 1.15 (Fig. 1b). Using  $^1\text{H}$  NMR spectroscopy, a chloromethyl styrene content of 14% was determined (see ESI† Chapter 3.1), and this copolymer was used as a platform for all reactions described in the current contribution. The described polymer is a random copolymer; therefore, all SCNP folding reactions reported here follow the repeat unit approach.<sup>2c</sup> As poly(styrene-*co*-chloromethyl styrene) was selected as open-chain precursor, a nucleophilic ferrocene derivative is necessary to induce single-chain collapse. The most simple one fulfilling this prerequisites is 1,1'-dilithioferrocene, which was therefore prepared *in situ*, and a solution of polymer **P1** slowly added (Scheme 1).

$^1\text{H}$  NMR spectroscopy indicated the quantitative conversion of the initial polymer by disappearance of the resonance of the chlorobenzyl functionality at  $\delta = 4.68\text{--}4.38$  ppm (dashed box in Fig. 1a). All resonances of SCNP **1** are broadened compared to the corresponding ones of **P1**, which might result from a decrease in relaxation time caused by reduced chain-segment mobility upon single-chain collapse.<sup>10a,16</sup>

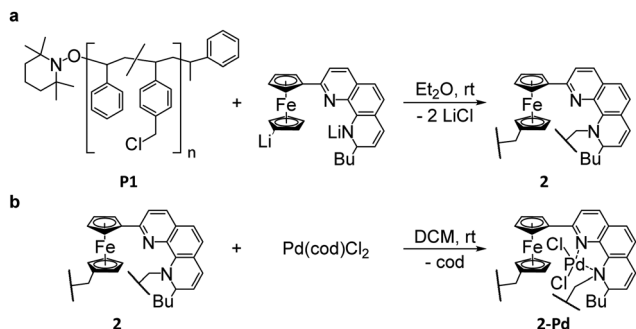
To ensure that only intramolecular crosslinking occurred, size sensitive techniques were employed. Fig. 1b shows the number-averaged size distributions of polymer **P1** as well as **1**, obtained *via* SEC in DMAc. The apparent peak molar mass ( $M_p$ ) of **1** is about  $5000 \text{ g mol}^{-1}$  lower than that of **P1**, indicating a decrease in the hydrodynamic volume, characteristic for SCNP compaction (see ESI† Fig. S7 for retention time plots).<sup>2a</sup>

To corroborate these findings, dynamic light scattering (DLS) measurements were conducted. Fig. 1c shows the number-averaged size distributions of polymer **P1** as well as **1**, recorded in tetrahydrofuran (THF). In line with the SEC results, a decrease in the hydrodynamic diameter  $D_h$  was observed for **1** ( $D_h = 4.68 \text{ nm}$ ) compared to **P1** ( $D_h = 5.69 \text{ nm}$ ), also indicative of SCNP folding. It is worth noting here that DLS data of particles with such small hydrodynamic diameters needs to be treated with caution as they only possess weak scattering abilities.<sup>2d</sup>

Additionally, SCNP folding was evidenced by diffusion-ordered NMR spectroscopy (DOSY). Fig. 1d shows the superimposed diffusion domains of **P1** and **1**, revealing an increase in the diffusion coefficient of **1** ( $D = 1.99 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ) compared to **P1** ( $D = 1.17 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ). According to the Stokes-Einstein equation, an increase in the diffusion coefficient goes in hand with a decrease in the hydrodynamic diameter, which again validates the assumed SCNP compaction.

For potential future applications of ferrocene-containing SCNPs, *e.g.* in redox-switchable catalysis, it is desirable to supplement them with an additional functionality. In an initial step, our interest focused on the combination of ferrocene with a second metal within an SCNP. To achieve this aim, two conceptually distinct approaches are conceivable. On the one hand, the synthesis of a terpolymer containing one comonomer for folding and another one for metal complexation





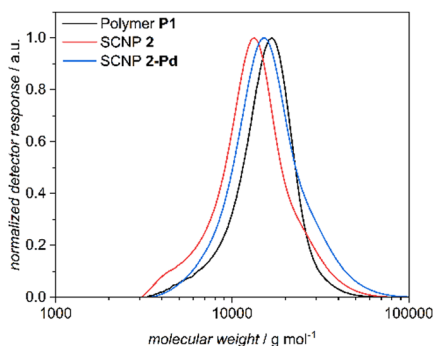
**Scheme 2** Synthesis of the 2-ferrocenyl-1,10-phenanthroline folded SCNP **2** (a) and Pd functionalization of SCNP **2** to obtain SCNP **2-Pd** (b) (simplified scheme).

is possible. On the other hand, SCNP folding and the introduction of a functional group for metal complexation can be combined in an elegant all-in-one approach using a donor-functionalized ferrocene derivative. One candidate for the latter approach is 2-ferrocenyl-1,10-phenanthroline.<sup>17</sup> Therefore, analogous to the reaction described above, 2-ferrocenyl-1,10-phenanthroline was lithiated (Scheme 2a). However, NMR studies show that the lithiation is not selective. Therefore, density functional theory (DFT) calculations were performed to deduce the most probable structure which is depicted in Scheme 2. The complexity of the reaction mixture obtained after lithiation of 2-ferrocenyl-1,10-phenanthroline and the determination of the most probable structure of the actual folding unit, based on DFT calculations, is discussed within the ESI† (Chapter 5.2).

The lithiated ferrocene derivative was subsequently reacted *in situ* with **P1** to obtain **2**. Again, <sup>1</sup>H NMR spectroscopy indicated the quantitative conversion of the chlorobenzyl functionalities ( $\delta = 4.68\text{--}4.38$  ppm) in **P1** (Fig. S5, ESI†).

SEC measurements in DMAc (Fig. 2) evidence that the apparent peak molar mass of **2** is decreased by approximately  $4000\text{ g mol}^{-1}$  compared to **P1**, indicating successful SCNP folding. Compared to **1**, the compaction is less pronounced.

DLS measurements in THF corroborated the SEC results. A hydrodynamic diameter of  $D_h = 5.35$  nm was observed for **2**. Compared to **P1** ( $D_h = 5.69$  nm), the compaction is still evident,



**Fig. 2** Number-averaged size distributions (SEC, DMAc, RI, PS cal.) of polymer **P1** (black), SCNP **2** (red) and SCNP **2-Pd** (blue).

however, it is less pronounced than that of **1** ( $D_h = 4.68$  nm). DOSY measurements gave a diffusion coefficient of  $D = 1.13 \cdot 10^{-10}\text{ m}^2\text{ s}^{-1}$ , similar to that of **P1** ( $D = 1.17 \cdot 10^{-10}\text{ m}^2\text{ s}^{-1}$ ).

SEC, DLS and DOSY clearly evidence SCNP compaction, however, it must be noted that **2** additionally contains an unidentified low molar mass impurity, as is evident from <sup>1</sup>H NMR spectroscopy and SEC measurements (Fig. S5 and S9, ESI†). Purification leads to interchain crosslinking, evidenced by SEC (Fig. S9, ESI†) and a drastic decrease in solubility.

To perform catalytic transformations, SCNP **2** needed to be supplemented with an additional metal. As important prerequisites, the metal must possess catalytic activity and should not undergo chemical reactions with either the SCNP crosslinker or the polymer backbone. To allow for future applications of the ferrocene redox switch, it is additionally necessary that the second metal does not interfere with oxidized ferrocenium moieties. One metal ion expected to fulfil these prerequisites is Pd(II). Therefore, SCNP **2** was reacted with [Pd(cod)Cl<sub>2</sub>] (cod = 1,5-cyclooctadiene) in a ligand substitution reaction to give SCNP **2-Pd** (Scheme 2b). Contrary to **2**, there is no evidence for the presence of a low molar mass impurity in the <sup>1</sup>H NMR spectrum (Fig. S6, ESI†) and the SEC chromatogram of **2-Pd**.

Relative to **2** and in agreement with the expectation that the Pd-functionalization leads to a less compact structure, and thus an increase in the hydrodynamic volume, an increase in the apparent molar mass is observed for **2-Pd** (Fig. 2).

DLS measurements of **2-Pd** in THF were conducted; however, only inconclusive data, with deviations larger than the actual estimated particle size, were obtained. Presumably, this is a consequence of absorption of the red laser light used in our DLS setup by the sample.

DOSY NMR corroborates the SEC findings as a slight increase in the diffusion coefficient of **2-Pd** ( $D = 1.35 \cdot 10^{-10}\text{ m}^2\text{ s}^{-1}$ ) compared to **P1** ( $D = 1.17 \cdot 10^{-10}\text{ m}^2\text{ s}^{-1}$ ) is observed.

Additionally, energy dispersive X-ray spectroscopy (EDX) measurements of **2-Pd** were conducted and unambiguously evidence that Pd is indeed present (Fig. S15 and Table S6, ESI†). Successful Pd functionalization was corroborated by UV/Vis measurements combined with time-dependent DFT (TDDFT) calculations (Fig. S16–S18 and ESI† Chapter 5.3) showing that an additional absorption present in the UV/Vis spectrum of **2-Pd**, which is absent in the corresponding spectrum of **2**, originates from the PdCl<sub>2</sub> moiety.

As a proof-of-principle illustrating that heterobimetallic ferrocene SCNPs are highly promising candidates for future applications, we assessed the ability of **2-Pd** to function as homogeneous catalyst. To avoid undesirable interferences with the ferrocene moieties, no redox step should be present in the catalytic cycle. One reaction fulfilling this prerequisite is the intramolecular hydroamination of the aminoalkyne 2,2-diphenyl-4-heptyn-1-amine displayed in Fig. S1 (ESI†), as it most probably proceeds *via* a mechanistic pathway in which Pd remains in the +II oxidation state.<sup>18</sup> The same reaction has already been used previously by our groups to demonstrate the catalytic activity of SCNPs.<sup>10f</sup> [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] is known to



be an efficient co-catalyst for hydroamination reactions.<sup>19</sup> The reaction progress was monitored by <sup>1</sup>H NMR spectroscopy (Fig. S1, ESI<sup>†</sup>), and virtually quantitative conversion of the substrate was achieved within three hours at 60 °C, compared to zero conversion to the desired product when only the cocatalyst is present (Fig. S2, ESI<sup>†</sup>).

In summary, we exploit ferrocene as a simple and efficient crosslinker to collapse individual polymer chains into compact single-chain nanoparticles (SCNPs). For the first time, this was solely achieved by covalently bonded ferrocene. SCNPs folding of poly(styrene-co-chloromethyl styrene) following the repeat unit approach was induced by *in situ* generated 1,1'-dilithioferrocene. Critically, we explored the ability of 2-ferrocenyl-1,10-phenanthroline to function as an elegant all-in-one SCNPs crosslinker, combining single-chain collapse with the concomitant introduction of a donor functionality allowing for subsequent metal functionalization. Pd(II) functionalization gave access to the first heterobimetallic ferrocene SCNPs, which proved to be an active catalyst for the intramolecular hydroamination of an aminoalkyne.

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## Conflicts of interest

There are no conflicts to declare.

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