Supplementary Material for: 

Hybrid Single-Chain Nanoparticles via Metal Induced Crosslinking of N-Donor Functionalized Polymer Chains

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1. Materials, Equipment and Methods

All air-sensitive operations were performed at a high vacuum line using Schlenk techniques. If not noted differently, chemicals were bought from Sigma. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from dry ethanol and dried in vacuo before use. Toluene and THF were passed through a PS-MD-4 solvent purification system (inert technology) for drying (<10 ppm H₂O). 4-Vinylpyridine was degassed, dried with CaH₂ over night and freshly distilled before use. n-Butyl acrylate was washed with NaOH (4 wt-%) and water, dried with CaCl₂ and freshly distilled before use. 4-Methoxybenzene was distilled before use. 1,4-Dioxane (Alfa Aesar) was dried with sodium/benzophenone and distilled before use. Ethyl 2-bromoisobutyrate (Ebib), tris(2-pyridylmethyl)amine (TPMA), tin(II) 2-ethylhexanoate, 2,5-dibromo-3,4-dinitrothiophene (TCI), phenylboronic acid (Alfa Aesar), d₄-THF (Deutero), PS standard (212 400 g mol⁻¹) Pd(PPh₃)₄, Pd(OAc)₂, Zn(BF₄)₂ (Alfa Aesar), NiCl₂, Cu(BF₄)₂, MgCl₂, CoCl₂ and FeCl₂ have been used as received. All polymers containing 4-vinylpyridine have been stabilized with small amounts of 2,6-di-tert-butyl-4-methylphenol.

Elemental analyses were performed with a Vario EL system (elementar). SEC measurements were carried out with a Waters 515 HPLC pump and a Knauer Smartline RI 2300 detector. For low molecular weight samples, 2 × 5 µm mixed-C and 1 PLgel 1000 Å column from Polymer Laboratories or 1 Ultrastyragel 100 Å, 2 × Ultrastyragel 200 Å from Waters and 1 Oligopore column from Polymer Laboratories were used. For high molecular weight samples, 4 × 20 µm mixed-A columns from Polymer Laboratories were used. THF with a flow rate of 1 mL/min at 25 °C was used as eluent. Molecular weights were obtained relative to poly(methyl metacrylate) calibration for molecular weights <12 000 g/mol and relative to polystyrene calibration for higher molecular weights. All molecular weights are referenced relative to poly(n-butyl acrylate) according to the universal calibration with Mark-Houwink coefficients given in literature (K₅₈ = 11.4·10⁻⁵ dL·g⁻¹, α₅₈ = 0.716, K₉₈ = 12.2·10⁻⁵ dL·g⁻¹ and α₉₈ = 0.700; K₂₈ = 7.56·10⁻⁵ dL·g⁻¹, α₂₈ = 0.731, K₇₈ = 6.47·10⁻⁵ dL·g⁻¹ and α₇₈ = 0.765). Dynamic light scattering measurements were performed with a ALV/CGS-3 (ALV) compact goniometer using a 22 mW HeNe Laser (1145P, JDS Uniphase) operating with vertically polarized light at λ₀ = 632.8 nm. Scattered light was detected with an ALV/HIGH QE Avalanche Photodiode. Intensity autocorrelation functions were recorded with an ALV-5000/EPP digital correlator. The hydrodynamic radii presented here were obtained from an inverse Laplace transformation using the regularized CONTIN algorithm with 150 grid points by the ALV-5000/EPP software version 3.0.2.5 from measurements at 90° scattering angle.

Diffusion coefficients have been transformed to Rᵣ assuming a logarithmic mass-weighting in all cases. NMR spectra have been recorded on a Bruker Avance 400 (Bruker Corporation) (400 MHz (¹H), 100 MHz (¹³C)) and Avance III 600 (600 MHz (¹H), 150 MHz (¹³C)) FT-NMR spectrometer. Chemical shifts are given in ppm relative to the residual solvent signal. Diffusion ordered NMR Spectroscopy (DOSY) data was recorded on the Bruker Avance III 600 spectrometer equipped with a broadband observed (BBO) probe with z-Gradient. The spectrometer was additionally provided with the NMR thermometer hardware (Bruker) that ensured highly stable temperature conditions. Initial calibration of the gradient strength G was conducted by means of a deuterium oxide sample containing H₂O-traces and was found to be 0.548 Tm⁻¹ for the BBO probe. The diffusion ordered spectra were performed in 3 mm NMR tubes (Wilmad 335) under calibrated (methanol thermometer) and carefully stabilized temperature conditions, i.e. T = 298±0.1 K. The probe head nitrogen gas flow was adjusted to 800 L/h. Optimized pulse repetition delays (d₁ = 10 s) were obtained from inversion-recovery experiments. Sample spinning was used in order to avoid convection. The applied
pulse sequence was the DOSY Oneshot experiment creating a series of 16 1-D spectra with squared increase of the gradient field strength from 10 to 80%. The intergradient delay (diffusion time) \( \Delta (\text{d20}) \) was set to 0.2 s. The corresponding length of the gradient pulse \( (\text{p30}; \delta/2) \) was adjusted to 3.0 ms (2.7 ms for \( \text{P3a-Cu} \)). Each single spectrum was processed with a line-broadening factor (LB) of 1.0 Hz. The DOSY data were analyzed with the DOSY Toolbox in order to calculate diffusion coefficients and generate the common DOSY plot. A viscosity of \( 0.501 \times 10^{-3} \text{ Pa·s} \) (25 °C) for \( d_8\text{-THF} \) has been used for the calculation of the hydrodynamic radii. Hydrodynamic radii were calibrated relative to a polystyrene standard \( (M_n = 212 \text{ 400 g mol}^{-1}, R_n = 14 \text{ nm}) \).
2. Free Radical Polymerization

A 50 mL round-bottom Schlenk flask equipped with a magnetic stirring bar was evacuated, heated and backfilled with nitrogen several times. The flask was charged with dry and degassed THF (15.0 mL), \( n \)-butyl acrylate (4.00 mL, 3.60 g, 0.03 mol) and the appropriate amount of 4-vinylpyridine. The flask was heated to 60 °C and the polymerization was started by addition of AIBN (0.5 mol-% vs. sum of monomers). The mixture was stirred at 60 °C for 24 h. The reaction mixture was cooled down and poured into methanol (200 mL). After 12 h at 4 °C, the resulting two phases were separated and the polymer dissolved in THF (15 mL) and precipitated in methanol (200 mL) again. After phase separation for 12 h at 4 °C, the polymer was isolated and roughly dried in vacuo. The polymer was dissolved in benzene (5 wt-%) and freeze-dried until complete removal of the solvents.
3. SCNP Formation of \( \text{P3}_a + \text{Cu(BF}_4\text{)}_2 \) Monitored by DOSY NMR

**Fig. S1** SCNP formation monitored via DOSY NMR upon addition of 0.5 eq Cu(BF\(_4\))\(_2\) (dissolved in d\(_8\)-THF, c = 1 mg/mL) to \( \text{P3}_a \) (dissolved in d\(_8\)-THF, c = 1 mg/mL). Grey: pure \( \text{P3}_a \), black: after addition of 0.5 eq Cu(BF\(_4\))\(_2\) (lines are guide to the eye).
4. Elemental Analysis

The copolymer-composition of P(BuA-co-4-VP) has been calculated from the elemental analysis according to:

\[
X_{4-VP} = \frac{w_N \cdot M_{BuA}}{n_{N,4-VP} \cdot M_N - w_N \cdot (M_{4-VP} - M_{BuA})}
\]

With \(X_{4-VP}\) = mol fraction of 4-vinylpyridine, \(w_N\) = mass percentage of nitrogen according to the elemental analysis of P(BuA-co-4-VP), \(M_{BuA}\) = molar mass of \(n\)-butyl acrylate, \(n_{N,4-VP}\) = number of nitrogen atoms of the monomer 4-vinylpyridine, \(M_N\) = molar mass of nitrogen, \(M_{4-VP}\) = molar mass of 4-vinylpyridine.
5. Overlap Concentration

Table ST1 Overlap concentration $c^*$ of the precursors $P3_a – P8_a$ (and control polymers $CP1_f, CP2_a$) calculated according to $c^* = \frac{3M_c}{4\pi N_A R^2}$.

<table>
<thead>
<tr>
<th>No.</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w/M_n$</th>
<th>$X$ (4-VP) (mol-%)</th>
<th>$c^*$ (mg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CP1_f$</td>
<td>82 000</td>
<td>3.13</td>
<td>-</td>
<td>28.9</td>
</tr>
<tr>
<td>$CP2_a$</td>
<td>12 100</td>
<td>1.20</td>
<td>-</td>
<td>59.5</td>
</tr>
<tr>
<td>$P3_a$</td>
<td>51 200</td>
<td>1.25</td>
<td>2.91</td>
<td>47.0</td>
</tr>
<tr>
<td>$P4_f$</td>
<td>69 700</td>
<td>4.37</td>
<td>9.10</td>
<td>27.7</td>
</tr>
<tr>
<td>$P5_a$</td>
<td>21 600</td>
<td>1.23</td>
<td>11.74</td>
<td>58.7</td>
</tr>
<tr>
<td>$P6_a$</td>
<td>13 300</td>
<td>1.50</td>
<td>13.75</td>
<td>65.4</td>
</tr>
<tr>
<td>$P7_f$</td>
<td>11 500</td>
<td>2.79</td>
<td>16.95</td>
<td>94.1</td>
</tr>
<tr>
<td>$P8_a$</td>
<td>5 700</td>
<td>2.21</td>
<td>21.81</td>
<td>-</td>
</tr>
</tbody>
</table>
6. Solvent Content of SCNPs

Table ST2 Solvent content\(^a\) (vol-%) of SCNPs obtained by addition of solutions of various metal salts to solutions of the polymers \(\text{P3}_a - \text{P7}_f\) and control experiments (\(\text{CP1}_f, \text{CP2}_a\)).

<table>
<thead>
<tr>
<th></th>
<th>CP1(_f)</th>
<th>CP2(_a)</th>
<th>P3(_a)</th>
<th>P4(_f)</th>
<th>P5(_a)</th>
<th>P6(_a)</th>
<th>P7(_f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ (\text{Cu(BF}_4\text{)}_2)</td>
<td>93</td>
<td>90</td>
<td>87</td>
<td>82</td>
<td>54</td>
<td>72</td>
<td>30</td>
</tr>
<tr>
<td>+ (\text{Pd(OAc)}_2)</td>
<td>91</td>
<td>89</td>
<td>87</td>
<td>90</td>
<td>64</td>
<td>80</td>
<td>40</td>
</tr>
<tr>
<td>+ (\text{Zn(BF}_4\text{)}_2)</td>
<td>93</td>
<td>93</td>
<td>86</td>
<td>91</td>
<td>54</td>
<td>82(^b)</td>
<td>56</td>
</tr>
<tr>
<td>+ (\text{NiCl}_2)</td>
<td>92</td>
<td>89</td>
<td>88</td>
<td>85</td>
<td>25</td>
<td>64</td>
<td>30</td>
</tr>
<tr>
<td>+ (\text{MgCl}_2)</td>
<td>89</td>
<td>77</td>
<td>84</td>
<td>82</td>
<td>25</td>
<td>54</td>
<td>30</td>
</tr>
<tr>
<td>+ (\text{CoCl}_2)</td>
<td>92</td>
<td>89</td>
<td>86</td>
<td>88</td>
<td>54</td>
<td>64</td>
<td>62</td>
</tr>
<tr>
<td>+ (\text{FeCl}_2)</td>
<td>94</td>
<td>90</td>
<td>83</td>
<td>89</td>
<td>85(^c)</td>
<td>64</td>
<td>-(^c)</td>
</tr>
</tbody>
</table>

\(^a\)Calcd. from \(R_h\) of SCNP and \(R_c\) of the compact globule. \(^b\)Aggregation visible in DLS. \(^c\)Oxidation occurred.
7. Calculations

Restricted and unrestricted density-functional theory (DFT)-calculations were carried out by using the Jaguar 9.1.013 software\(^8\) running on Linux 2.6.18-238.el5 SMP (x86_64) on five AMD Phenom II X6 1090T processor workstations (Beowulf-cluster) parallelized with OpenMPI. MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the LACVP* (Hay-Wadt effective core potential (ECP) basis on heavy atoms, N31G6* for all other atoms) basis set and with the hybrid B3LYP density functional. All calculated structures were proven to be true minima by the absence of imaginary frequencies. Spin contamination was below 1% for all calculated copper complexes \((S(S+1) = 0.75)\). Plots were obtained using Maestro 10.5.013, the graphical interface of Jaguar. Molecular Dynamics (MD) calculations have been performed with Chem3D 16.0.0.82 (PerkinElmer Informatics) on one AMD Phenom II X6 1090T processor workstation. The polymer structures have been preminimized to the nearest local minimum with the MM2 force field as input geometry. For the generation of the copper crosslinked input structures, the fully MD-equilibrated free polymer structure has been used. MM2-MD has been equilibrated for 2.5 ns at 300 K with a step interval of 1 fs. Heating has been performed at 1 kcal atom\(^{-1}\) ps\(^{-1}\). Beginning at 2.5 ns, snapshots were taken every 200 ps for a total run time of 5.3 ns. Snapshots were minimized on the MM2 force field to the nearest local minimum. Radii of gyration \((R_g)\) and solvent accessible surface areas \((A_{sa})\) have been calculated on the geometry of the minimized snapshots with VMD 1.9.2.\(^9\) Copper atoms have been removed before calculation of \(R_g\) if appropriate. Semi-empirical single-point energy (SPE) calculations have been performed with MOPAC2016 version 17.138W.\(^10\) MM2 optimized geometries of the snapshots have been taken as input structure and copper atoms have been removed before the calculation if appropriate. The PM7 method has been applied with localized molecular orbitals (LMO). The structures derived from the crosslinked geometry were slightly lower in energy (within the range of 1%), which obviously is physically not meaningful but can readily be explained by the MD/minimization (MM2) and single point calculation (PM7) on a different level of theory.
Fig. S2 Radius of gyration ($R_g$) of the free polymer chain (empty circles) (150 monomer units $n$-butyl acrylate and 30 monomer units 4-vinylpyridine randomly distributed), the copper cross linked chain with 5 (black circles) and 10 (black triangles) cross links. Snapshots have been taken after equilibration for 2.5 ns. $R_g$ has been calculated on the MM2 minimized snapshots and after subsequent removal of the copper atoms if appropriate.
Fig. S3. Heat of Formation ($\Delta H_f$) of the free polymer chain (150 monomer units $n$-butyl acrylate and 30 monomer units 4-vinylpyridine randomly distributed) calculated on the PM7 level of theory on the MM2 minimized snapshots of the MD simulation.

Fig. S4. Heat of Formation ($\Delta H_f$) of the copper cross linked polymer chain (5 cross links) calculated on the PM7 level of theory on the MM2 minimized snapshots of the MD simulation after removal of the copper atoms.
Fig. S5. Heat of Formation ($\Delta H_f$) of the copper cross linked polymer chain (10 cross links) calculated on the PM7 level of theory on the MM2 minimized snapshots of the MD simulation after removal of the copper atoms.
8. Polymer Characterization

**CP1f:**

*N*-content (%): 0.03

\[ M_n \text{ (rel. PS)}: 76\,700 \text{ g/mol}; M_w: 240\,400 \text{ g/mol} \]

\(^1\)H-NMR (CDCl\(_3\)):
CP2$_a$:

$N$-content (%): 0.02

$M_n$ (rel. PS): 11 490 g/mol; $M_w$: 13 740 g/mol

$^1$H-NMR (CDCl$_3$):
P3a:

N-content (%): 0.32

\[ M_n \text{ (rel. PS)}: 48 \text{ 160 g/mol; } M_w: 59 \text{ 970 g/mol} \]

\(^1\text{H-NMR (CDCl}_3\):
P4f:

N-content (%): 1.01

\[ M_n \text{ (rel. PS): 56 300 g/mol; } M_w: 285 314 \text{ g/mol} \]

\(^1\text{H-NMR (CDCl}_3\):
**PSₐ:**

N-content (%): 1.31

$M_n$ (rel. PS): 20450 g/mol; $M_w$: 25249 g/mol

$^1$H-NMR (CDCl₃):
P6\textsubscript{a}:

\( N \)-content (\%): 1.54

\[ \begin{array}{cccccccccccc}
0 & 5 & 10 & 15 & 20 & 25 & 30 & 35 & 40 & 45 & 50 \\
\end{array} \]

\[ \begin{array}{cccccccccccc}
mV & & & & & & & & & & \\
0 & 5 & 10 & 15 & 20 & 25 & 30 & 35 & 40 & 45 & 50 \\
\end{array} \]

\( t \) [min]

\( M_n \) (rel. PS): 12 690 g/mol; \( M_w \): 19 080 g/mol

\( ^1 \text{H}-\text{NMR} (\text{CDCl}_3) \):

\[ \text{ppm} \]

\[ \begin{array}{cccccccccccc}
8.5 & 8.0 & 7.5 & 7.0 & 6.5 & 6.0 & 5.5 & 5.0 & 4.5 & 4.0 & 3.5 & 3.0 & 2.5 & 2.0 & 1.5 & 1.0 \\
\end{array} \]
P7f:

N-content (%): 1.91

\[ M_n \text{ (rel. PS): 12 640 g/mol; } M_w: 35 220 g/mol \]

\(^1\)H-NMR (CDCl\(_3\)): 

![1H-NMR spectrum](image-url)
P8ₐ:

N-content (%): 2.48

\[ M_n \text{ (rel. PS): 5 430 g/mol; } M_w: 12 000 \text{ g/mol} \]

\[^1\text{H-NMR (CDCl}_3\text{):}\]
$N$-content (%): 2.80

$M_n$ (rel. PS): 1 880 g/mol; $M_w$: 4 550 g/mol
9. NMR Spectra of 3,4-Dinitro-2,5-diphenylthiophene (3)

$^{1}H$-NMR (CDCl$_3$)

$^{13}C$-NMR (CDCl$_3$)
$^1$H-NMR (d5-pyridine)

\[
\begin{align*}
&\text{S} \\
&\text{O}_2\text{N} \\
&\text{NO}_2
\end{align*}
\]

$^{13}$C-NMR (d5-pyridine)

$^{13}$C{[1H]} (100 MHz, nujol)
10. References