## Supporting Information

Realizing Shape and Size Control for the Synthesis of Coordination Polymer Nanoparticles templated by Diblock Copolymer Micelles

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#### 1. Characterization of the dBCPs

#### 1.1. NMR

**Figure S1.** <sup>1</sup>H NMR spectra of the five dBCPs SV-15 (A), SV-21 (B), SV-35 (C), SV-42 (D), and SV-61 (E) and an exemplary calculation for the composition of the dBCPs (F).



#### **1.2. GPC**

**Figure S2.** Apparent molecular weight distributions from GPC for the five dBCPs SV-15 (black), SV-21 (red), SV-35 (green), SV-42 (blue), and SV-61 (light blue) (PS calibration).



### 1.3. DSC

**Figure S3.** DSC measurements of the five dBCPs SV-15 (black), SV-21 (red), SV-35 (green), SV-42 (blue), and SV-61 (light blue) showing the glass transition temperature  $T_g$  of PS and P4VP at 109 °C and 157 °C, respectively.



# 1.4. DLS

**Figure S4.** DLS autocorrelation functions and intensity weighted hydrodynamic diameter distributions of the five dBCPs SV-15 (black), SV-21 (red), SV-35 (green), SV-42 (blue), and SV-61 (light blue).



#### **1.5. TEM and cryo-TEM**

**Figure S5**. TEM (left) and cryo-TEM (right) images of micelles formed by the dBCPs SV-15 (A, B), SV-21 (C, D), SV-35 (E, F), SV-42 (G, H) and SV-61 (I, J) in THF ( $c = 2.5 \text{ g L}^{-1}$ ). Only spherical micelles were observed for all neat dBCPs. The corresponding P4VP core size distributions are given on the right.



# 2. Characterization of the SCO CP-dBCP nanocomposites

# 2.1. TEM

**Figure S6.** TEM images of the samples **1a** (A), **1b** (B), **1c** (C), and **1d** (D). The core size distributions of the nanocomposite micelles are given in the insets.



**Figure S7.** TEM images of the samples **2a** (A), **2b** (B), **2c** (C), and **2d** (D). The core size distributions of the nanocomposite micelles are given in the insets.



**Figure S8.** TEM images of the samples **3a** (A), **3b** (B), **3c** (C), and **3d** (D). The core size distributions of the nanocomposite micelles are given in the insets.



**Figure S9.** TEM images of the samples **4a** (A), **4b** (B), **4c** (C), and **4d** (D). The core size distributions of the nanocomposite micelles are given in the insets.



**Figure S10.** TEM (left) and cryo-TEM (right) micrographs of the SCO CP-dBCP nanocomposite particles **1e** (A, B), **2e** (C, D), **3e** (E, F), and **4e** (G, H) that show spherical nanoparticles in both characterization methods. The size distributions are given on the right.



#### 2.2. DLS

Figure S11. DLS autocorrelation functions (left) and intensity weighted hydrodynamic diameter distributions (right) of the nanocomposite samples 1a (black), 1b (red), 1c (green), 1d (blue), and 1e (light blue).



Figure S12. DLS autocorrelation functions (left) and intensity weighted hydrodynamic diameter distributions (right) of the nanocomposite samples 2a (black), 2b (red), 2c (green), 2d (blue), and 2e (light blue).



Figure S13. DLS autocorrelation functions (left) and intensity weighted hydrodynamic diameter distributions (right) of the nanocomposite samples 3a (black), 3b (red), 3c (green), 3d (blue), and 3e (light blue).



Figure S14. DLS autocorrelation functions (left) and intensity weighted hydrodynamic diameter distributions (right) of the nanocomposite samples 4a (black), 4b (red), 4c (green), 4d (blue), and 4e (light blue).



Figure S15. DLS autocorrelation functions (left) and intensity weighted hydrodynamic diameter distributions (right) of the nanocomposite samples **5a** (black), **5b** (red), **5c** (green), **5d** (blue), and **5e** (light blue).



#### 2.3. IR

Figure S16. IR spectra of the samples 1a-e (A), 2a-e (B), 3a-e (C), 4a-e (D), and 5a-e (E).





4000 3500 3000 2500 2000 1500 1000 500 wavenumber v [cm<sup>-1</sup>]

# 2.4. Room temperature PXRD

**Figure S17.** Powder X-ray diffraction patterns of the samples **1a-e** (A), **2a-e** (B), **3a-e** (C), **4a-e** (D), and **5a-e** (E).



#### 2.5. Room temperature Mössbauer spectroscopy

**Figure S18.** Room temperature <sup>57</sup>Fe Mössbauer spectrum of the sample **1d** showing only one doublet characteristic for the CP. The spectrum is displayed in respect to  $\alpha$ -Fe as reference.



**Figure S19.** Room temperature <sup>57</sup>Fe Mössbauer spectrum of the samples **2c** and **2d** showing only one doublet characteristic for the CP. The spectrum is displayed in respect to  $\alpha$ -Fe as reference.



Figure S20. Room temperature <sup>57</sup>Fe Mössbauer spectrum of the samples 3c and 3d showing only one doublet characteristic for the CP. The spectrum is displayed in respect to  $\alpha$ -Fe as reference.



Figure S21. Room temperature <sup>57</sup>Fe Mössbauer spectrum of the samples 4c and 4d showing only one doublet characteristic for the CP. The spectrum is displayed in respect to  $\alpha$ -Fe as reference.



**Figure S22.** Room temperature <sup>57</sup>Fe Mössbauer spectrum of the samples **5c** and **5d** showing only one doublet characteristic for the CP. The spectrum is displayed in respect to  $\alpha$ -Fe as reference.



**Table S1.** Isomer shift  $\delta$ , quadrupole splitting  $\Delta E_Q$ , line width  $\Gamma_{\text{HWHM}}$ , and the area of the iron(II) HS sites of the samples **1d** and **2–5,c–d**.

Sample	δ [mm s <sup>-1</sup> ]	$\Delta E_Q$ [mm s <sup>-1</sup> ]	$\Gamma_{\rm HWHM}$ [mm s <sup>-1</sup> ]	Area [%]
1d	0.937(6)	2.177(13)	0.193(10)	100
2c	0.951(10)	2.16(2)	0.191(15)	100
2d	0.962(17)	2.20(3)	0.20(3)	100
3c	0.940(7)	2.158(13)	0.176(10)	100
3d	0.944(6)	2.157(11)	0.173(9)	100
4c	0.940(9)	2.151(18)	0.216(14)	100
4d	0.934(7)	2.186(15)	0.184(11)	100
5c	0.939(5)	2.16(10)	0.160(7)	100
5d	0.930(6)	2.166(12)	0.186(10)	100

#### 2.6. SQUID magnetometry

**Figure S23.** Magnetic susceptibility data for the samples **1c** (left), **1d** (middle), and **1e** (right) given as  $\chi_M T$  vs. *T* plot measured in sweep (measurement 1-5) and settle mode (measurement 6) in the whole measured temperature range from 50 K to 400 K.



**Figure S24.** Magnetic susceptibility data for the samples **2c** (left), **2d** (middle), and **2e** (right) given as  $\chi_M T$  vs. *T* plot measured in sweep (measurement 1-5) and settle mode (measurement 6) in the whole measured temperature range from 50 K to 400 K.



**Figure S25.** Magnetic susceptibility data for the samples **3c** (left), **3d** (middle), and **3e** (right) given as  $\chi_M T$  vs. *T* plot measured in sweep (measurement 1-5) and settle mode (measurement 6) in the whole measured temperature range from 50 K to 400 K.



**Figure S26.** Magnetic susceptibility data for the samples **4c** (left), **4d** (middle), and **4e** (right) given as  $\chi_M T$  vs. *T* plot measured in sweep (measurement 1-5) and settle mode (measurement 6) in the whole measured temperature range from 50 K to 400 K.



**Figure S27.** Magnetic susceptibility data for the samples **5c** (left), **5d** (middle), and **5e** (right) given as  $\chi_M T$  vs. *T* plot measured in sweep (measurement 1-5) and settle mode (measurement 6) in the whole measured temperature range from 50 K to 400 K.



**Table S2.** Summary of the cooling and heating cycles and the data derived from the magnetic susceptibility measurements for the samples 1–5e, showing the transition temperatures  $T_{1/2}\downarrow$  and  $T_{1/2}\uparrow$ , the hysteresis width, the  $\chi_M T$  value at 50 K, and the  $\gamma_{HS}$  value at 50 K. The results for 1e and 5e are given in the main manuscript.

Sample	Temperature range [K]	Mode	<i>T</i> <sub>1/2</sub> ↓ [K]	<i>T</i> <sub>1/2</sub> ↑ [K]	Hysteresis width [K]	<i>χ</i> <sub>M</sub> <i>T</i> at 50 K [cm³Kmol⁻¹]	γ <sub>HS</sub> [%]
	300-50-370 <sup>a)</sup>		160	166	6	1.71	53
	370-50-380 <sup>b)</sup>		171	181	10	1.74	54
	380-50-400 <sup>c)</sup>	sweep	186	201	15	1.63	50
1e	400-50-400 <sup>d)</sup>		199	216	17	1.41	43
	400-50-300 <sup>e)</sup>		204	222	18	1.18	36
	300-50-300 <sup>f)</sup>	settle	208	221	13	0.97	30
	300-50-370 <sup>a)</sup>		163	172	9	1.78	55
	370-50-380 <sup>b)</sup>		170	182	12	1.79	55
20	380-50-400 <sup>c)</sup>	sweep	185	200	15	1.60	49
Ze	400-50-400 <sup>d)</sup>		201	216	15	1.26	39
	400-50-300 <sup>e)</sup>		209	225	16	0.98	30
	300-50-300 <sup>f)</sup>	settle	212	223	11	0.85	26
	300-50-370 <sup>a)</sup>		162	167	5	1.76	54
	370-50-380 <sup>b)</sup>		172	186	14	1.81	56
2-	380-50-400 <sup>c)</sup>	sweep	189	205	16	1.57	48
36	400-50-400 <sup>d)</sup>		200	216	16	1.26	39
	400-50-300 <sup>e)</sup>		205	222	17	1.05	32
	300-50-300 <sup>f)</sup>	settle	208	220	12	0.87	27
	300-50-370 <sup>a)</sup>		164	170	6	1.79	55
	370-50-380 <sup>b)</sup>		174	193	19	1.82	56
40	380-50-400 <sup>c)</sup>	sweep	193	212	19	1.47	45
40	400-50-400 <sup>d)</sup>		202	220	18	1.10	34
	400-50-300 <sup>e)</sup>		206	224	18	0.92	28
	300-50-300 <sup>f)</sup>	settle	209	222	13	0.69	21
	300-50-370 <sup>a)</sup>		169	174	5	1.61	50
	370-50-380 <sup>b)</sup>		183	210	27	1.42	44
50	380-50-400 <sup>c)</sup>	sweep	195	218	23	1.09	34
Je	400-50-400 <sup>d)</sup>		203	223	20	0.77	24
	400-50-300 <sup>e)</sup>		207	226	19	0.62	19
	300-50-300 <sup>f)</sup>	settle	211	224	13	0.47	14

See **Figure 4 and Figures S23-S27**, respectively, <sup>a)</sup> curve 1; <sup>b)</sup> curve 2; <sup>c)</sup> curve 3; <sup>d)</sup> curve 4; <sup>e)</sup> curve 5; <sup>f)</sup> curve 6.

# 2.7. Temperature-dependent PXRD

**Figure S28.** Temperature-dependent powder X-ray diffraction patterns of the samples **1e** (A), **2e** (B), **3e** (C), **4e** (D), and **5e** (E) at five different temperatures and their comparison with the bulk material [FeL(bipy)]<sub>n</sub>.



#### 2.7. Temperature-dependent Mössbauer spectroscopy

**Figure S29.** Selected example spectra of the temperature-dependent zero-field <sup>57</sup>Fe Mössbauer measurements on compounds **5e** (as-synthesized, left panel) and **5e\*** (after thermal annealing at T = 393 K for 3 h under nitrogen atmosphere, right panel). The measurements were carried out starting with T = 300 K upon zero-field cooling to  $T = 250^{\#}$ ,  $215^{\#}$ , 175,  $135^{\#}$  and 80 K (<sup>#</sup>: not shown), followed by a corresponding zero-field warming sequence from T = 80 back to 300 K. Symbols: Experimental data. Lines: The spectra were analyzed with one or two doublets of Lorentzian lines, respectively. The colored lines represents the individual sub-spectra of the fit, which are attributed to Fe(II) low-spin (green) and Fe(II) high-spin sites (red), respectively (see main text). The parameters of the fits are summarized in **Table S3**.



**Table S3.** Summary of Mössbauer parameters determined for compounds **5e** (as-synthesized) and **5e**\* (after thermal annealing at T = 393 K for 3 h under nitrogen atmosphere) by fits with one or two doublets of Lorentzian lines, respectively, with isomer shift  $\delta$ , quadrupole splitting  $\Delta E_Q$  and Lorentzian line width  $\Gamma_{\text{FWHM}}$  (full width at half maximum).  $A_2/A_1$  describes the relative intensities of the two corresponding lines of a given doublet, while AREA quotes the relative (integral) intensities of the individual doublets. The measurements were carried out starting with T = 300 K upon zero-field cooling to T = 250, 215, 175, 135 and 80 K, followed by a corresponding zero-field warming sequence from T = 80 back to 300 K.

<i>T</i> (K)	$\delta$ <sup>a)</sup> [mm s <sup>-1</sup> ]	$\Delta E_Q$ [mm s <sup>-1</sup> ]	Γ <sub>FWHM</sub> [mm s <sup>-1</sup> ]	$A_2/A_1^{\ \rm b)}$	AREA [%]
300	0.944(2)	2.212(4)	0.264(5)	1.07(2)	85.0
	0.389(15)	1.007(31)	0.301(32)	1*	15.0
250	0.978(5)	2.221(12)	0.267(4)	1.05(2)	83.1
	0.412(29)	1.047(63)	0.310(27)	1*	16.9
215	1.008(2)	2.216(3)	0.287(3)	1.03(2)	83.9
	0.404(5)	1.165(5)	0.249(16)	1*	16.1
175	0.994(2)	2.297(3)	0.360(5)	0.98(1)	68.8
	0.500(3)	1.050(6)	0.314(8)	1*	31.2
135	0.996(2)	2.364(3)	0.311(5)	0.99(2)	48.3
	0.502(2)	1.120(3)	0.310(4)	1*	51.7
80	1.015(1)	2.376(2)	0.278(4)	1.03(2)	43.7
	0.508(1)	1.134(3)	0.284(3)	1*	56.3
135	0.993(2)	2.356(4)	0.299(6)	0.96(2)	47.3
	0.501(2)	1.122(4)	0.306(5)	1*	52.7
175	1.001(1)	2.326(3)	0.281(4)	1.02(2)	61.1
	0.493(3)	1.104(5)	0.275(8)	1*	38.9
215	0.997(2)	2.273(3)	0.300(3)	1.00(1)	79.3
	0.477(3)	1.018(9)	0.281(11)	1*	20.7
250	0.991(2)	2.221(4)	0.348(4)	1.00(1)	88.4
	0.358(9)	1.110(17)	0.282(26)	1*	11.6
300	0.945(1)	2.229(3)	0.384(5)	1.00(1)	87.9
	0.462(12)	0.879(20)	0.348(29)	1*	12.1

Before thermal annealing (as-synthesized)

Values marked with an asterisk (\*) were fixed in the fit. **a**): Isomer shifts ( $\delta$ ) were specified relative to metallic iron at T = 300 K, but were not corrected in terms of the second-order Doppler shift. **b**): In case of polycrystalline powders with random orientations of the crystallites, the expectation value of this parameter is  $A_2/A_1 = 1$ .<sup>[1]</sup> Deviations from this value are attributed to the presence of marginal texture effects due to partial orientations of crystallites on compacting the powder in the sample containment.

<i>T</i> (K)	$\delta$ <sup>a)</sup> [mm s <sup>-1</sup> ]	$\Delta E_Q$ [mm s <sup>-1</sup> ]	Г <sub>FWHM</sub> [mm s <sup>-1</sup> ]	$A_2/A_1^{\ \  m b)}$	AREA [%]
300	0.955(1)	2.232(3)	0.272(4)	1.02(1)	100
	-	-	-	-	-
250	0.989(1)	2.252(3)	0.280(4)	1.00(1)	100
	-	-	-	-	-
215	1.009(3)	2.270(6)	0.284(5)	1.02(2)	84.1
	0.420(12)	1.179(27)	0.267(25)	1*	15.9
175	0.968(3)	2.394(5)	0.285(7)	1.00(3)	42.8
	0.459(2)	1.147(4)	0.276(5)	1*	57.2
135	0.977(2)	2.438(4)	0.246(6)	0.99(2)	31.1
	0.462(1)	1.165(2)	0.279(3)	1*	68.9
80	0.994(3)	2.437(4)	0.258(6)	0.93(3)	29.8
	0.466(1)	1.154(2)	0.287(3)	1*	70.2
135	0.978(3)	2.442(6)	0.253(8)	1.02(4)	29.4
	0.457(2)	1.175(3)	0.282(4)	1*	70.6
175	0.961(3)	2.400(4)	0.271(7)	0.96(3)	35.9
	0.451(2)	1.171(3)	0.278(4)	1*	64.1
215	0.976(2)	2.340(3)	0.286(5)	1.00(3)	64.7
	0.461(3)	1.106(6)	0.251(8)	1*	35.3
250	0.991(1)	2.252(3)	0.292(4)	1.03(1)	100
	-	-	-	-	-
300	0.954(1)	2.232(3)	0.340(5)	1.02(1)	100
	-	-	-	-	-

### After thermal annealing

Values marked with an asterisk (\*) were fixed in the fit. [a]: Isomer shifts ( $\delta$ ) were specified relative to metallic iron at T = 300 K but were not corrected in terms of the second-order Doppler shift. [b]: In case of polycrystalline powders with random orientations of the crystallites, the expectation value of this parameter is  $A_2/A_1 = 1$ .<sup>[1]</sup> Deviations from this value are attributed to the presence of marginal texture effects due to partial orientations of crystallites on compacting the powder in the sample containment.

**Table S4.** Comparison of the molar fraction of high-spin molecules  $\gamma_{HS}$  determined by Mössbauer spectroscopy and magnetic susceptibility measurements of the samples **5e** and **5e**<sup>\*</sup>.

	Mössbauer spectroscopy		SQUID magnetometry	
<i>T</i> [K]	<b>5e</b> , $\gamma_{\rm HS}^{a)}$ [%]	<b>5e*</b> , $\gamma_{HS}^{b)}$ [%]	<b>5e</b> , γ <sub>HS</sub> <sup>c)</sup> [%]	<b>5e*</b> , γ <sub>HS</sub> <sup>d)</sup> [%]
300	85	100	100	100
250	83	100	99	99
215	84	84	98	73
175	69	42	80	23
135	48	31	57	17
80	44	30	51	15
135	47	29	57	17
175	61	36	76	19
215	79	65	98	40
250	88	100	99	99
300	88	100	100	100

a) and b): Values for **5e** (as-synthesized) before (a) and **5e**\* after (b) thermal annealing determined by Mössbauer spectroscopy (cf., **Table S3**). c) and d): Values determined by magnetic susceptibility measurements before (c) and after (d) thermal annealing, assuming that the value of  $\chi T = 3.26 \text{ cm}^3 \text{ K mol}^{-1}$  measured at T = 300 K corresponds with  $\gamma_{\text{HS}} = 100\%$  (cf., **Figure S27**).

The systematically lower  $\gamma_{\rm HS}$  values of the annealed sample obtained by SQUID magnetometry can be explained by the different annealing environments for the two measurements. For the magnetic susceptibility measurements, the neat sample was annealed over several measurement cycles inside the magnetometer under He/vacuum atmosphere until its final annealing temperature of 400 K, remaining inside the device for about 25 h. In contrast, the annealing of the Mössbauer sample was performed by heating the sample holder inside a Schlenk tube under nitrogen atmosphere in a drying oven at 393 K for 3 h.

# 2.9. SEM

**Figure S30.** SEM image of the samples **1e** before (left) and **1e**\* after thermal annealing (right) showing the absence of microcrystals on the polymer surface.



**Figure S31.** SEM image of the samples **2e** before (left) and **2e**\* after thermal annealing (right) showing the absence of microcrystals on the polymer surface.



Figure S32. SEM image of the samples 3e before (left) and 3e\* after thermal annealing (right).



Figure S33. SEM image of the samples 4e before (left) and 4e\*after thermal annealing (right).



Figure S34. SEM image of the samples 5e before (left) and 5e\* after thermal annealing (right).



#### 2.10. DLS (after thermal annealing)

Figure S35. DLS autocorrelation functions (left) and intensity weighted hydrodynamic diameter distributions (right) of the nanocomposite samples  $1e^*$  (black),  $2e^*$  (red),  $3e^*$  (green),  $4e^*$  (blue), and  $5e^*$  (light blue) after thermal annealing.



**Table S5.** Comparison of the hydrodynamic diameter and the core diameter/width measured by DLS and TEM, respectively, before annealing (as-synthesized samples; 1-5e) and after thermal annealing ( $1-5e^*$ ).

Sample	Hydrodynamic diameter Dh	Core diameter/width
	[nm]	D <sub>core</sub> [nm]
1e	113 ± 67	14 ± 2
1e <sup>*</sup>	106 ± 67	14 ± 2
2e	118 ± 55	28 ± 3
2e*	109 ± 39	27 ± 3
3e	139 ± 38	$48 \pm 4$
3e*	$123 \pm 34$	48 ± 5
4e	139 ± 36	$58 \pm 4$
4e <sup>*</sup>	140 ± 39	$53 \pm 4$
5e	242 ± 147	60 ± 8
5e*	246 ± 149	65 ± 5

# **2.11. TEM (after thermal annealing)**

**Figure S36.** TEM images of the samples  $1e^*$  (A),  $2e^*$  (B),  $3e^*$  (C),  $4e^*$  (D), and  $5e^*$  (E) after thermal annealing. The core size distribution of the nanomposite micelles are given in the insets.



# 2.12. TEM and SQUID magnetometry (on a sample prepared in toluene with microcrystals)

**Figure S37.** Exemplary TEM image of a sample synthesized in toluene containing microcrystals of the SCO CP (A) and the corresponding magnetic measurement revealing bulk-like behaviour in the as-synthesized sample before thermal annealing (B).



# 2.13. Comparison between dried up toluene and THF solutions by optical light microscopy

A toluene dispersion containing a mixture of nanocomposite particles and microcrystals and a THF nanocomposite particles dispersion were kept until complete evaporation of the solvents. A comparison of the two different dried up dispersions was done using optical light microscopy. As observed before, CP crystals precipitated from the toluene dispersion, while the nanocomposite particles dispersion in THF resulted in the formation of a polymeric solid/film (**Figure S38**). As reference, a dried up dBCP/bipy solution in THF and a powdered sample of the CP [FeL(bipy)]<sub>n</sub> were used. The bipyridine crystallized in a starshaped structure, which was also detected for the dried up SCO CP-dBCP dispersion from THF (see **Figure S39A, B**). Images of the powdered CP and the crystal obtained from a dried up SCO CP-dBCP dispersion from toluene revealed unshaped structures (**Figure S39C**) and block shaped crystals (**Figure S39D**), respectively. Both latter CP samples were additionally much darker in colour than the SCO CP-dBCP sample from THF. Thus, the crystals observed by optical light microscopy and SEM are presumably 4,4'-bipyridine which was used in excess during the synthesis.

**Figure S38.** Photographs of two different dried up solutions for TEM preparation. In the sample from toluene solution on the left, large microcrystals precipitated upon drying. In the nanocomposite sample from THF on the right, a polymeric solid/film remained.



**Figure S39.** Images taken by optical light microscopy from dried up solutions of dBCP/bipy showing the crystallization of bipy (A) and SCO CP-dBCP nanocomposite from THF suggesting a similar crystallization behavior like pure bipy (B). Additionally, the powder sample of the CP [FeL(bipy)]<sub>n</sub> (C) and a crystal (D) obtained from a dried up toluene solution (cf. Figure S36), were imaged showing much darker colors, indicating that the crystals in image (B) are bipy crystals.



#### 2.14. TEM-EDX HAADF

**Figure S40.** TEM-EDX HAADF image of sample **5d** with the overlays of the iron, nitrogen, carbon, and silicon signals. The areas marked 1 (on the coordination polymer in the 4VP core of the micelles) and 2 (area without coordination polymer, the PS corona cannot be differentiated from the carbon grit) are equal in size and correspond to the respective spectra showing that iron is only found inside the polymeric structure.



#### References

[1] N. N. Greenwood, T. C. Gibb, *Mössbauer Spectroscopy*, Chapman and Hall Ltd., London, **1971**.