Supporting Information for

Coordination polymer particles with ligand-centred pH-responses and spin transition

F. Nador,^{*a*} F. Novio^{*a,b*} and D. Ruiz-Molina^{*a,b*}

Index

S1. Synthesis of L₁

S2. pH-response of L₁ monitored by ¹H NMR

- S2.1. By-product obtained after exposure L_1 at pH~5 treatment
- S2.2. Time dependence stability of L_1 at pH~5
- S2.3. Time dependence stability of L_1 at pH~5 and pH~7

S3. Synthesis and full characterization of CPP₁

- S3.1. Interfacial Polymerization
- S3.2. Magnetic Stirring
- S3.3. SEM and TEM
- S3.4. FT-IR
- S3.5. UV-Vis
- S3.6. XPS
- S3.7. EDX

S4. pH-response studies of CPP₁

S5. pH-response of L₂ monitored by ¹H NMR

S6. Synthesis and full characterization of CPP₂

- S6.1. Interfacial Polymerization
- S6.2. Magnetic Stirring
- S6.3. SEM and TEM
- *S6.4. FT-IR*
- S6.5. UV-Vis
- S6.6. EDX

S7. pH-response studies of CPP₂

S1. Synthesis of N-(3,4-dihydroxybenzylidene)-2-(3,4-dihydroxyphenyl)ethaneamine (L_1)

A mixture of dopamine hydrochloride (1.5 mmol, 284 mg) and 3,4-dihydroxybenzaldehyde (1.5 mmol, 207 mg) in methanol absolute (36 mL) was stirred at room temperature under argon atmosphere. After complete dissolution, triethylamine (1.5 mmol, 210 μ L) was slowly added by syringe. After six hours a yellow solid started to precipitate. The reaction was left overnight under magnetic stirring and after that the methanol was evaporated under reduced pressure. The solid was washed with water (3x10 mL), filtered and dried to obtain L₁: 83% yield. ¹H NMR: δ = 2.68 (t, *J* = 6.9 Hz, 2H), 3.63 (t, *J* = 6.9 Hz, 2H), 6.45 (d, *J* = 7.7 Hz, 1H), 6.60-6.61 (m, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 7.17 (s, 1H), 8.01 (s, 1H). ¹³C NMR: δ = 35.8, 53.2, 109.0, 112.5, 117.2, 119.8, 121.7, 128.7, 135.5, 144.1, 144.6, 148.4, 164.0, 170.8. IR-KBr (cm⁻¹) 3310.9, 3246.5, 1659.0, 1610.7, 1514.1, 1356.3, 1282.2, 1127.7. Anal. (%) Calcd. for C₁₅H₁₅NO₄: C, 65.96; H, 5.49; N, 5.13. Found: C, 65.87; H, 5.37; N, 5.15.

S2. pH-response of L₁ monitored by ¹H NMR

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-400 and ARX-250 spectrophotometer using methanol- d_4 and dimethyl sulfoxide- d_6 as solvent.

S2.1. By-product obtained after exposure L_1 at pH~5 treatment



Figure S1. Mechanism of Pictet-Spengler cyclization of L_1 in acid medium



S2.2. Time dependence stability of L_1 at pH~5

b) 90min and c) 150min. The integrals are shown below the signals.

S2.3. Time dependence stability of L_1 at pH~5 and pH~7



9.8 9.6 9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 f1 (ppm)

Figure S3. ¹H NMR spectra of L_1 after a) 105 min at pH~5 and b) 300 min at pH~7. The integrals are shown below the signals.

S3. Synthesis and full characterization of CPP₁

S3.1. Interfacial Polymerization

<u>Synthesis of $[Co(Bix)(L_1)]$ CPP_1</u>: A mixture of L_1 (0.5 mmol, 136.5 mg) and 1,4-bis(imidazole-1ylmethyl)benzene (bix, 0.5 mmol, 118.5 mg) was dissolved in DMSO (5 mL), and later ethanol (40 mL) was added. On the other hand, $Co(CH_3COO)_2 \cdot 4H_2O$ (0.5 mmol, 124.6 mg) was placed in a vial of and dissolved in water (5 mL). The mixture of ligands was slowly added on the aqueous solution forming a new phase. A black solid started to form in the interphase, precipitating after few hours. The reaction left during 72h without moving and finally the precipitate was centrifuged (8000 rpm) and washed with water and ethanol several times. The solvent was removed and the solid dried under vacuum. Anal. (%) Calcd. For $C_{29}H_{25}N_5O_4Co$: C, 61.52; H, 4.42; N, 12.36. Found: C, 52.69; H, 3.46; N, 10.59.

S3.2. Magnetic Stirring

<u>Synthesis of $[Co(Bix)(L_1)] CPP_1</u>$: A mixture of L_1 (0.5 mmol, 136.5 mg) and bix (0.5 mmol, 118.5 mg) was dissolved in DMSO (5 mL), and later ethanol (40 mL) was added. Under magnetic stirring (700 rpm) the addition of an aqueous solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (0.5 mmol, 124.6 mg in 5 mL of water) led to a color change to black. Rapidly a fine precipitate was formed and after stirring at room temperature for 24 hours, the precipitate was centrifuged (10000 rpm) and washed with water and ethanol several times. The solvent was removed and the solid dried under vacuum. TEM images of the resulting spherical nanoparticles showed a size distribution around 40 ± 20 nm.</u>

S3.3. SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Miscroscopy)

SEM images were performed on a scanning electron microscope (FEI Quanta 650 FEG) at acceleration voltages of 2–5 kV. Aluminium was used as support.

TEM images were obtained with a FEI Tecnai G2 F20. One drop of a solution of the materials was deposited on a carbon coated copper grid and left to dry. The observation was performed at room temperature at a voltage of 200 kV.



Figure S4. TEM image of CPP1' and histogram with the size distribution

S3.4. FT-IR (Infrared Spectroscopy)

FT-IR spectra were collected on a Tensor 27 FT-IR Spectrometer (Bruker) in the range of 400-4000 cm⁻¹ using KBr pellets.



S3.5. UV-Vis (Ultraviolet–Visible Spectroscopy)

UV-Vis spectra were obtained on a Cary 4000 spectrophotometer (Agilent) using quartz cuvettes.



Figure S6. UV-Vis of CPP₁

S3.6. X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were performed with a Phoibos 150 analyzer (SPECS GmbH, Berlin, Germany) in ultra-high vacuum conditions (base pressure 1E-10mbar) with monochromatic aluminium Kalpha X-ray source (1486.74eV).

The presence of cobalt was determined by X-ray Photoelectron Spectroscopy (XPS). Firstly, a sample of $Co(CH_3COO)_2 \cdot 4H_2O$ was analysed as reference, and then the **CPP**₁ and **CPP**₂. All the spectra were

referenced to the aliphatic carbon at binding energy (BE) of 284.8 eV. High-resolution Co 2p spectrum showed two important signals, the more intense from Co $2p_{3/2}$ at 781.1 eV and the less intense from Co2p1/2 at 796.7 eV. Moreover, two satellite peaks at 785.9 and 802.4 eV were found, which supports even more the presence of Co(II).



Figure S7. XPS of **CPP**₁ (—), **CPP**₂ (—) and Co(AcO)₂·4H₂O (—)

S3.7. Energy Dispersive X-ray (EDX)

The analysis on several sections confirmed the presence of cobalt, with energy bands of 6.9, 7.7 keV (K lines) and 0.8 keV (L line). The analysis also showed carbon, oxygen and nitrogen.



Figure S8. EDX of CPP₁. Al and Si peaks come from the Aluminium tape used

S4. pH-response studies of CPP₁



Figure S9. Time dependence stability of **CPP**₁ monitored by SEM. (a) after 6h at pH~5 (CBS buffer) and (b) after 14h at pH~7 (PBS buffer)



Figure S10. FT-IR of **CPP**₁ before (—) and after treatment at pH~7 for 3h (—), 6h (—), 9h (—) and 14h (—)



Figure S11. FT-IR of **CPP**₁ before (—) and after treatment at pH~5 for 3h (—), 6h (—), 9h (—) and 14h (—)

S5. pH-response of L₂ monitored by ¹H NMR





S6. Synthesis and full characterization of CPP₂

S6.1. Interfacial Polymerization

<u>Synthesis of $[Co(Bix)(L_2)]$ CPP₂: A mixture of nordihydroguaiaretic acid (L₂) (0.5 mmol, 151.2 mg)</u> and bix (0.5 mmol, 118.5 mg) was dissolved in ethanol (16 mL). On the other hand, $Co(CH_3COO)_2 \cdot 4H_2O$ (0.5 mmol, 124.6 mg) was placed in a vial and dissolved in water (5 mL). The mixture of ligands was slowly added on the aqueous solution forming a new phase. A grey precipitate started to form in the interphase, precipitating after few hours. The reaction left during 72h without moving and finally the precipitate was centrifuged (8000 rpm) and washed with water and ethanol several times. The solvent was removed and the solid dried under vacuum. Anal. (%) Calcd. For $C_{32}H_{32}N_4O_4Co$: C, 64.54; H, 5.37; N, 9.41. Found: C, 60.03; H, 4.47; N, 8.11.

S6.2. Magnetic Stirring

<u>Synthesis of $[Co(Bix)(L_2)] CPP_2'</u>$: A mixture of L_2 (0.5 mmol, 151.2 mg) and bix (0.5 mmol, 118.5 mg) was dissolved in ethanol (16 mL). Under magnetic stirring (700 rpm) the addition of an aqueous solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (0.5 mmol, 124.6 mg in 5 mL of water) led to a color change to violet. Rapidly a precipitate was formed and after stirring at room temperature for 24 hours, the precipitate was centrifuged (10000 rpm) and washed with water and ethanol several times. The solvent was removed and the solid dried under vacuum. TEM images of the resulting spherical nanoparticles showed a size distribution around 100 ± 60 nm.</u>

S6.3. SEM and TEM



Figure S13. SEM image of CPP₂ and histogram with the size distribution



Figure S14. TEM image of CPP₂' and histogram with the size distribution



Figure S15. FT-IR of L_2 (----), CPP_2 (----) and bix (----)





Figure S16. UV-Vis of CPP₂

S6.6. EDX



Figure S17. EDX of **CPP**₂. Al and Si peaks come from the Aluminium tape used

S7. pH-response studies of CPP₂



Figure S18. Time dependence stability of **CPP**₂ before and after exposure at pH~5 (CBS buffer) at the times thereby indicated



Figure S19. Time dependence stability of **CPP**₂ before and after exposure at pH~4 (MES buffer) at the times thereby indicated



Figure S20. FT-IR of **CPP**₂ before (—) and after treatment at pH~5 for 4.3h (—), 9h (—) and 24h (—)



Figure S21. χ T values as a function of temperature for CPP₂ before (**■**) and after acidic treatment at pH~5 for 14h (**▲**)