Supporting Information for

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

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S1. Synthesis of \( \text{N-(3,4-dihydroxybenzylidene)-2-(3,4-dihydroxyphenyl)ethaneamine (L1)} \)

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 \( \mu \)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 \( \text{L1} \): 83% yield. \( \text{^1H NMR:} \delta = 2.68 (t, \ J = 6.9 \text{ Hz}, 2\text{H}), 3.63 (t, \ J = 6.9 \text{ Hz}, 2\text{H}), 6.45 (d, \ J = 7.7 \text{ Hz}, 1\text{H}), 6.60-6.61 (m, 2\text{H}), 6.73 (d, \ J = 8.0 \text{ Hz}, 1\text{H}), 6.93 (d, \ J = 8.0 \text{ Hz}, 1\text{H}), 7.17 (s, 1\text{H}), 8.01 (s, 1\text{H}). \text{^13C NMR:} \delta = 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. \text{IR-KBr (cm}^{-1}) 3310.9, 3246.5, 1659.0, 1610.7, 1514.1, 1356.3, 1282.2, 1127.7. \text{Anal. (%) Calcd. for C}_{15}\text{H}_{15}\text{NO}_4: C, 65.96; H, 5.49; N, 5.13. \text{Found: C, 65.87; H, 5.37; N, 5.15.}

S2. pH-response of \( \text{L1} \) monitored by \( \text{^1H NMR} \)

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 \( \text{L1} \) at pH\( \sim \)5 treatment

![Figure S1. Mechanism of Pictet-Spengler cyclization of \( \text{L1} \) in acid medium](figure.png)
S2.2. Time dependence stability of L₁ at pH~5

Figure S2. ¹H NMR spectra of L₁ at pH~5 after a) 30min, b) 90min and c) 150min. The integrals are shown below the signals.

S2.3. Time dependence stability of L₁ at pH~5 and pH~7

Figure S3. ¹H NMR spectra of L₁ 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

Synthesis of [Co(Bix)(L₁)] CPP₁: A mixture of L₁ (0.5 mmol, 136.5 mg) and 1,4-bis(imidazole-1-ylmethyl)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(CH₃COO)₂·4H₂O (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 C₂₉H₂₅N₅O₄Co: C, 61.52; H, 4.42; N, 12.36. Found: C, 52.69; H, 3.46; N, 10.59.

S3.2. Magnetic Stirring

Synthesis of [Co(Bix)(L₁)] CPP₁': A mixture of L₁ (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(CH₃COO)₂·4H₂O (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.

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

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.

![FT-IR Spectra](image)

**Figure S5. FT-IR of L\(_1\) (---), CPP\(_1\) (---) and bix (---)**

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

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

![UV-Vis Spectra](image)

**Figure S6. UV-Vis of CPP\(_1\)**

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\(_3\)COO)\(_2\)·4H\(_2\)O was analysed as reference, and then the CPP\(_1\) and CPP\(_2\). All the spectra were
referred 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 Co2p_{1/2} 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 CPP₁ (▬), CPP₂ (▬) and Co(AcO)₂·4H₂O (▬)](image)

**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](image)
S4. pH-response studies of CPP₁

**Figure S9.** Time dependence stability of CPP₁ 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 CPP₁ before (▬) and after treatment at pH~7 for 3h (▬), 6h (▬), 9h (▬) and 14h (▬)
S5. pH-response of L2 monitored by $^1$H NMR

![Figure S12](image.png)

The integrals are shown below the signals

S6. Synthesis and full characterization of CPP$_2$

S6.1. Interfacial Polymerization

Synthesis of [Co(Bix)(L$_2$)]CPP$_2$: A mixture of nordihydroguaiaretic acid (L$_2$) (0.5 mmol, 151.2 mg) and bix (0.5 mmol, 118.5 mg) was dissolved in ethanol (16 mL). On the other hand, Co(CH$_3$COO)$_2$·4H$_2$O (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\textsubscript{32}H\textsubscript{32}N\textsubscript{4}O\textsubscript{4}Co: C, 64.54; H, 5.37; N, 9.41. Found: C, 60.03; H, 4.47; N, 8.11.

**S6.2. Magnetic Stirring**

Synthesis of [Co(Bix)(L\textsubscript{2})] CPP\textsubscript{2}¨: A mixture of L\textsubscript{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\textsubscript{3}COO)\textsubscript{2}·4H\textsubscript{2}O (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.

**S6.3. SEM and TEM**

![Figure S13. SEM image of CPP\textsubscript{2} and histogram with the size distribution](image)

![Figure S14. TEM image of CPP\textsubscript{2}¨ and histogram with the size distribution](image)
S6.4. FT-IR

Figure S15. FT-IR of L₂ (-----), CPP₂ (-----) and bix (-----)

S6.5. UV-Vis

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 CPP$_2$**

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 (▬).

Key:
A, $\nu$C=C
B, $\delta$C$_{\text{al}}$-H
C, $\nu$C-O
D, $\delta$C$_{\text{ar}}$-H
Figure S21. $\chi_T$ values as a function of temperature for CPP$_2$ before (■) and after acidic treatment at pH~5 for 14h (▲)