A coloring tool for spiropyans: Solid state metal-organic complexation versus salification

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Experimental section

Synthesis

(Ia) 150.49 mg (0.543 mmol) of SPH and 76.04 mg (0.559 mmol) ZnCl$_2$ were separately dissolved in a total amount of 2 mL acetone in a round-bottom flask. After reflux heating for 10 min, an orange precipitate occurred. After cooling down, filtration of the precipitate with subsequent acetone and 1,4 dioxane washing yielded in 170.09 mg (76.1%) of the complex (Ia).

A 149.80 mg (0.540 mmol) SPH and 73.50 mg (0.540 mmol) ZnCl$_2$ slurry in 2 mL acetone yielded orange precipitate after 1 day. The filtered and with acetone washed precipitate resulted in 193.56 mg (86.6%) of (Ia).

(IIa) 507.91 mg (1.55 mmol) SPBenz and 209.91 mg (1.54 mmol) ZnCl$_2$ were partially dissolved in 10 mL acetone. Reflux heating for 1h resulted in a red precipitate. After cooling down the precipitate was filtered and washed with acetone and 1,4-dioxane. 576.08 mg (76.6%) of the acetone solvate (IIa) was obtained.

(IIb) 500.07 mg (1.53 mmol) SPBenz and 346.50 mg (1.54 mmol) ZnBr$_2$ were partially dissolved in 10 mL acetone. Reflux heating for 1h resulted in a red precipitate. After cooling down the precipitate was filtered and washed with acetone and 1,4-dioxane. 490.70 mg (55.2%) of the acetone solvate (IIb) was obtained.

(IVa) 149.83 mg (0.465 mmol) SPNO$_2$ mixed with 65.65 mg (0.482 mmol) ZnCl$_2$ in 3 mL acetone were reflux heated for 10 min until orange precipitate occurred. The solution was left for cooling down. Washing of the precipitate with acetone and 1,4-dioxane yielded in 137.66 mg (63.9%) of the product (IVa).

(IVb) 150.41 mg (0.4657 mmol) SPNO$_2$ mixed with 160.55 mg (0.473 mmol) ZnBr$_2$ in 3 mL acetone were reflux heated for 10 min until orange precipitate occurred. The solution was left for cooling down. Washing of the precipitate with acetone and 1,4-dioxane yielded in 109.16 mg (42.5%) of the product (IVf).

(IVf) A solution of 110.71 mg (0.465 mmol) CoCl$_2$·6H$_2$O in acetone was added to acetone solution of 150.46 mg (0.467 mmol) SPNO$_2$ and reflux heated until red/brown precipitate occurred (3 mL of acetone in total). Filtration of the precipitate and subsequent washing with acetone and 1,4-dioxane yielded in 183.38 mg (70.3%) of (IVf).

(IVk) A slurry in 0.75 mL acetone with 249.99 mg (0.775 mmol) SPNO$_2$ and 92.20 mg (0.388 mmol) CoCl$_2$·6H$_2$O were left for stirring for 2 days and resulted in red-brown precipitate. Filtration and washing with acetone and 1,4-dioxane yielded in 104.04 mg (66.1%) of the product (IVk).

(IVm) A slurry in 1.5 mL acetone with 150.50 mg (0.777 mmol) SPNO$_2$ and 186.40 mg (0.783 mmol) CoCl$_2$·6H$_2$O were left for stirring for 2 days and resulted in green precipitate. Filtration and washing with acetone and 1,4-dioxane yielded in 234.57 mg (69.9%) of the product (IVm).
Crystal packings

Figure S1: A partial packing diagram of MCH coordinated to ZnBr₂ (Ia) showing isolated dimers.

Figure S2: A partial packing diagram of MCH with ZnCl₂ forming the hydrate (lc) with chains running along the α axis.

Figure S3: Partial packing diagrams of MCBenz coordinated to ZnCl₂ (IIa; left) and ZnBr₂ (IIb; right). Both packings show disordered acetone molecules over two positions.
Figure S4: A partial packing diagram of MCOME coordinated to ZnCl$_2$ (IIIa) and ZnBr$_2$ (IIIb) with ethanol and H$_2$O in the case of (IIIa) in the crystal structure. Hydrogen bonds are indicated as dashed lines. Only the main occupied site is shown.

Figure S5: Partial packing diagrams of MCNO$_2$ coordinated to ZnCl$_2$ ((IVa); upper left) in a 1:1 ratio and in a 2:1 ratio ((IVb); upper right). Analogous for the isomorphous forms with ZnBr$_2$ ((IVf) and (IVg); below).
Figure S6: Two hydrate structures of MCNO2 coordinated to ZnCl$_2$ in different ratios ((IVd) left; (IVe) right).

Figure S7: A partial packing diagram of MCNO2 coordinated to ZnBr$_2$ with two acetonitrile molecules in the asymmetric unit (IVh); one coordinated to the metal center and one freely in the packing (not displayed).
Figure S8: Partial packing diagrams of MCNO2 with ZnCl$_2$ (IVc); left), ZnBr$_2$ (IVi); middle) and CoCl$_2$ (IVk); right) showing their isomorphous structures with one protonated MCNO2 molecule and one molecule coordinated to the metal center. Hydrogens bonds are indicated as dashed lines.
Figure S9: (a) X-ray powder diffraction patterns of (Ia) obtained by reflux (light blue curve) and by slurry (purple curve) in acetone. (b) The calculated powder X-Ray pattern of (Ib) (black curve) compared to the bulk material obtained by reflux (blue curve).
Figure S10: X-ray powder diffraction patterns of (Ila) and (Iib) comparing the calculated powder X-Ray patterns (black curves) with the from reflux obtained bulk material (light blue curves). In comparison the resulting ansolvate (Ila') and (Iib') after evaporation of acetone (dark blue curves) and the recrystallized solvates in an atmosphere of acetone (red curves).
Figure S11: (a) X-ray powder diffraction patterns of (IVa) in comparison of the from single crystal calculated pattern (black curve) with the bulk material from reflux (light blue curve) and slurry (purple curve). (b) Comparison of the X-ray powder diffraction patterns of the from single calculated powder patterns (black curve) and the bulk material obtained from reflux (light blue curve). (c) Calculated powder x-ray patterns of (IVg) (black curve) in comparison with the bulk material obtained after evaporation of the filtrate from the reflux reaction of (IVf) (purple curve).
**Figure S12:** (a) X-ray powder diffraction patterns of the from reflux obtained product (light blue curve) compared to the from single crystal calculated x-ray pattern of (IVj) (black curve). (b) Calculated powder x-ray patterns of (IVk) (black curve) compared to the bulk material obtained by a 1:1 Slurry of SPNO2 with CoCl2·6H2O (purple curve). (c) Calculated powder x-ray patterns of (IVm) (black curve) compared to the bulk material obtained by a 2:1 Slurry of SPNO2 with CoCl2·6H2O (purple curve). Obtained product of (IVk) and (IVj) after exposure to an atmosphere of HCl (green curves).
Figure S13: X-ray powder diffraction patterns of the obtained ZnO products obtained after burning (IIa), and (IVi) under oxygen flow in comparison of the simulated powder patterns of ZnO.
Figure S14: $^1$H-NMR of SPH in DMSO-$d_6$ ($\delta$ (ppm): 2.50). Traces of $H_2O$ ($\delta$ (ppm): 3.33) present.

Figure S15: $^{13}$C-NMR of SPH in DMSO-$d_6$ ($\delta$ (ppm): 39.51).
Figure S16: HMQC-NMR of SPH in DMSO-d$_6$ (δ (ppm): 2.50/39.51).
Figure S17: HMBC-NMR of SPH in DMSO-$d_6$ ($\delta$ (ppm): 2.50/39.51).
Figure S18: $^1$H-NMR of (Ia) in DMSO-d$_6$ ($\delta$ (ppm): 2.50). Traces of H$_2$O ($\delta$ (ppm): 3.33) and acetone ($\delta$ (ppm): 2.08) present.

Figure S19: $^1$H-NMR of (Ib) in DMSO-d$_6$ ($\delta$ (ppm): 2.50). Traces of H$_2$O ($\delta$ (ppm): 3.34) and acetone ($\delta$ (ppm): 2.08) present.
Figure S20: $^1$H-NMR of SPBenz in DMSO-d$_6$ ($\delta$ (ppm): 2.50). Traces of H$_2$O ($\delta$ (ppm): 3.33) present.

Figure S21: $^1$H-NMR of (Ila) in DMSO-d$_6$ ($\delta$ (ppm): 2.50). Traces of H$_2$O ($\delta$ (ppm): 3.33) present. The acetone signal ($\delta$ (ppm): 2.08) derives from the solvate.
Figure S22: $^1$H-NMR of the ansolvate (IIa') in DMSO-d$_6$ ($\delta$ (ppm): 2.50). Traces of H$_2$O ($\delta$ (ppm): 3.33) present.

Figure S23: $^1$H-NMR of (IIb) in DMSO-d$_6$ ($\delta$ (ppm): 2.50). Traces of H$_2$O ($\delta$ (ppm): 3.33) present. The acetone signal ($\delta$ (ppm): 2.08) derives from the solvate.
Figure S24: $^1$H-NMR of the ansolvate (IIb') in DMSO-d$_6$ ($\delta$ (ppm): 2.50). Traces of H$_2$O ($\delta$ (ppm): 3.33) present.

Figure S25: $^1$H-NMR of SPNO2 in DMSO-d$_6$ ($\delta$ (ppm): 2.50). Traces of H$_2$O ($\delta$ (ppm): 3.33) present.
Figure S26: $^1$H-NMR of (IVa) in DMSO-d$_6$ ($\delta$ (ppm): 2.50) showing the SP (highlighted in the spectra below) and MC form (highlighted in the upper spectra) of SPNO$_2$/MCNO$_2$. Traces of H$_2$O ($\delta$ (ppm): 3.33) and acetone ($\delta$ (ppm): 2.08) present.
Figure S27: $^1$H-NMR of (IVa) in DMSO-$d_6$ ($\delta$ (ppm): 2.50) showing only the SP form of SPNO2/MCNO2 after exposing to sunlight. Traces of H$_2$O ($\delta$ (ppm): 3.33) and acetone ($\delta$ (ppm): 2.08) present.
**Figure S28**: $^1$H-NMR of (IVf) in DMSO-d$_6$ ($\delta$ (ppm): 2.50). Traces of H$_2$O ($\delta$ (ppm): 3.33) and acetone ($\delta$ (ppm): 2.08) present.

**Figure S29**: NMR tube of (IVj) in DMSO-d$_6$ directly after dissolution (left), after exposing for several seconds to sunlight (middle) and exposing to sunlight until complete discoloration.
**Figure S30**: $^1$H-NMR of (IVj) in DMSO-d$_6$ ($\delta$ (ppm): 2.50). Traces of H$_2$O ($\delta$ (ppm): 3.41) and acetone ($\delta$ (ppm): 2.07) present.

**Figure S31**: $^1$H-NMR of (IVk) in DMSO-d$_6$ ($\delta$ (ppm): 2.50).
Figure S32: $^1$H-NMR of (IVm) in DMSO-d$_6$ ($\delta$ (ppm): 2.50). Traces of H$_2$O ($\delta$ (ppm): 3.51) and acetone ($\delta$ (ppm): 2.05) present.
Figure S33: Diffuse reflectance spectroscopy of the parent spirogyran compounds, a) SPH/MCH, b) SPBenz/MCBenz and c) SPNO2/MCNO2, as well as their formed complexes with ZnCl$_2$/ZnBr$_2$.
Thermal gravimetric analysis

**Figure S34**: TGA analysis of SPH. (25-800 °C; 10°C/min; N₂)

**Figure S35**: TGA analysis of MCH coordinated to ZnCl₂ (Ia). (25-800 °C; 10°C/min; N₂)
Figure S36: TGA analysis of MCH coordinated to ZnBr$_2$ (lb). (25-800 °C; 10°C/min; N$_2$)

Figure S37: TGA analysis of SPBenz. (25-800 °C; 10°C/min; N$_2$)
Figure S38: TGA analysis of MCBenz coordinated to ZnCl$_2$ (IIa) showing the loss of acetone starting around 150°C. (25-800 °C; 10°C/min; N$_2$)

Figure S39: TGA analysis of MCBenz coordinated to ZnBr$_2$ (IIb) showing the loss of acetone starting around 147°C. (25-800 °C; 10°C/min; N$_2$)
**Figure S40**: TGA analysis of SPNO₂. (25-800 °C; 10°C/min; N₂)

**Figure S41**: TGA analysis of MCNO₂ coordinated to ZnCl₂ (IVa). (25-800 °C; 10°C/min; N₂)
Figure S42: TGA analysis of MCNO2 coordinated to ZnBr₂ (IVf). (25-800 °C; 10°C/min; N₂)

Figure S43: TGA analysis of MCNO2 coordinated to CoCl₂ (IVj). (25-800 °C; 10°C/min; N₂)
Figure S44: TGA analysis of MCNO2 with CoCl₂ forming the mix form (IVk). (25-800 °C; 10°C/min; N₂)

Figure S45: TGA analysis of MCNO2 with CoCl₂ forming the hydrated salt (IVm). (25-800 °C; 10°C/min; N₂)