

### Experimental Section

**Materials.**  $\text{CuCl}_2$  (99.999%),  $\text{MnCl}_2$  (99+%) and cyanamide (99%) were purchased from Aldrich. Benzylamine was obtained from Fluka. All the chemicals (except the solvents used for washing, which were technical grade) were anhydrous and analytical grade. They were all used without further purification.

**Synthesis.** All experiments were started in a glovebox under Argon atmosphere. Centrifugation and washing was then performed outside the glovebox. **(a)**  $\text{CuNCN}$  synthesis. 15 mmol of cyanamide was melted at  $50^\circ\text{C}$ , followed by the addition of anhydrous  $\text{CuCl}_2$  (1 mmol) to the molten cyanamide under vigorous stirring. The solution turns to deep green. Finally, an excess of benzylamine (76 mmol) was slowly dropped into this mixture. The dark green solution immediately became black. The black solid phase was separated from the liquid by centrifugation, consecutively washed with ethanol and acetone, and dried at  $60^\circ\text{C}$  in air. The yield of the reaction is 78% with respect to  $\text{CuCl}_2$ . The whole synthesis does not take longer than 90 minutes. **(b)**  $\text{MnNCN}$  synthesis. The synthesis of  $\text{MnNCN}$  was analogous to the synthesis of  $\text{CuNCN}$  described above. 15 mmol of cyanamide was melted at  $50^\circ\text{C}$ . Then, anhydrous  $\text{MnCl}_2$  (1 mmol) was added under vigorous stirring. The solution turns to pastel green. Finally, an excess of benzylamine (76 mmol) was slowly dropped to this mixture. In contrast to the  $\text{CuNCN}$  synthesis, the light green cloudy solution becomes dark green only after contact with surrounding air outside the glovebox. The solid phase was separated from the liquid by centrifugation, consecutively washed with ethanol and acetone, and dried at  $60^\circ\text{C}$  in air. **Characterization.** Powder XRD patterns of the nanoparticles were recorded on a PANalytical PW 1800 diffractometer equipped with secondary monochromator in reflection mode using  $\text{CuK}\alpha$  radiation. For the transmission electron microscopy (TEM) investigation, the material was deposited onto a carbon foil supported on a copper grid. TEM investigations were performed with a CM30ST microscope (FEI), operated at 300 kV). FTIR transmission spectra were recorded with  $2\text{ cm}^{-1}$  resolution on a Bruker 66v FTIR Spectrometer equipped with DLTG detector. KBr was used as a reference.

DC resistance measurements were performed on pellets of 6 mm diameter and 0.6 (MnNCN) and 1.2 mm (CuNCN) thickness. A Keithley Source Measure Unit 236 was used as a programmable constant current source, and a Keithley Digital Multimeter DMM 2002 was used for measuring the voltage drop across the sample. Resistance across the pellet was measured in the van der Pauw four-probe mode in the temperature range RT -  $170^\circ\text{C}$ .