

Electronic Supplementary Information

Amino *versus* imino-transition metallic complexes in functionalized mesoporous silica-a lone pair degenerated into a singlet electron system

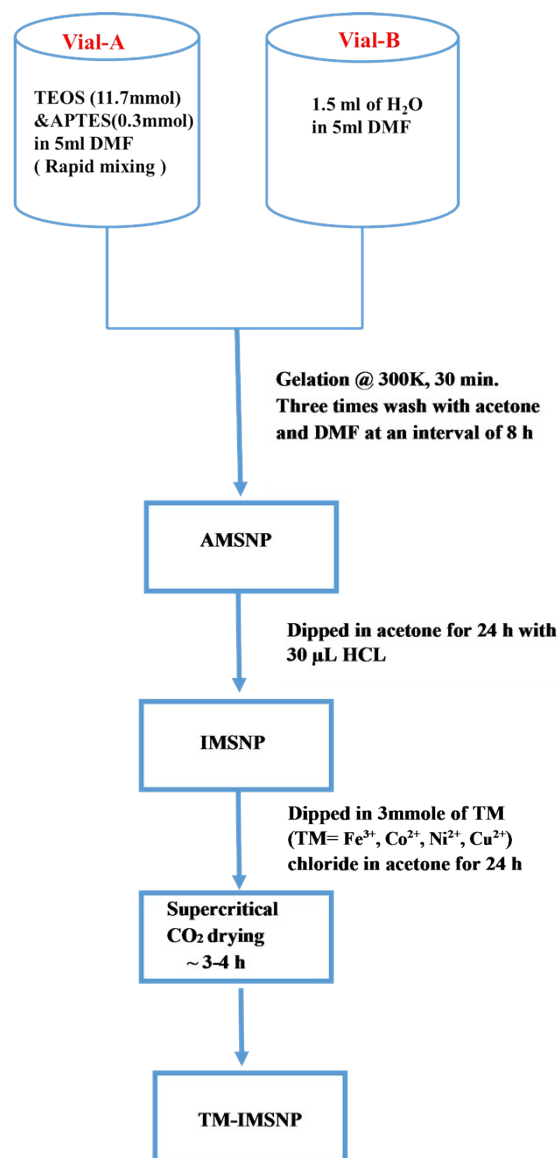


Figure S1. Flowchart on sol-gel synthesis of IMSNP complexing with TM ions through AMSNP

Experimental Section

Amine modified silica gels were prepared by mixing TEOS (11.7 mmol) and APTES (0.3 mmol) in 5 mL DMF in vial A and followed by addition of 1.5 mL of water in 5 mL DMF in vial B. The gelation time was found to be ~30 min. The obtained wet gels were washed with DMF (3x) followed by acetone (3x) washes. In order to obtain imine modified silica gel, the amine terminated silica gel was dipped in acetone for 1 day in room temperature. The imine modified gels were found to be yellowish in colour. The metal ions were coordinated with imine modified gels by dipping the gels in respective TM chloride (TM: Fe³⁺, Co²⁺, Cu²⁺ and Ni²⁺). The amine,

imine and metal ion terminated silica gels were dried supercritically in an autoclave using $scCO_2$ at a pressure and temperature of 1200 psi and 40 °C respectively.

Characterization

For functional group analysis, IR spectra were recorded using a Bruker Tensor 27 FT-IR spectrometer. Photoluminescence spectra were recorded using a JASCO FP8500 spectrofluorometer (model name: ESC-842, made in Japan). For optical absorption studies, diffused reflectance spectra (DRS) were recorded using Cary 7000 (Agilent technologies, UV-Vis-NIR) spectrometer. For identification of free radicals, paired/unpaired electron states, Electron spin resonance spectra were obtained using Bruker Biospin, X Band ESR spectrometer.

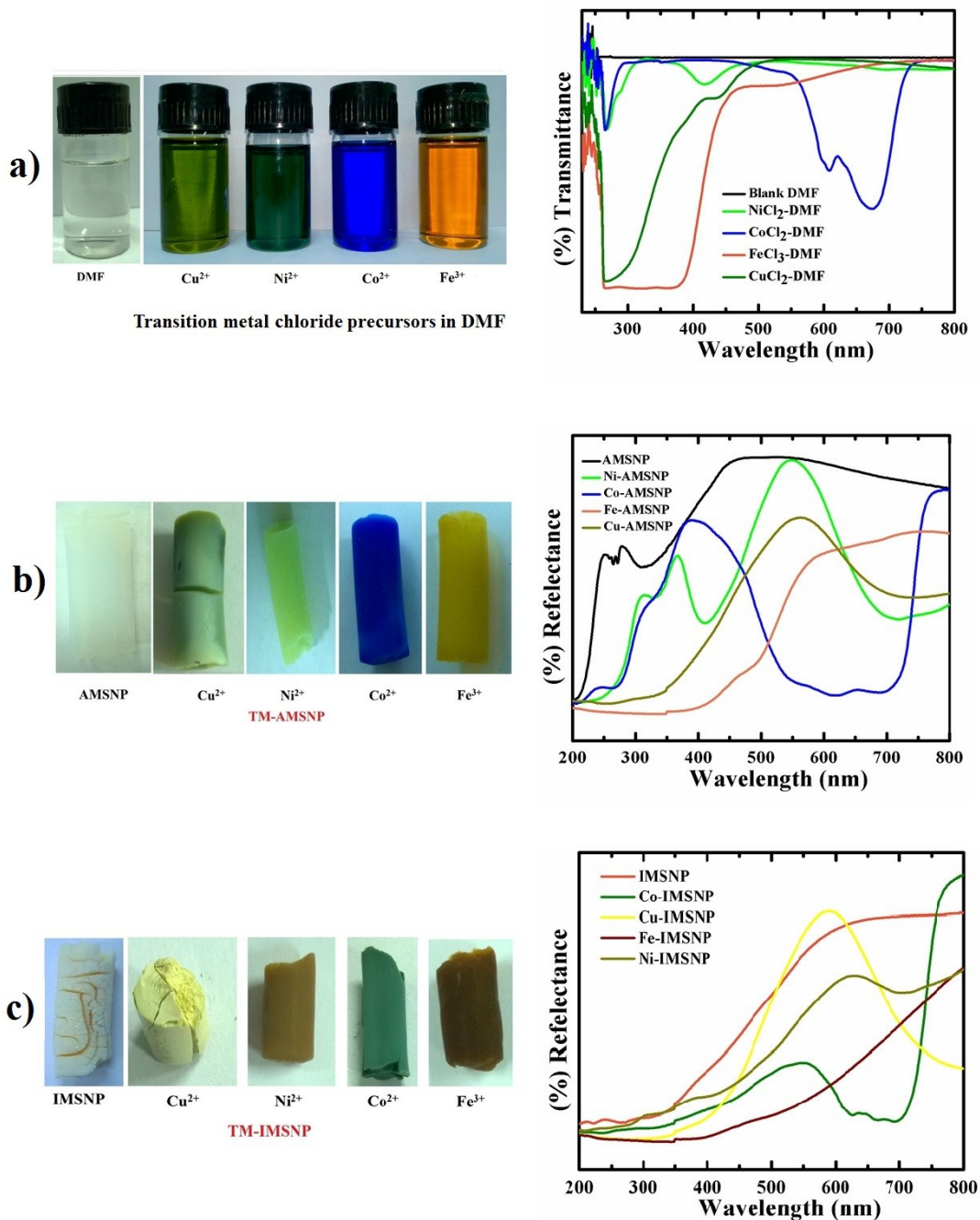


Figure S2: (Right column) UV-Vis transmittance spectra of TM chloride precursors in DMF and diffuse reflectance spectra of TM-AMSNP and TM-IMSNP. (Left column) From these photographs we can observe substantial change in body color of IMSNP upon complexing with TM ions. In the case of AMSNP system such change in colour from the respective colour of the precursor TM chloride solutions is not observed.

Additional note: Furthermore it is important to note that repeated washings using DMF solvent, the TM-IMSNP samples did not show any change/fade in colour and also the decanted DMF solution after washing remained colourless. On the other hand, in the case of TM-AMSNP samples we observed substantial colour fading of the TM-AMSNP samples and also the decanted DMF solution after washing acquired the respective colours of the precursor TM chloride solutions. This concludes the effective complexing ability of IMSNP with TM ions while AMSNP samples did not exhibit such behaviour.