

SUPPLEMENTARY INFORMATION

Preparation, Characterization and Activity of CuZn and Cu₂ Superoxide Dismutase Mimics Encapsulated in Mesoporous Silica

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Elemental Analyses for complexes 1 – 3

Complex 1. Anal. Calc. for CuZnC₁₁Cl₃N₈H₃₃O₁₄: C 17.7, Cu 8.8, H 4.5, N 15.2, Zn 8.9%; found: C 17.8, Cu 8.9, H 4.5, N 15.3, Zn 9.0%.

Complex 2. Anal. Calc. for Cu₂C₁₁Cl₃N₈H₂₉O₁₂: C 18.8, H 4.3, N 16.0, Cu 18.3%; found: C 18.6, H 4.4, N 15.8, Cu 18.1%.

Complex 3. Anal. Calc. for CuZnC₁₇Cl₂H₁₆N₂O₂: C 42.4, H 3.4, N 5.8, Cu 13.5, Zn 13.6%. Found: C 42.5, H 3.3, N 5.7, Cu 13.8, Zn 13.6%.

IR measurements and PCA analysis. Solid samples of silica, neat complexes and hybrid materials were run in ATR (attenuated total reflectance) mode on a diamond crystal. Principal components analysis (PCA) of IR spectral data [1,2] from multiple spectra taken on all samples was performed using the Statistica software [3], in the 1200–1800 cm⁻¹ spectral region, selecting 313 wave numbers, with 34 principal components that justify 100% variance.

Cu and Zn K-edge XANES measurements. The beam energy was selected using an Si(220) N₂ cryo-cooled double-crystal monochromator with an experimental resolution close to that theoretically predicted (namely ~0.5 eV) [4]. The beam spot on the sample was approximately 300 × 200 μm² (H × V, FWHM). Spectra were recorded in absorption mode with a 30-element solid state Ge detector (Canberra). The temperature was kept at 10 K during data collection to prevent sample damage and the absence of significant photo-reduction of the Cu(II) samples was checked. The energy was calibrated with Cu and Zn metallic foils, such that the maximum of the first derivative was set at 8979 and

9659 eV, respectively. Cu data were collected from 8840 to 8960 eV using a 5 eV step of 2 s, from 8960 to 9020 eV using a 0.5 eV step of 3 s, and from 9020 to 9300 eV with a k-step of 0.05 Å⁻¹ and an increasing time of 2–10 s per step. Zn data were collected from 9510 to 9630 eV using a 5 eV step of 2 s, from 9630 to 9700 eV using a 0.5 eV step of 3 s, and from 9700 to 10,000 eV with a k-step of 0.05 Å⁻¹ and an increasing time of 2–10 s per step. XANES spectra were background-corrected by a linear regression through the pre-edge region and a polynomial through the post-edge region and normalized to the edge jump. Samples of neat powder were prepared in a BN matrix (diluted at approx. 5%) and both the diluted neat powder and the complexes inserted in the material were under the form of a pastille taped on the sample holder.

N₂ adsorption-desorption isotherms. The samples were degassed at 10⁻³ Torr and 200 °C for 6 h prior to the adsorption experiment. Surface area (S_{BET}) were calculated using the Brunauer-Emmett-Teller (BET) [5] equation over the pressure range (p/p^0) of 0.05-0.20. The volume of micropores and mesopores (V_{UP} and V_{MP}) was determined by the alpha-plot method [5] using the standard Licrospher isotherm. The total pore volume (V_{TP}) was determined with the Gurvich rule [5] at 0.98 p/p^0 . The pore size distributions were calculated using the Villarroel-Barrera-Sapag (VBS) model [6], on the adsorption branch of the N₂ isotherms.

- [1] I. T. Jolliffe, *Principal Component Analysis*, 2nd ed. Springer, 2002, p 487.
- [2] R. A. Johnson, D. W. Wichern, *Applied Multivariate Statistical Analysis*, sixth ed. Pearson Education Limited, 2008, p 761.
- [3] Statistica - Data analysis software system, version 11, StatSoft, INC., 2012.
- [4] O. Proux, V. Nassif, A. Prat, O. Ulrich, E. Lahera, X. Biquard, J. J. Menthonnex, J.-L. Hazemann, *J. Synchrotron Radiat.* 13 (2006) 59–68.
- [5] M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K. S. W. Sing, *Pure Appl. Chem.* 87 (2015) 1051–1069.
- [6] J. Villarroel Rocha, D. Barrera, K. Sapag, *Top Catal.* 54 (2011) 121–134.

Table S1. EPR parameters of solids at 120 K

	g_{\parallel}	g_{\perp}	$A_{\parallel} / 10^4 \text{ cm}^{-1}$	g_1, g_2, g_3
1	2.20	2.05		
1@MCM-41	2.21	2.06	192	
2				2.06
2@MCM-41	2.23	2.03	190	
3				2.08, 1.94, 2.32
3@MCM-41	2.18	2.06		
CuZn-SOD^a	2.26	2.05	151	

^aK. M. Beem, W. E. Rich, K. V. Rajagopa, J. Biol. Chem. 249 (1974) 7298–7305

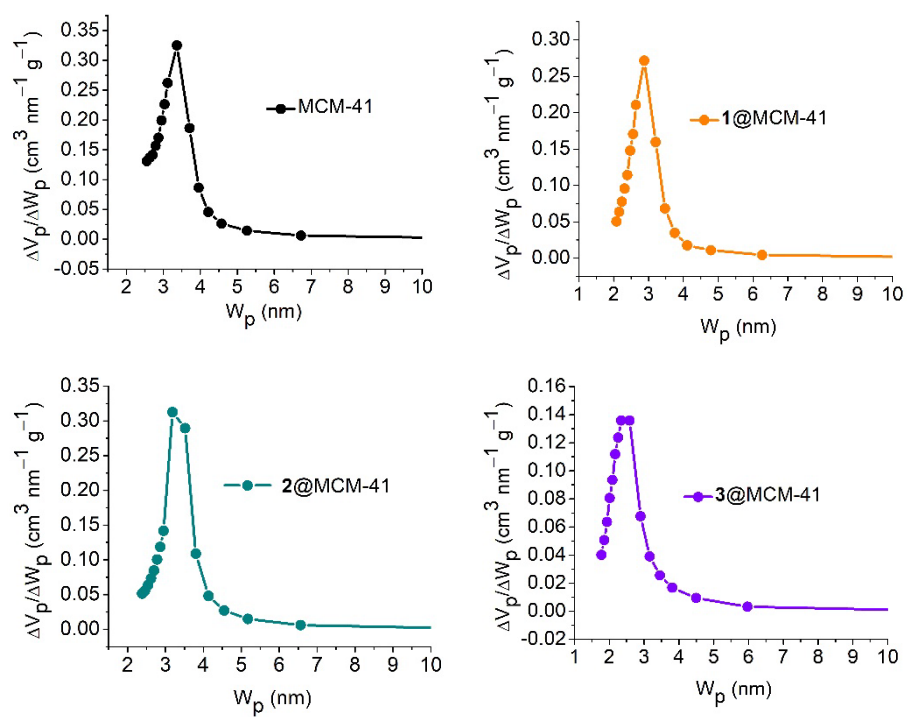


Figure S1: Pore size distribution of MCM-41 and hybrid materials.

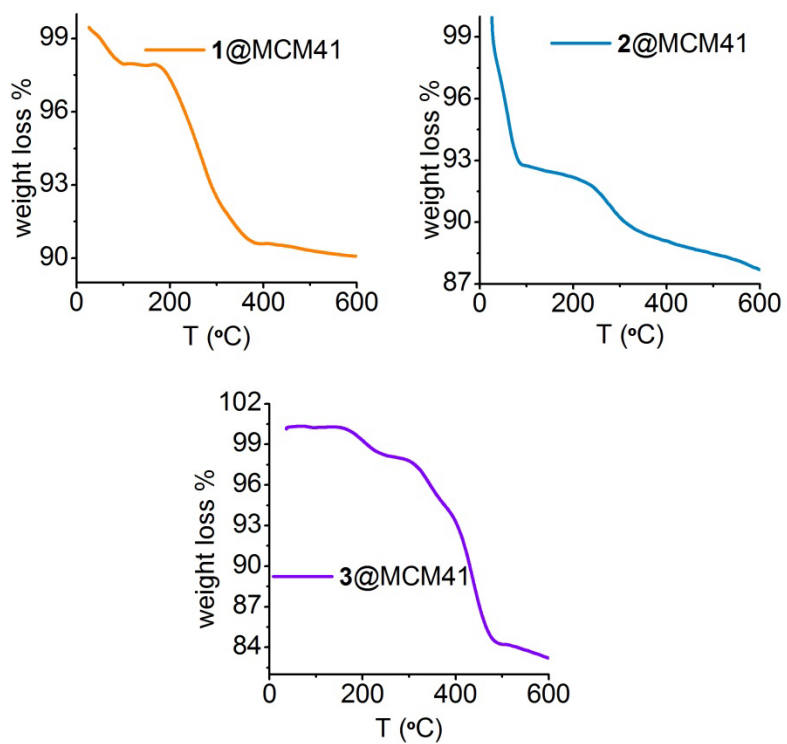


Figure S2. TGA profile of hybrid materials. Heating rate = 10°C min⁻¹; carrier gas (air) flow rate = 50 mL min⁻¹.

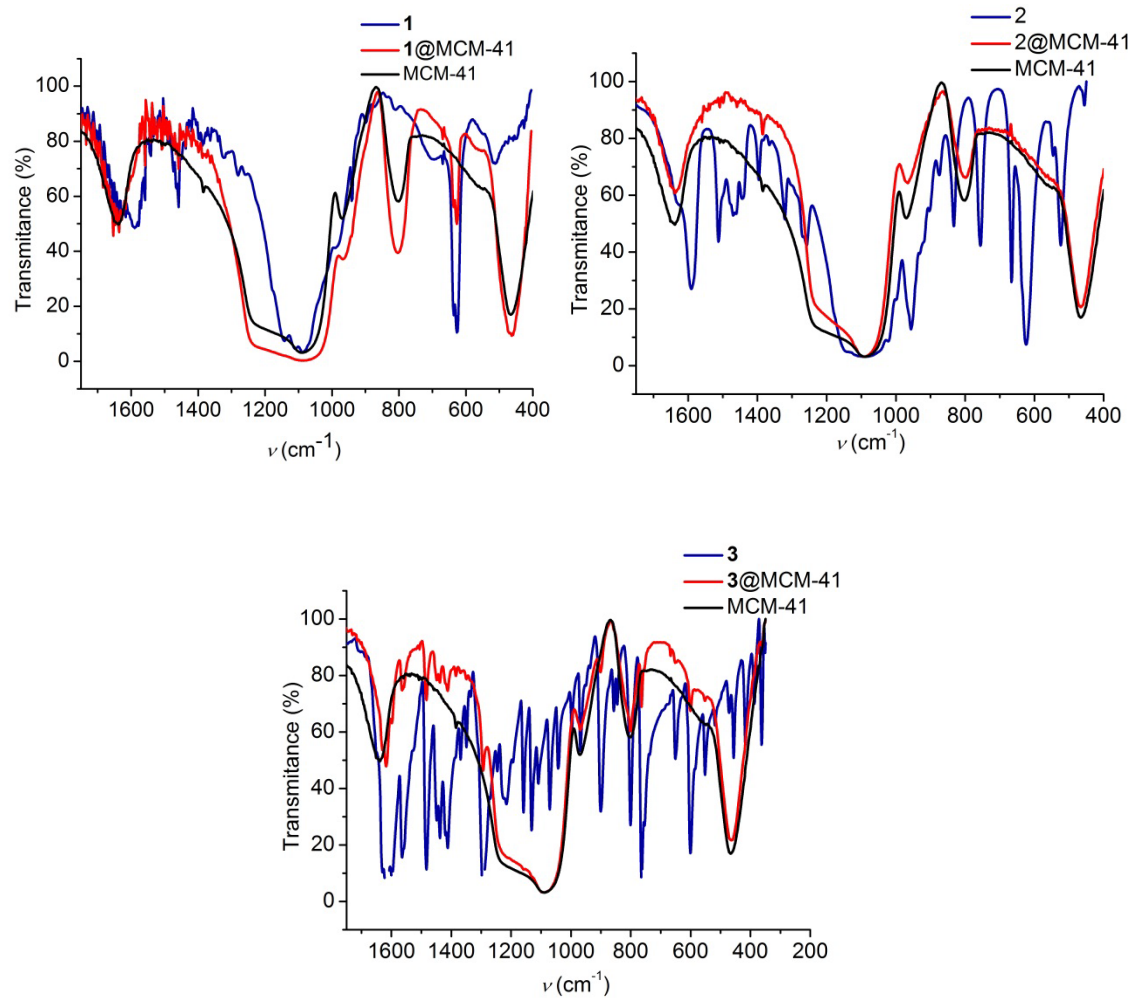


Figure S3. IR spectra of complexes and hybrid materials

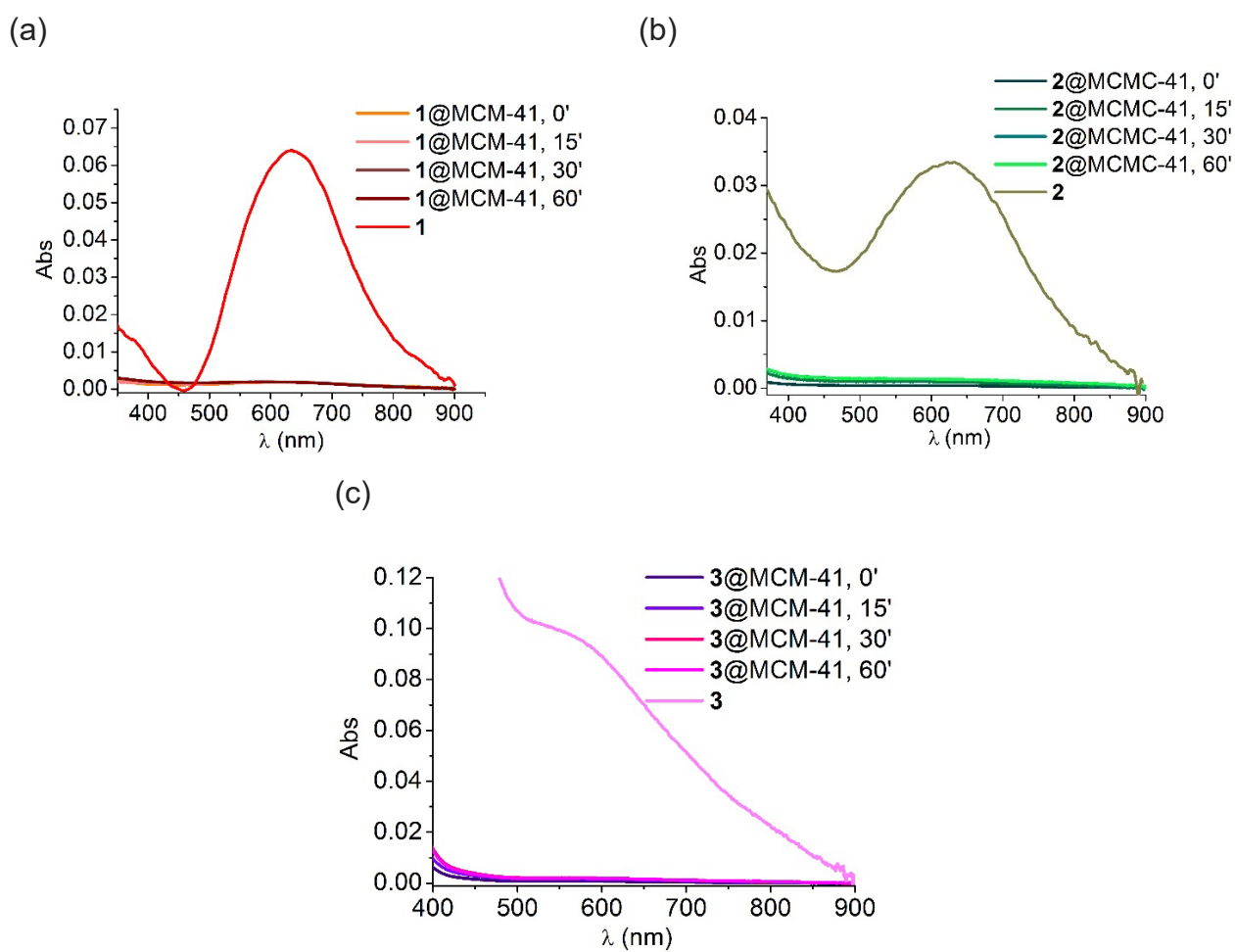


Figure S4. Electronic spectra of supernatant of hybrid suspensions after several incubation times in phosphate buffer of pH 7.8. (a) 1.3 mg/mL 1@MCM-41, [1] = 0.43 mM; (b) 1.5 mg/mL 2@MCM-41, [2] = 0.20 mM; (c) 1.1 mg/mL 3@MCM-41, [3] = 0.54 mM

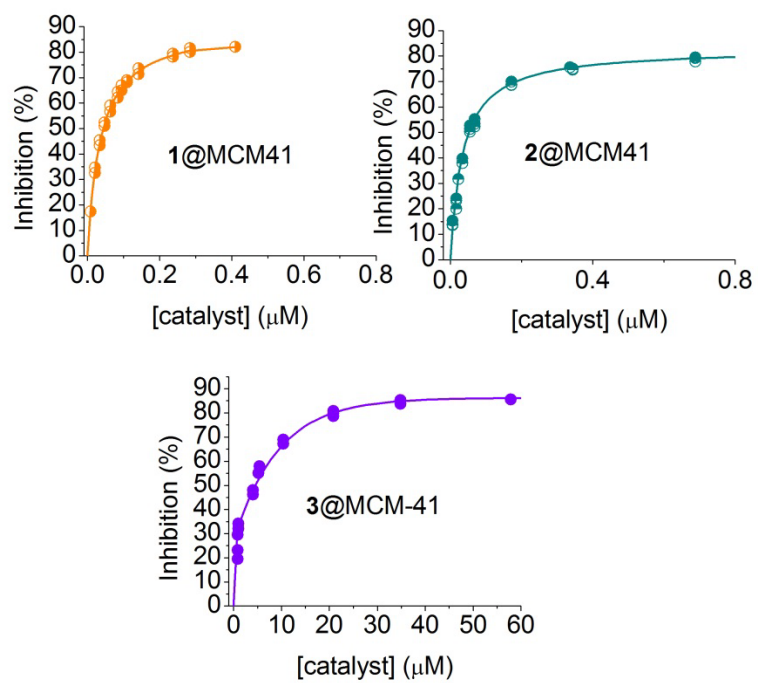


Figure S5. SOD activity of hybrids in the riboflavin-methionine-NBT assay