

Supplementary information

Catalyzed stereodivergent hydrosilylation with Onium Salts stabilized M(0) Nanocatalysts prepared in scCO₂

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Materials Characterization.

Powder XRD analysis on the above mentioned systems were performed using an X-ray diffractometer with Cu $\lambda_{K\alpha}$ radiation (PANalytical X'Pert Pro). For FTIR reflection measurements was used a Bruker spectrophotometer working in the range 7500-400 cm⁻¹.

Onim Salts with liquid crystal behavior during metal nanocrystals synthesis

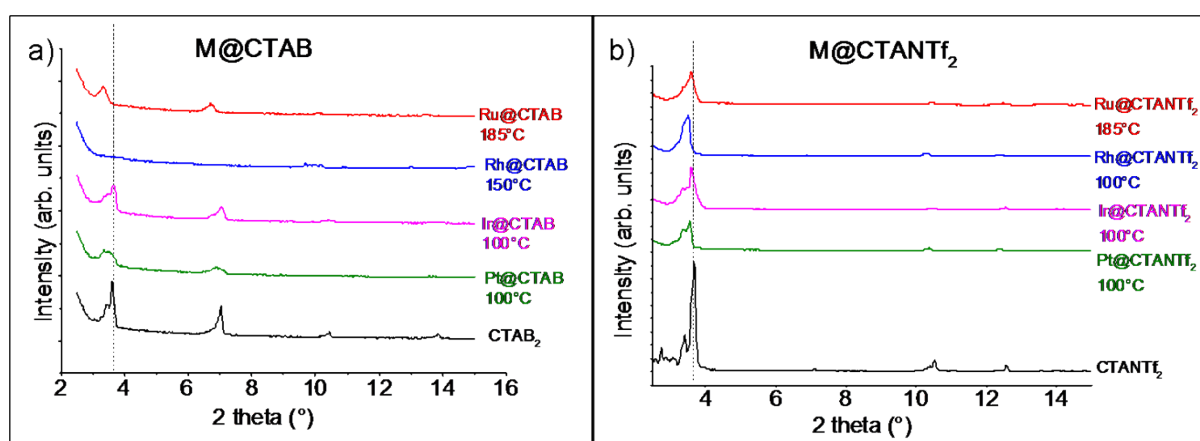


Figure 1S. XRD spectra of the systems M behaving as thermotropic liquid crystals showing a broader peak at low angle (2theta of 3.6 degree) compared with the pristine ionic salt

At the end of reaction, these liquid crystals will have an isotropic form, but still retaining some order.^{1,2,3} Experimentally, this was translated by the presence of a broad peak at very low angle in XRD spectra as proof for a layered structure (Figure 1S). The presence of this peak at low angle, demonstrate a layered structure during melting with a basal distance d , calculated using the Bragg law: $2d \cdot \sin \theta = \lambda$, where λ is the incident wavelength of 1.54 Å of Cu $\lambda_{K\alpha}$, making the angle θ with the surface. The sharp peak in the pristine ionic salt demonstrate a crystalline order which undergo a mesophase transition to a liquid crystal during melting and reaction, and by cooling at the end of the chemical reaction, will be transformed to isotropic form - peak position shifted and broadened (Table S1)

Table S1. Basal distance d (Å) calculated for each system.

CTAB	Ru@CTAB	Rh@CTAB	Ir@CTAB	Pt@CTAB
24.37	26.35	-	24.12	26.27
CTANTf ₂	Ru@CTANTf ₂	Rh@CTANTf ₂	Ir@CTANTf ₂	Pt@CTANTf ₂
24.12	24.71	25.22	24.54	24.98

¹ Scurto, A. M.; Newton, E. Weikel, R. R.; Draucker, L.; Hallet, J.; Liotta, Ch. L.; Leitner, W.; Eckert, Ch. A. *Ind. Eng. Chem. Res.* **2008**, *47*, 493-501;

² Kazarian, S. G.; Sakellarios, N.; Gordon, Ch. M. *Chem. Comm.* **2002**, 1314-1315;

³ Bradley, A. E.; Hardacre, C.; Holbrey, J. D.; Johnston, S.; McMath, S. E.; Nieuwenhuyzen, M. *Chem. Mater.* **2002**, *14*, 629-635.

Temperature influence in the size of the nanocrystals

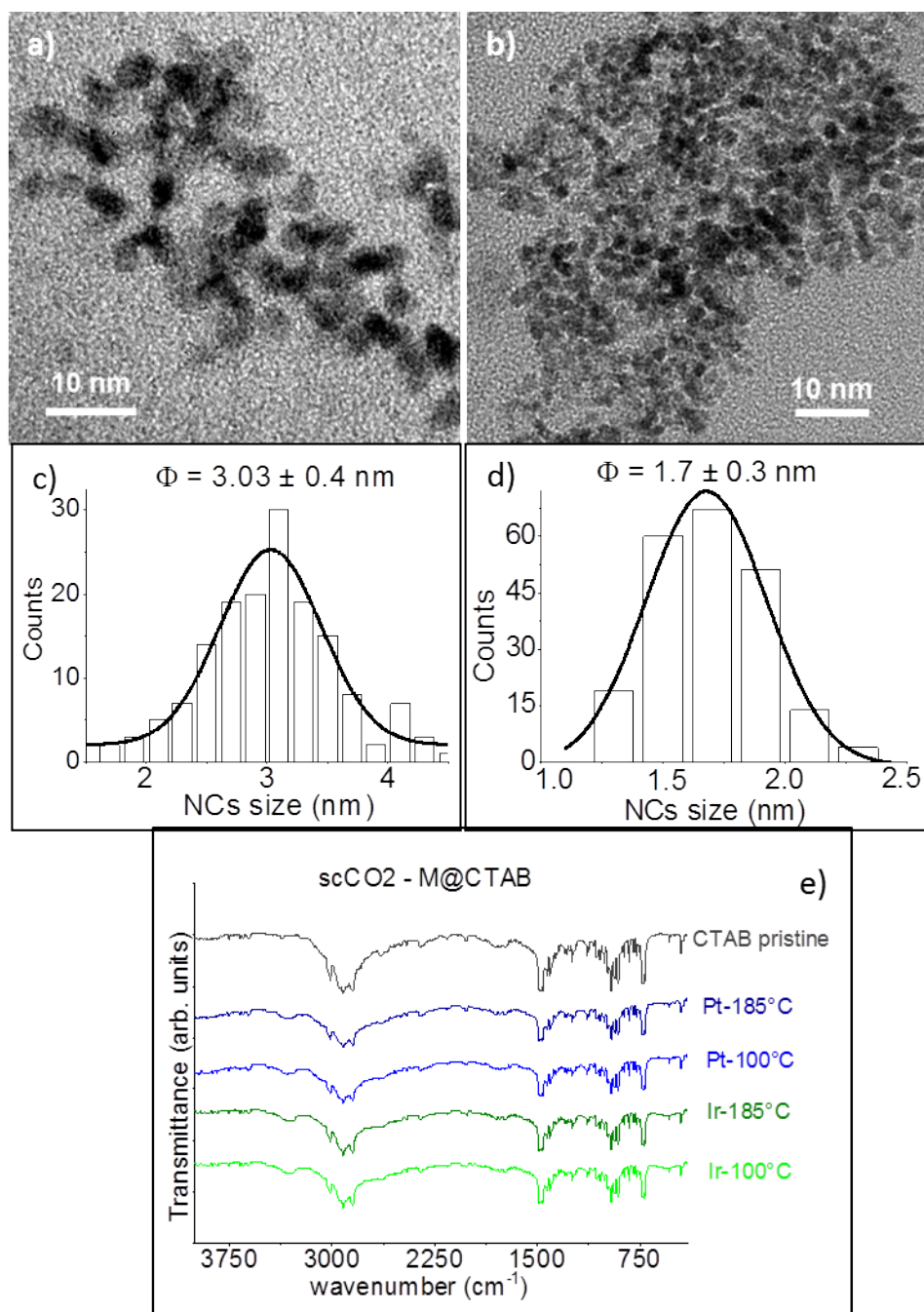


Figure 2S. TEM images of Ir@CTAB system prepared at two different reaction temperatures: **a)** at 100°C and **b)** at 185°C with the Gaussian size distribution (**c** and **d**); FTIR analysis of Ir and Pt@CTAB, at the two synthesis temperatures, in comparison with pristine CTAB. No changes in spectra after NCs formation.

Influence of metal nanocrystals formation and scCO₂ environment over the organic ionic solid structure

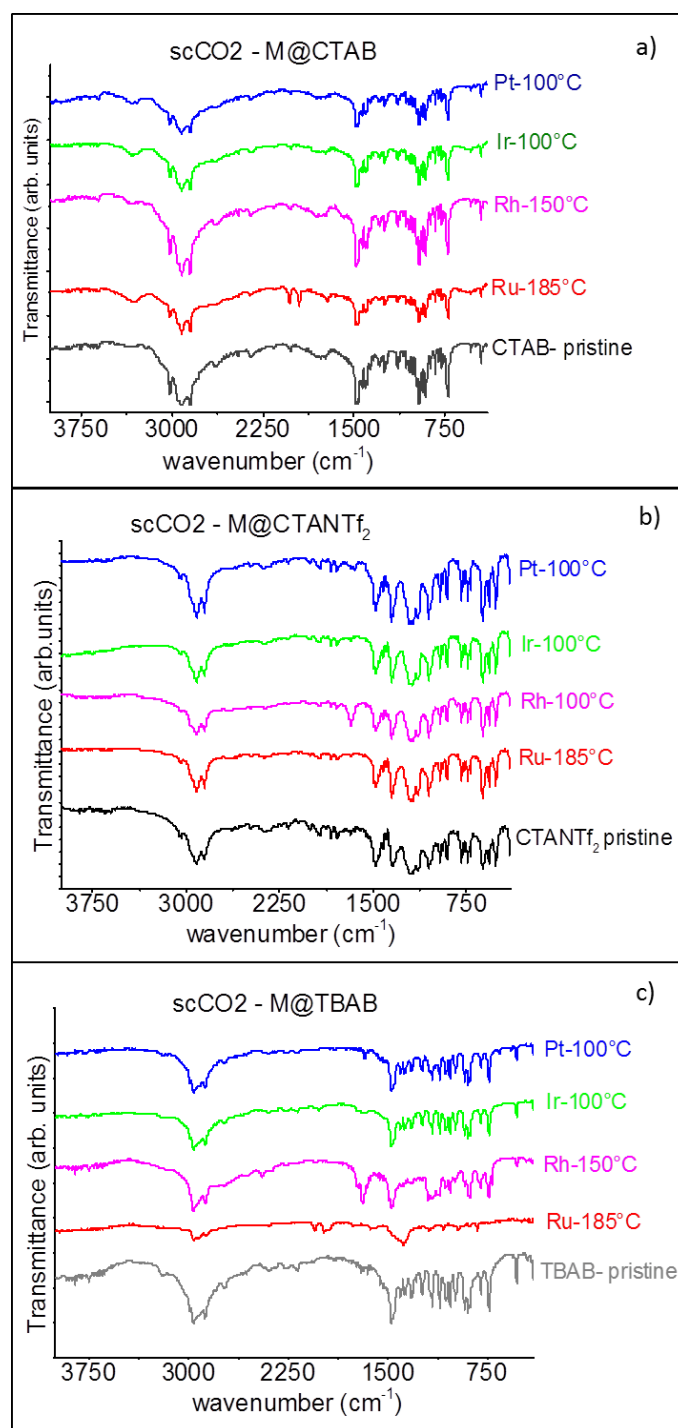
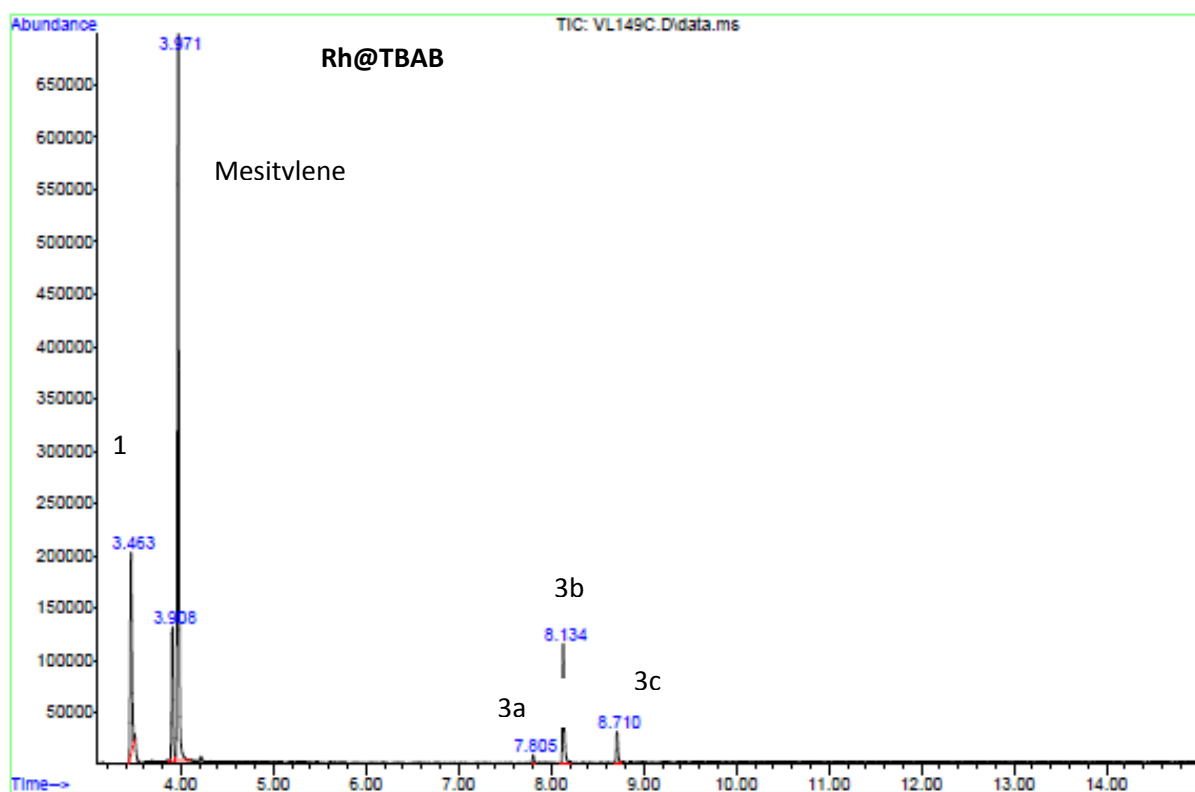
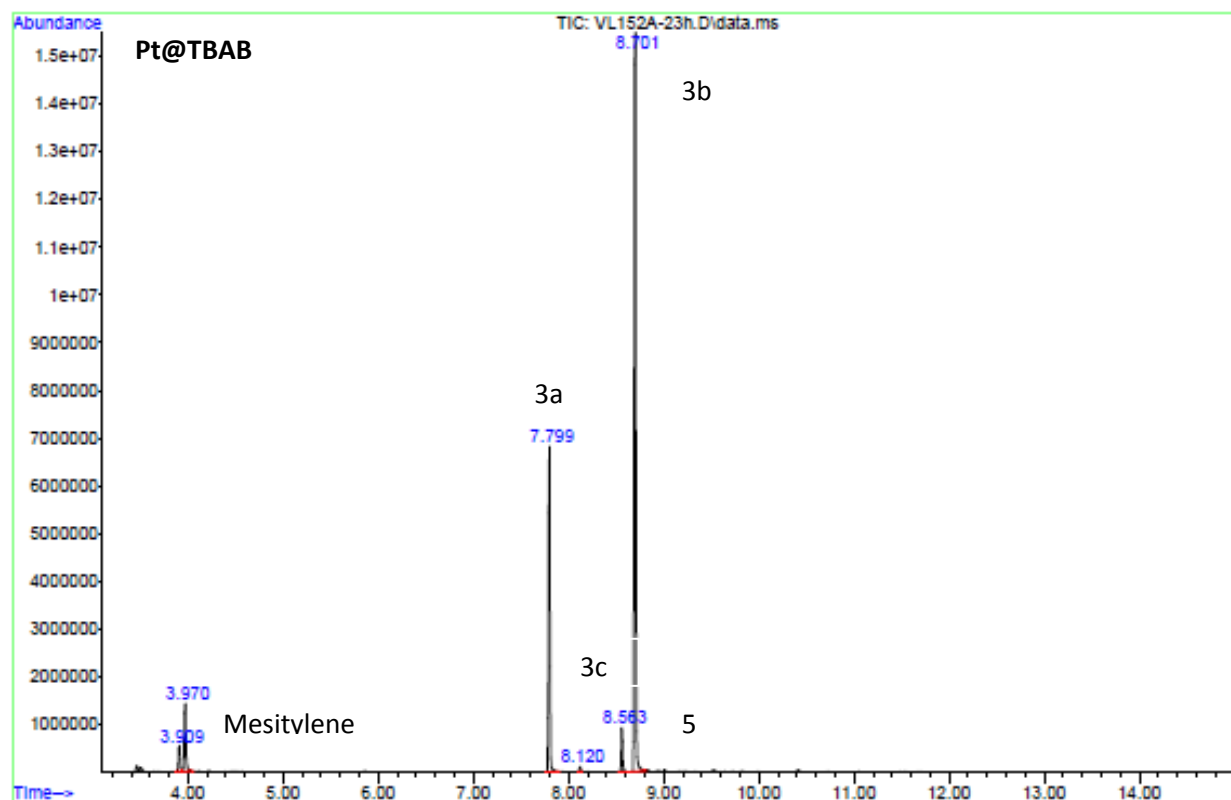


Figure 3S. Comparative FTIR spectra of pristine OS and M@OS.

GC/MS Chromatogram:



¹H NMR Spectra

