Topochemical Polymerization of Phenylacetylene Macrocycles Under Pressure

Andrea Lapini,[†,‡] Samuele Fanetti,[*,†,¶] Margherita Citroni,[†] Roberto Bini,[†,¶] Charles-Olivier Gilbert,[§] Simon Rondeau-Gagné,[‖] and Jean-Francois Morin[§]

†*European Laboratory for Nonlinear Spectroscopy (LENS), via Nello Carrara 1, 50019 Sesto Fiorentino (FI), Italy*

‡*Istituto Nazionale di Ottica (INO), Largo Fermi 6, Firenze (FI), Italy*

¶*Dipartimento di Chimica "Ugo Schiff", Università di Firenze, via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy*

§*Département de Chimie and Centre de Recherche sur les Matériaux Avancés (CERMA), Université Laval, 1045 Ave de la Médecine, Pavillon Alexandre-Vachon, Québec, QC, Canada G1V 0A6*

‖ *Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Ave. Windsor,Ontario, ON, Canada N9B3P4*

E-mail: fanetti@lens.unifi.it

Phone: +39 055 457 2536

Supporting Information Available

PAM2 and PBM2 were synthesizes according to previous reports.[1,2] For each sample, the powder was dissolved in chloroform (Sigma Aldrich) in concentration of 30 mg/ml. The solution rapidly formed a white gel. For each high-pressure run, a drop of gelified sample was loaded into a high-pressure cell with a micropipette. The sapphire anvil cells (SACs) were equipped with high-purity, low fluorescence sapphire anvils with culet diameter of 1 mm. Preindented beryllium-copper gaskets were used, and the initial sample's dimensions were ∼50-80 μm in thickness and ∼500 μm in diameter. In one run, a diamond anvil cell (DAC) was used to reach a pressure of 5.5 GPa. The DAC was equipped with IIa type diamonds, a stainless steel gasket was used and the initial sample dimensions were 150 μm in diameter and 50 μm in thickness. Both SACs and DAC were membrane anvil cells, where the pressure was applied remotely and finely tuned using Helium gas flowing into or out of the membrane. In all the runs, a ruby chip with diameter $\leq$10μm was loaded within the sample as pressure gauge. The pressure was then measured with the ruby fluorescence method[3] using $\leq$5 mW of the 2nd harmonic of a Nd:Yag laser (532 nm) focused on the ruby. Irradiation of the samples to induce the reactivity was performed by focusing the beam of an Ar^+ laser with a lens (f = 200 mm) placed at such distance as to uniformly irradiate the whole sample's surface. For visible irradiation we used the 514 nm with power of 70 mW. For near-UV irradiation we used the UV multiline, centered at 350 nm, with power of 100 mW. The reflections on the two surfaces of the front anvil are of the order of 5-10 % for the visible and 15-20 % for the near UV, for sapphire and diamond respectively. Heating of the sample was achieved by inserting the SAC into a resistively heated *clamp* and the temperature was measured by a K-thermocouple touching one anvil.

Fourier-transform Infrared Spectra were measured with a Bruker IFS 120 HR spectrometer adapted for in-situ measurements in the diamond or sapphire anvil cells,[4] using ellipsoidal mirror for focusing the IR beam on the sample. The spectra were measured with a resolution of 1 cm^{-1} in the region 600 - 5000 cm^{-1}.

As a preliminary step, we checked that PBM2 is non-reactive under UV irradiation at ambient pressure. To do that, the gelified sample was loaded into a room-pressure cell, between CaF_2 windows with a PTFE spacer 50 μm thick and was irradiated for 15 h with the 514 nm line of an CW Ar^+ laser (70 mW), and then for 15 h with the 266 nm line III harmonic of a Ti:Sapphire amplified laser (5-10 mW). In both cases, the beam was focused to a spot matching the sample's diameter 8 mm. No changes in the IR spectra measured before and after irradiation as well as in the sample appearance were detected thus excluding the occurrence of the polymerization reaction.

The formation of a non-negligible amount of diacetylene units would be able to change the colour to an intense blue.[2] The lack of reactivity of PBM2 at room pressure, under UV irradiation, was thus confirmed.

Raman characterization of both PBM2 and product was prevented by a strong fluorescence background independently of the excitation wavelength (458-657 nm).

TEM images of the recovered products were recorded with a *TEM CM 12 PHILIPS* instrument. The recovered samples were dispersed in chloroform and sonicated at 60° C for 24 h. A drop of the suspension was then deposited onto a Cu grid. The TEM resolution Range was from 20 a 120 kV, giving rise to a resolving power of 0.034 nm.

The XRD patterns were measured at ID27 of the ESRF, European Synchrotron Radiation Facility, with $\lambda = 0.3738$ Å and a beam diameter of approximately 3 μm, on the recovered solid samples in air, removed from the sapphire anvil cell.

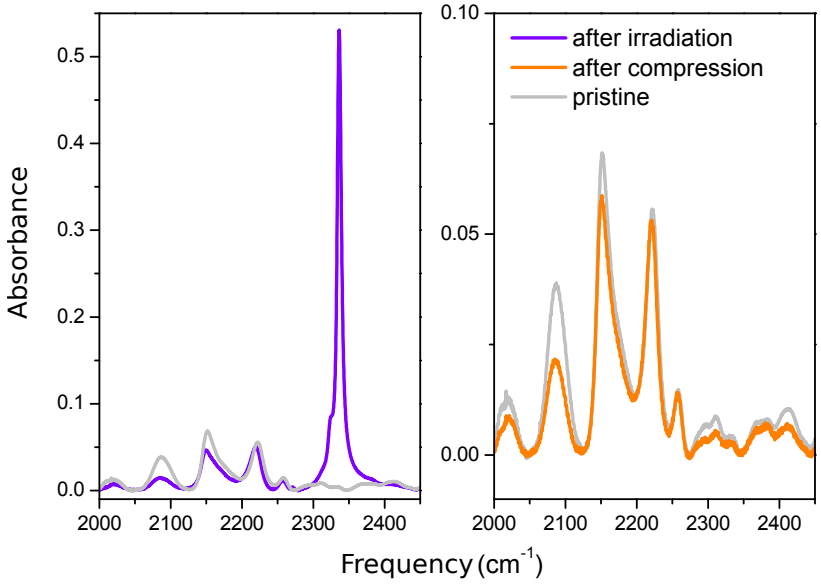

Figure S1: IR spectra of the reaction products of PAM2 in the sapphire anvil cell, in the region of C≡C and CO_2 stretching. Gray lines: spectrum of PAM2 gel as loaded. Left: violet line, spectrum of the product obtained at room temperature and nearly room pressure ($<$ 1 kbar) after 45 minutes of Ar^+ CW Laser irradiation at 350 nm (100 mW). Right: orange line, spectrum of the product obtained by compression to 3.4 GPa and decompression.

References

(1) Rondeau-Gagné, S.; Néabo, J. R.; Desroches, M.; Larouche, J.; Brisson, J.; Morin, J.-F. Topochemical Polymerization of Phenylacetylene Macrocycles: A New Strategy for the Preparation of Organic Nanorods *J. Am. Chem. Soc.* **2013**, *135*, 110-113.

(2) Rondeau-Gagné, S.; Néabo, J. R.; Desroches, M.; Levesque, I.; Daigle, M.; Cantin, K.; Morin, J.-F. Rigid Organic Nanotubes Obtained from Phenylene-Butadiynylene Macrocycles *Chem. Commun.* **2013**, *49*, 9546-9548.

(3) Mao, H. K.; Bell, P. M.; Shaner, J. V.; Steinberg, D. J. Specific Volume Measurements of Cu, Mo, Pd, and Ag and Calibration of the Ruby R1 Fluorescence Pressure Gauge from 0.06 to 1 Mbar *J. Appl. Phys.* **1978**, *49*, 3276-3283.

(4) Bini, R.; Ballerini, R.; Pratesi, G.; Jodl, H. J. Experimental Setup for Fourier Transform Infrared Spectroscopy Studies in Condensed Matter at High Pressure and Low Temperatures *Rev. Sci. Instrum.* **1997**, *68*, 3154-3160.