Single Molecule Raman Spectra of Porphycene: Isotopologues Compete for Hot Spots

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Supporting Information

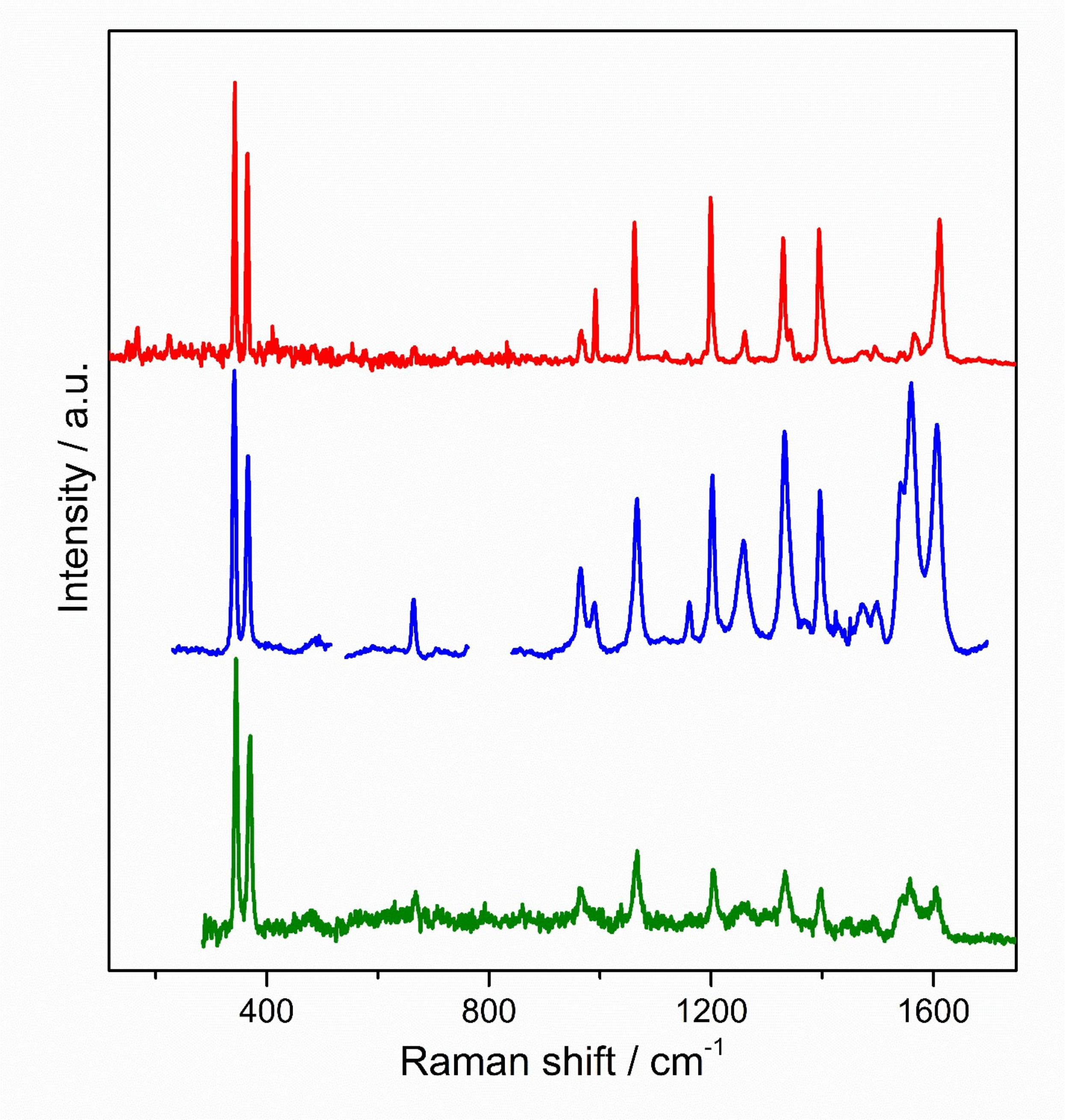

Figure S1. Raman and SERS spectra of Pc-d_0 at 293 K obtained for different environments with 785 nm excitation. Raman spectrum of a crystalline sample (red); Raman spectrum in acetone solution (blue); averaged SERS spectrum on gold nanobars (green). Regions affected by the acetone bands have been removed.

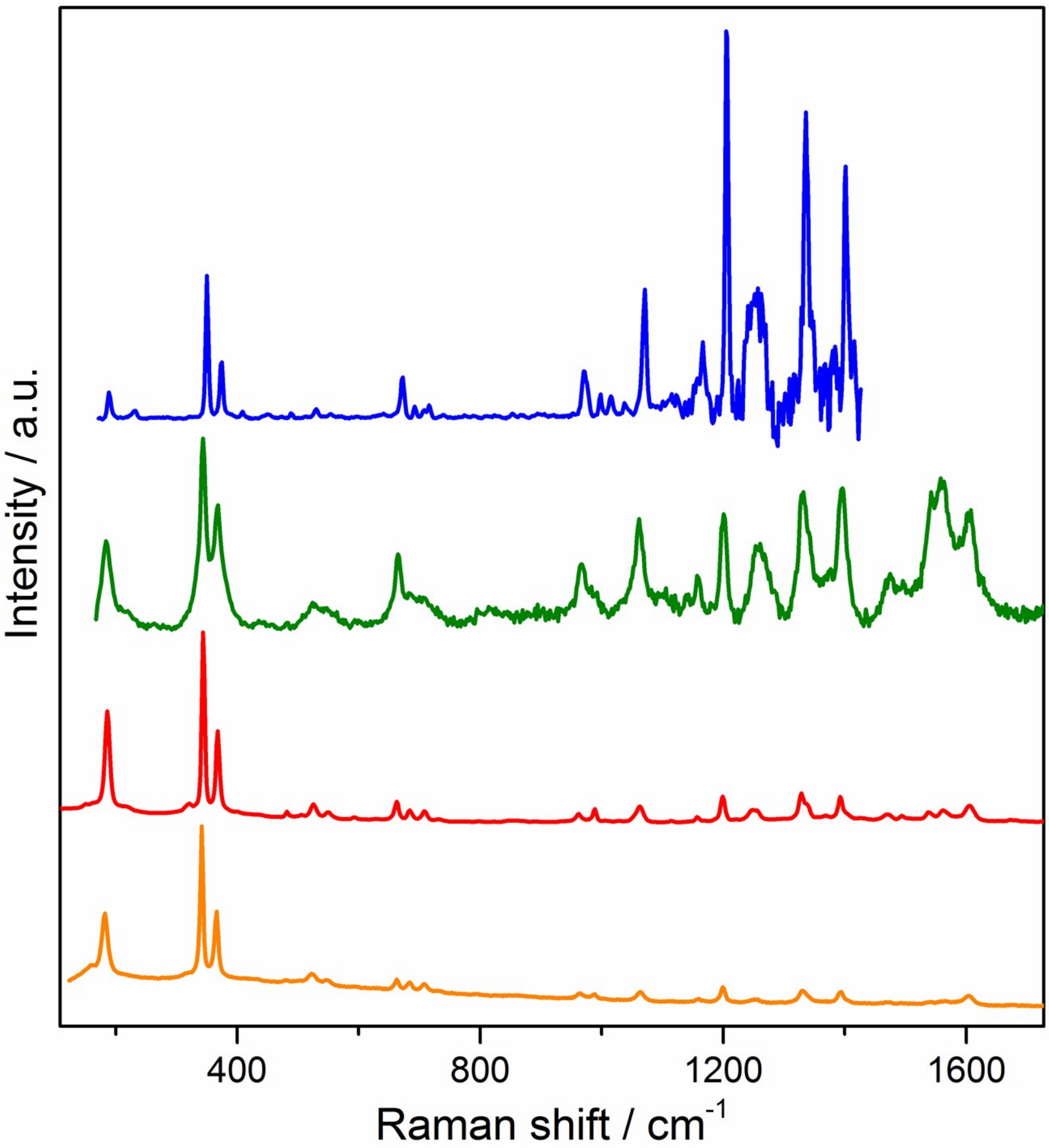

Figure S2. Raman and SERRS spectra of Pc-d_0 obtained for different environments with 632.8 nm excitation. Raman spectra of a monocrystal at 77 K (blue) and polycrystalline thin film smashed on glass at 293 K (green); averaged SERS spectra on gold nanostructures measured at 77 K (red) and at room temperature (orange).

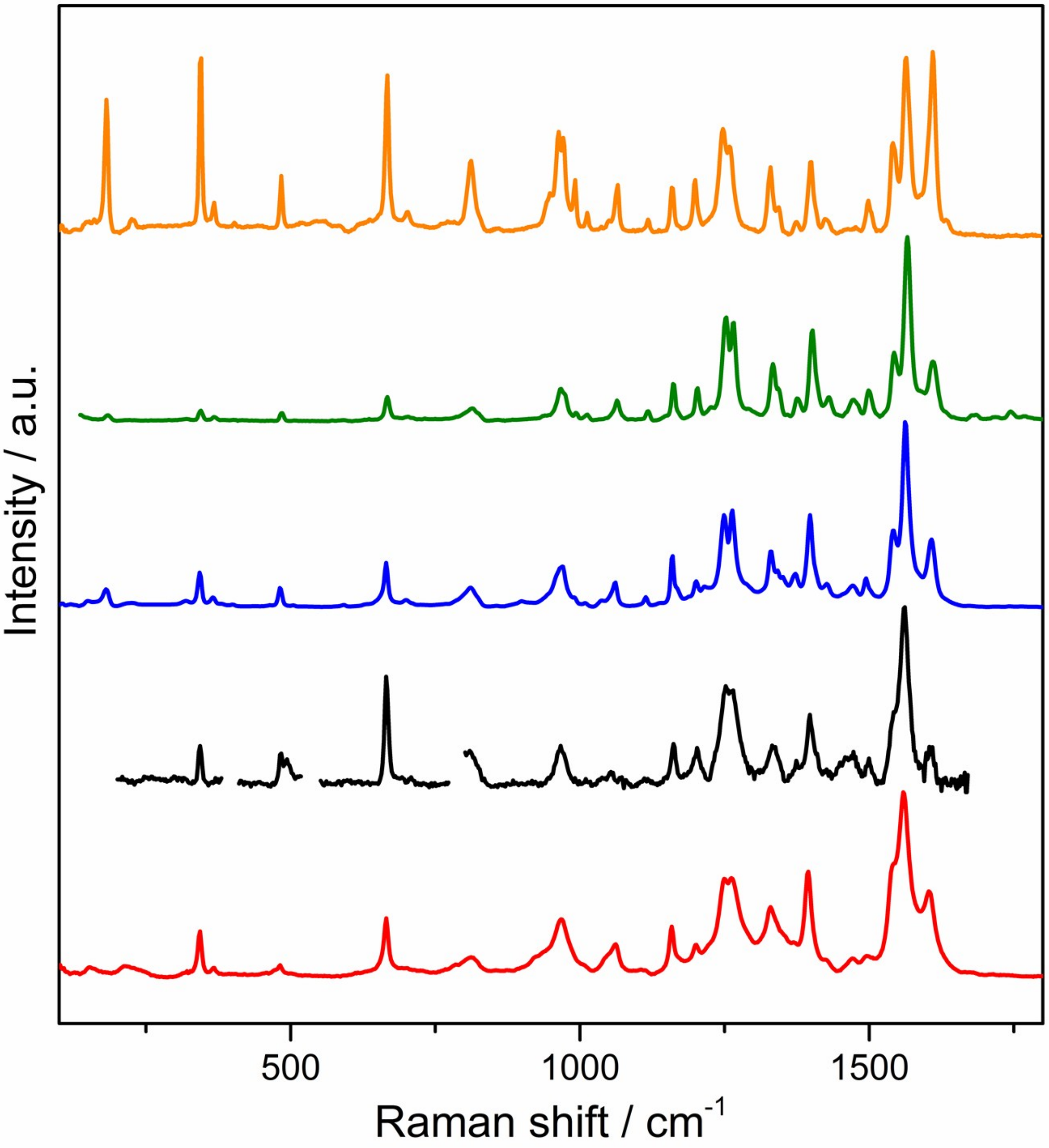

Figure S3. Raman and SERRS spectra of Pc-d_0 obtained for different environments with 514.5 nm excitation: Raman spectra of a crystalline sample at 77 K (orange); Raman spectra in Ar (green) and Xe (blue) matrices measured at 6 K; Raman spectra in acetone solution recorded at room temperature (black); averaged SERS spectra on gold nanostructures measured at 293 K (red). Regions affected by the acetone bands have been removed.

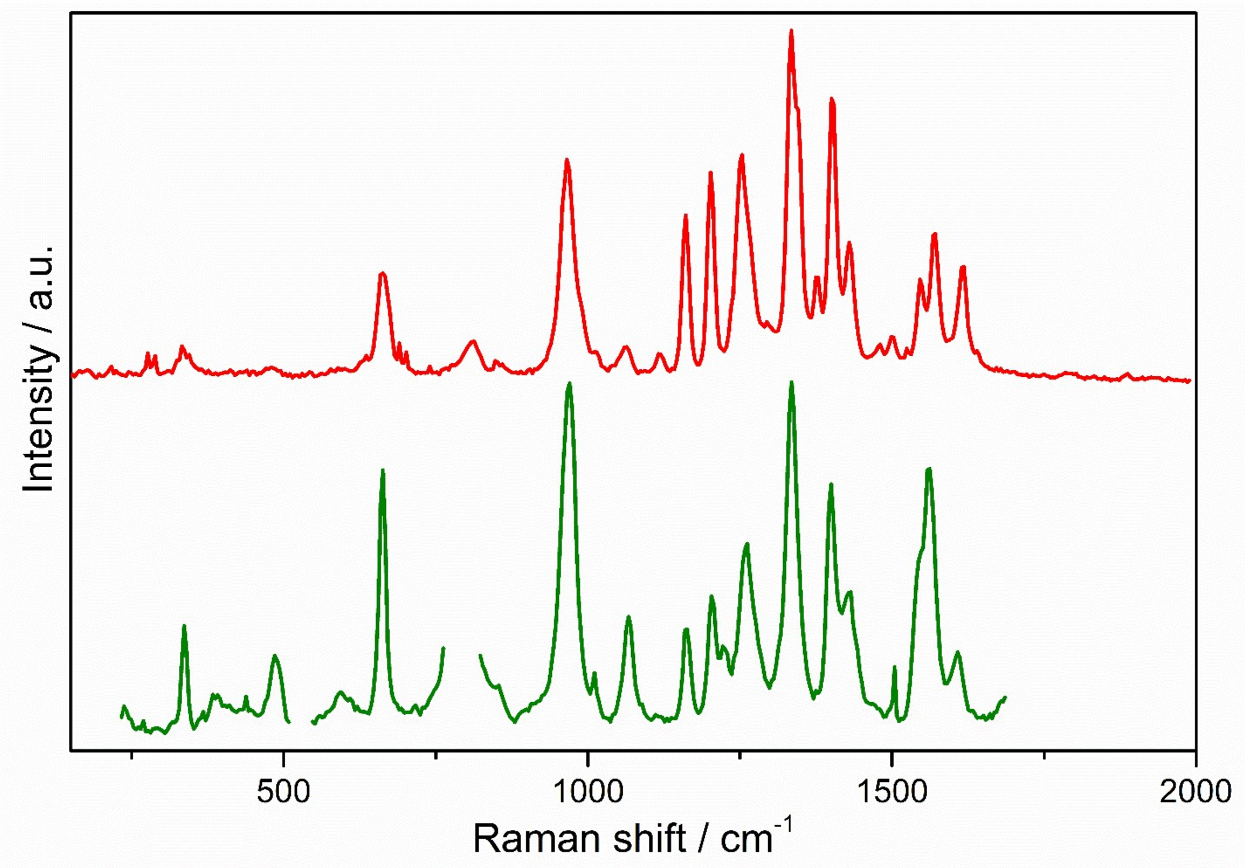

Figure S4. Raman spectra of Pc-d_0 obtained with 325 nm excitation from a crystal (red) and from solution in acetone (green). Regions affected by the acetone bands have been removed.

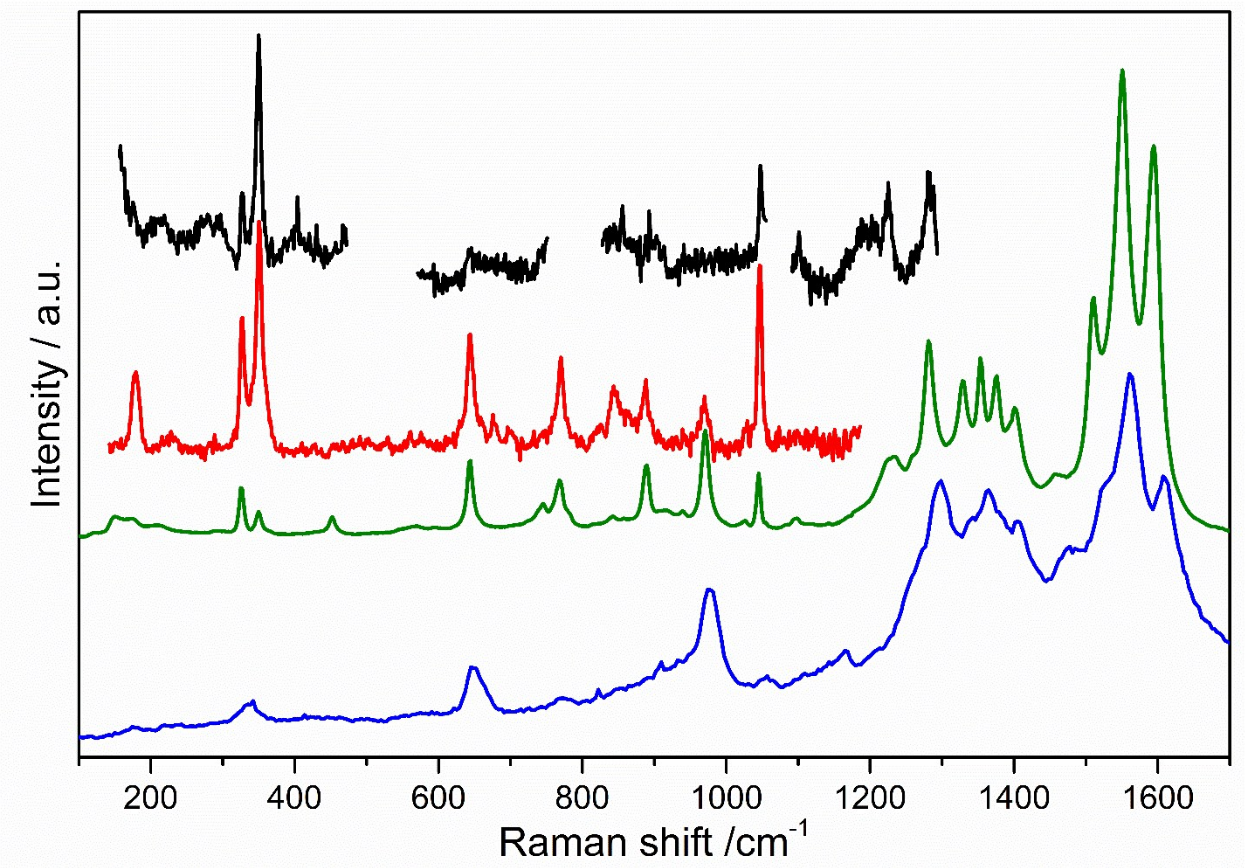

Figure S5. Raman spectra of Pc-d_{12} solution in acetone excited at 785 nm (black) and from crystal excited at 633 nm (red), 514 nm (green), and 325 nm (blue).

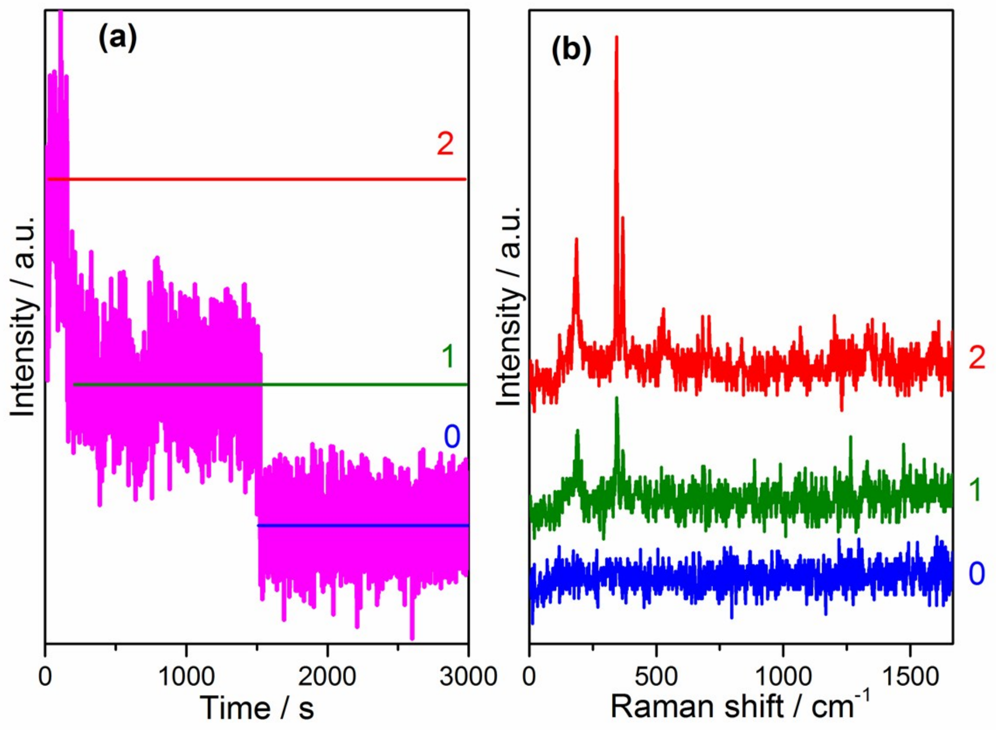

Figure S6. Left: time evolution of the intensity of the 343 cm^{-1} peak of Pc-d_0 deposited from "medium" concentration (~10^{-8} M) ethanol solution (20 μW laser power at the sample, acquisition time 300 ms/spectrum). Right, Raman spectra recorded at three different times.

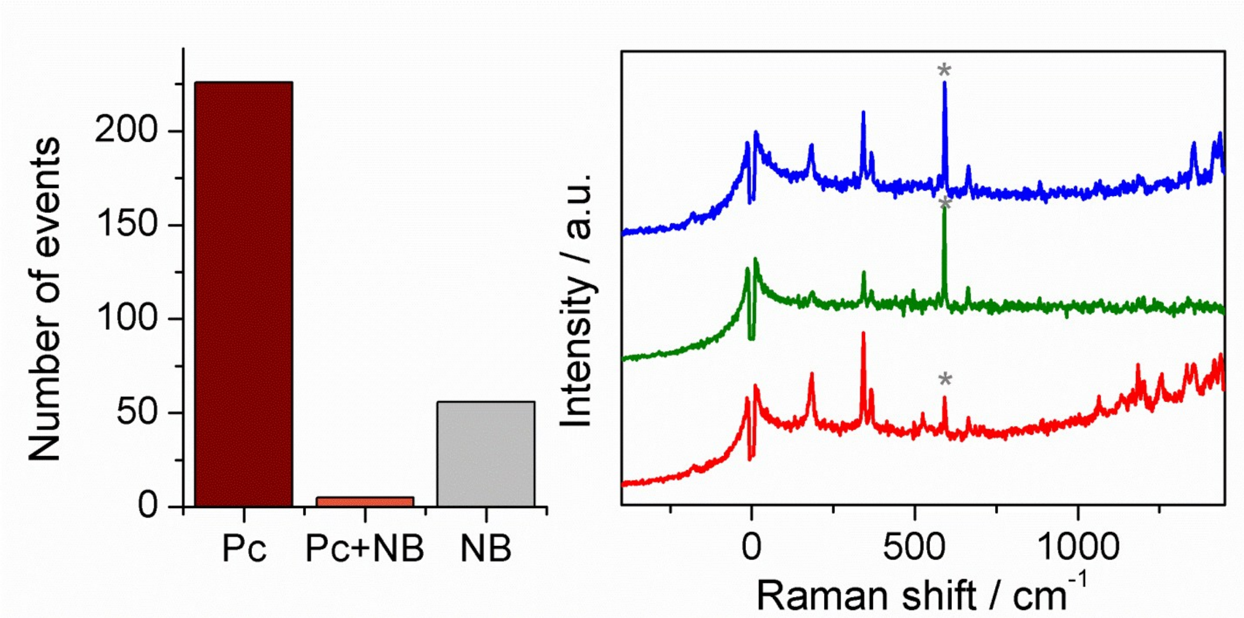

Figure S7. Histograms showing the occurrence of single chromophore vs mixed chromophore events, obtained for 1:1 Pc-d_0:Nile blue mixtures of 10^{-8} M concentration. Electrochemically prepared Au NPs, 50 μW laser power, 293 K.

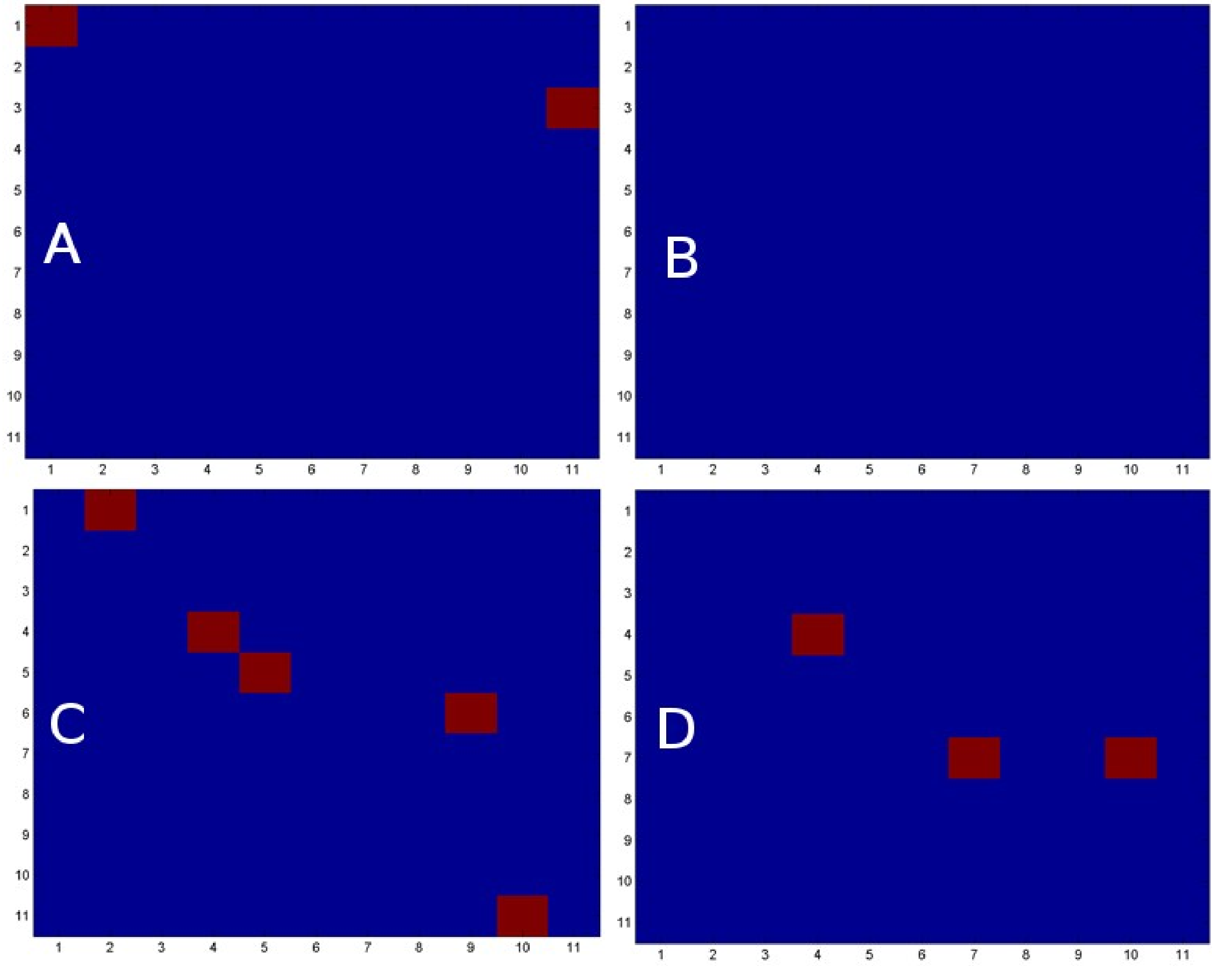

Figure S8. Selected frames from consecutive 200 SERS maps of Pc-d_0 deposited from 10^{-9} M solution on gold NPs/glass substrate, registered after: 0 min. (A), 22 min. (B), 30 min. (C), 57 min. (D). Attached gif file (map.gif) shows time evolution during the recording of the first 100 maps (500 ms/spectrum, 50 μW laser power, registration time of every single map was 73 s).

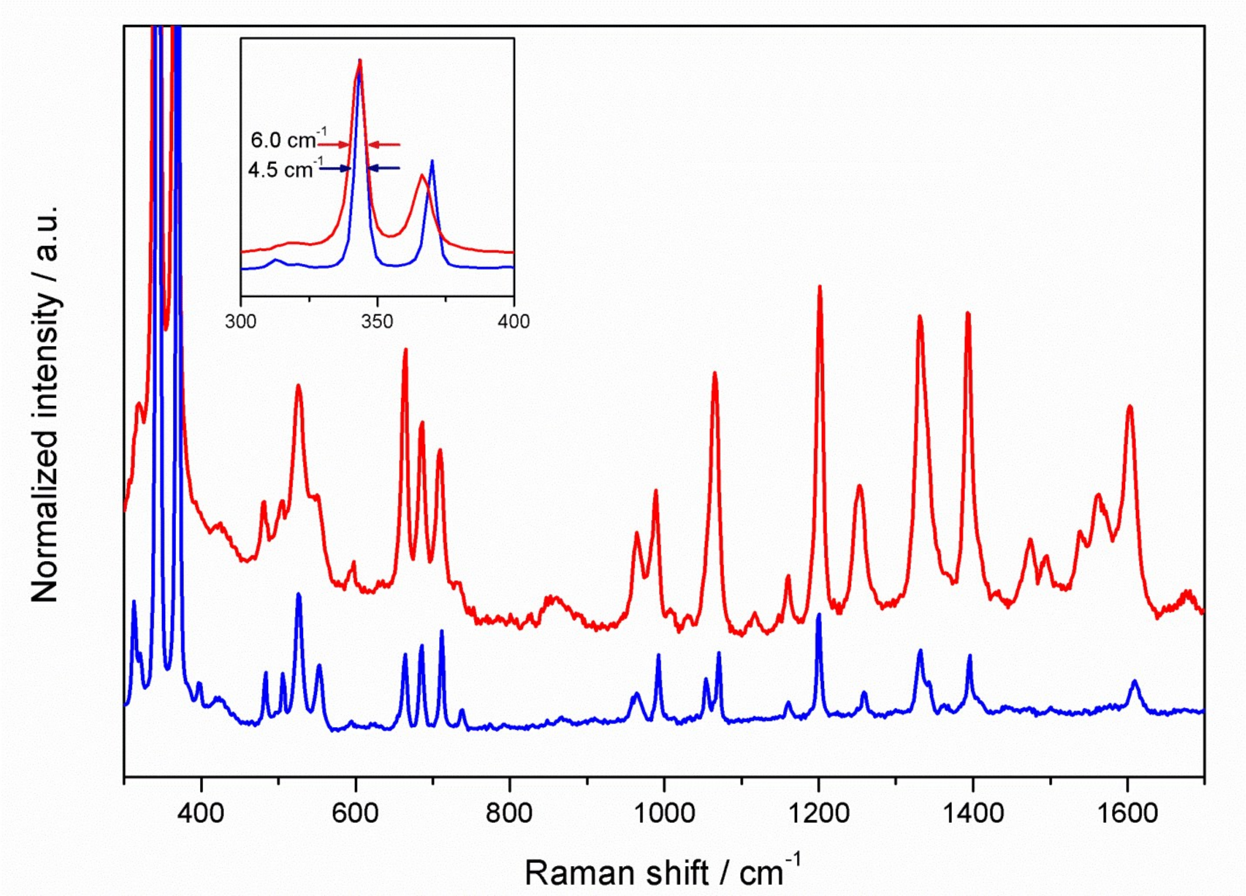

Figure S9. Spectra from two hot spots, averaged over 500s, measured at different temperatures: 123K (bottom, blue) and 293 K (top, red). Chemically synthesized Au NPs, 50 μW laser power.

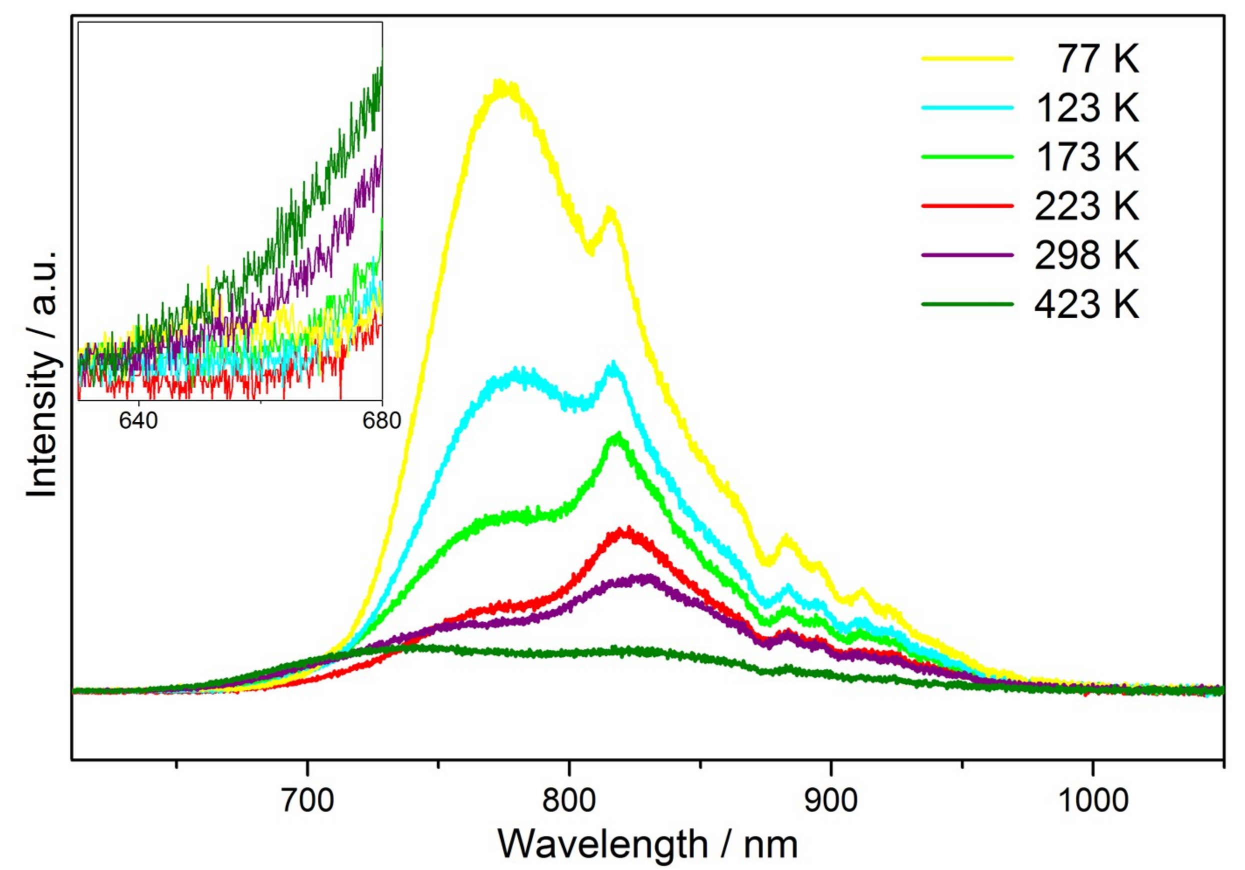

Figure S10. Fluorescence of Pc d_0 crystal excited with 633 nm laser line at different temperatures.

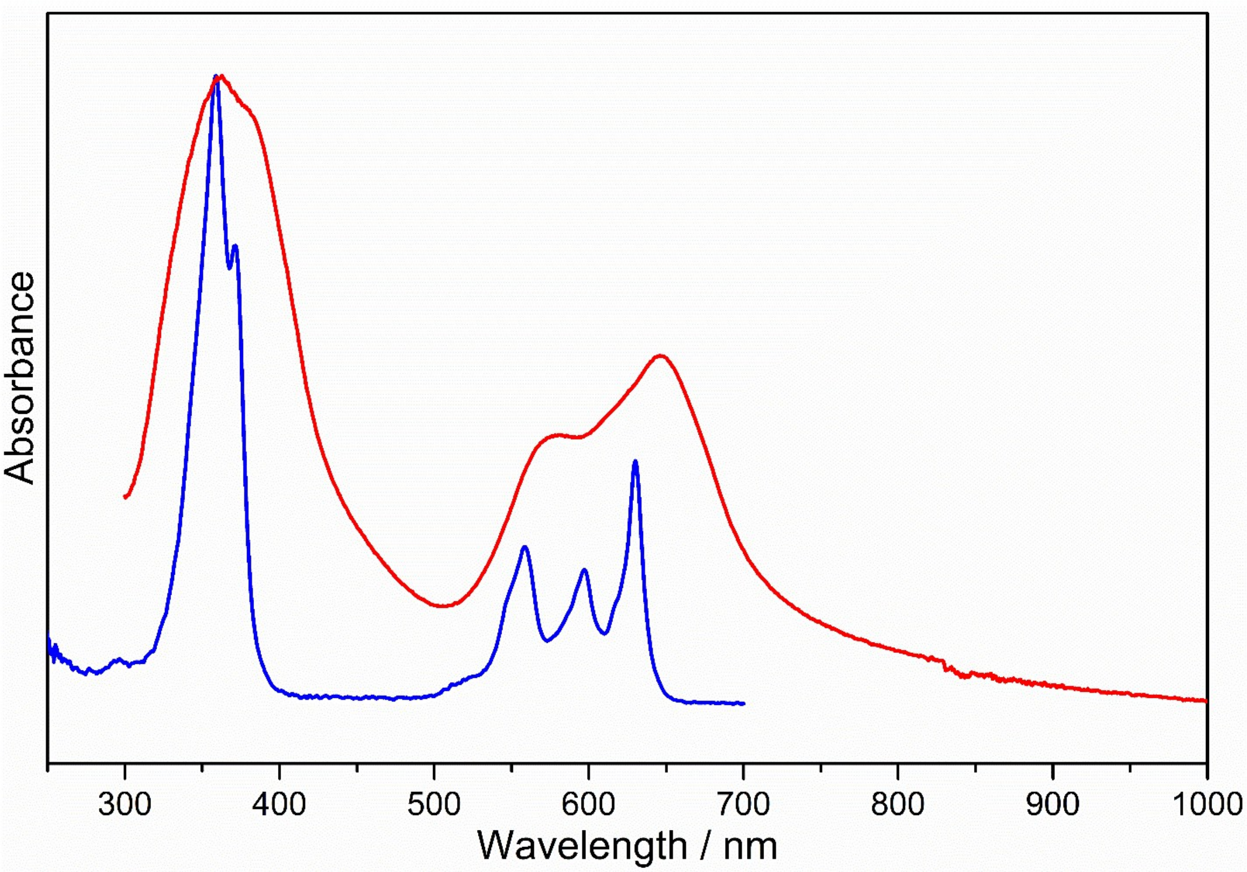

Figure S11. Normalized absorption spectra of Pc-d_0 in tetrahydrofuran solution (blue) and of thin polycrystalline film on glass (red) at room temperature.

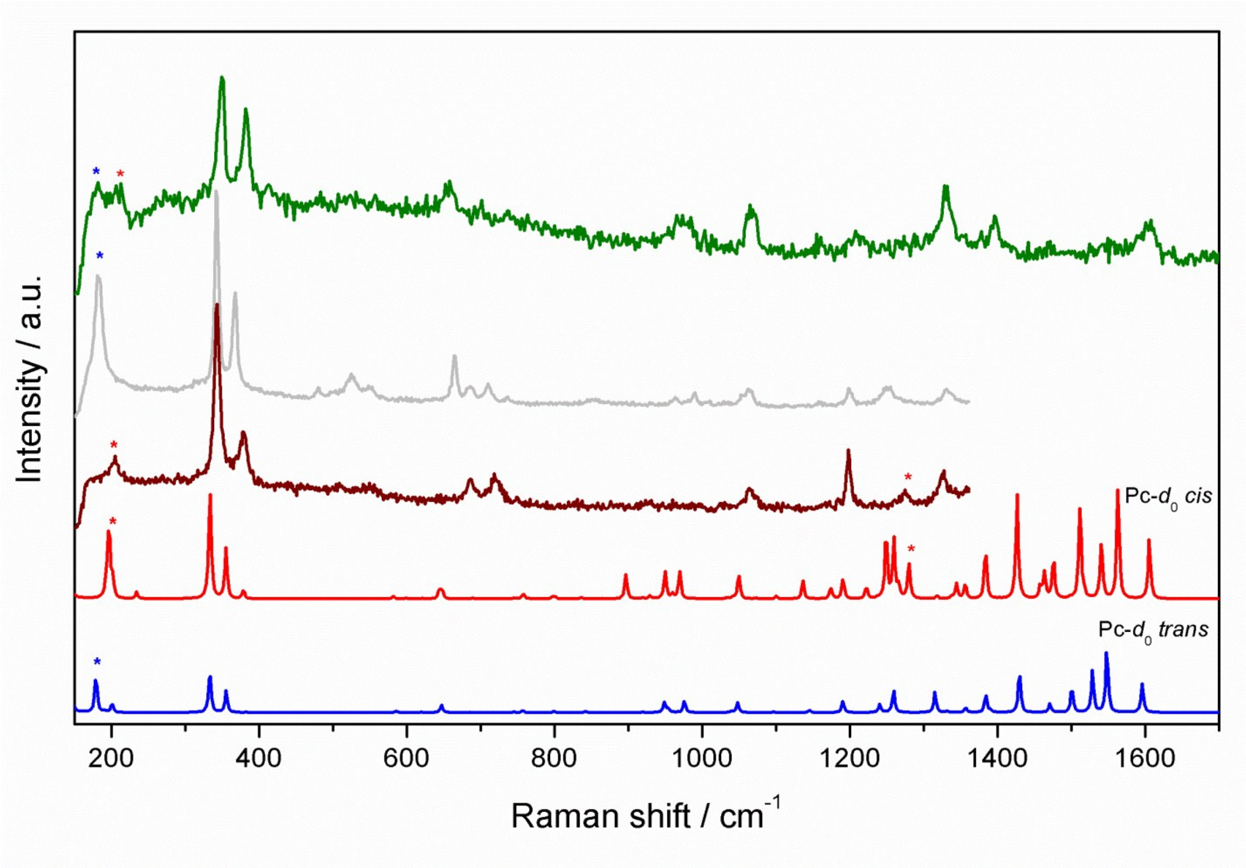

Figure S12. Three SMR spectra recorded from different hot spots (632.8 nm excitation, 298 K), compared with theoretical (B3LYP/6-31G(d,p), frequencies scaled by 0.96) predictions of Raman intensities for *trans* (blue) and *cis* (red) tautomeric forms. The asterisks mark the bands that reveal different frequencies in the two isotopologues.