Electronic Supplementary Material (ESI) for Faraday Discussions.

SUPPORTING INFORMATION

Chameleon-like Behaviour of Cyclo[n]paraphenylenes in Complexes with C_{70}. On Their Impressive Electronic and Structural Adaptability as probed By Raman spectroscopy.

Miriam Peña Alvarez [a], Paula Mayorga Burrezo[b], Takahiro Iwamoto[c], Lili Qiu[d], Miklos Kertesz[d], Mercedes Taravillo[a], Valentín G. Baonza[a] , Juan T. López Navarrete[b],*, Shigeru Yamago[c], Juan Casado[b,]

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[a]*MALTA-Consolider Team, Department of Physical Chemistry, Chemistry faculty, University Complutense of Madrid, 28040 Madrid, Spain.*

[b]*Department of Physical Chemistry, University of Málaga, CEI Andalucía Tech, Campus de Teatinos s/n, 29071-Málaga, Spain.* Fax: 0034952132000; Tel: 0034952131868; E-mail: *casado@uma.es*

[c]*Institute for Chemical Research, Kyoto University, Uji 611-0011, Japan.*

[d]*Department of Chemistry and Institute of Soft Matter, Georgetown University, 37th and O Streets, NW, Washington, D.C. 20057-1227, USA.*

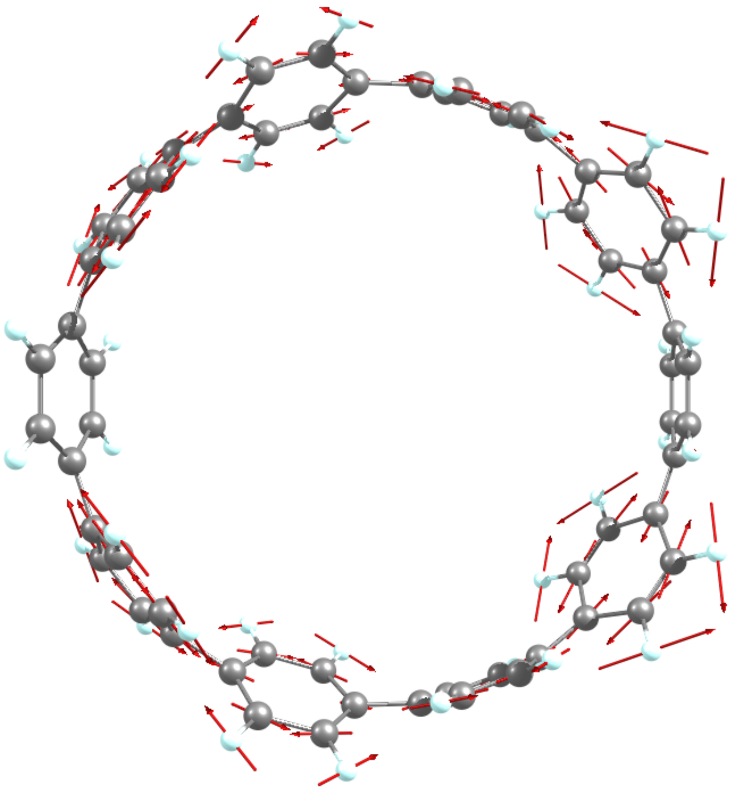
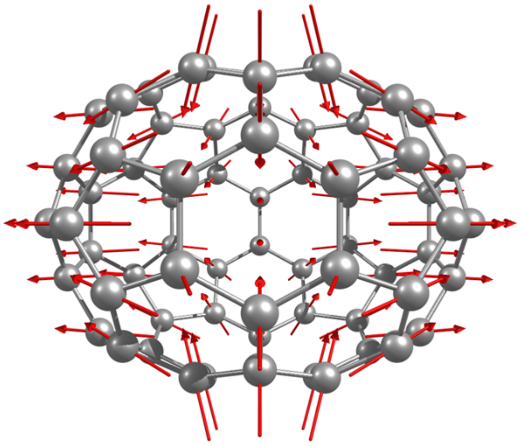
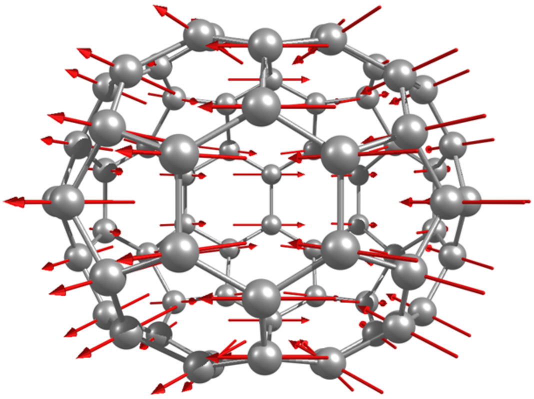


Figure S1. Vibrational modes associated to the G2 band of [10]CPP

Cage squashing mode 1, 261 cm^{-1}



Cage squashing mode 2, 252 cm^{-1}



Cage squashing mode 21, 224 cm^{-1}

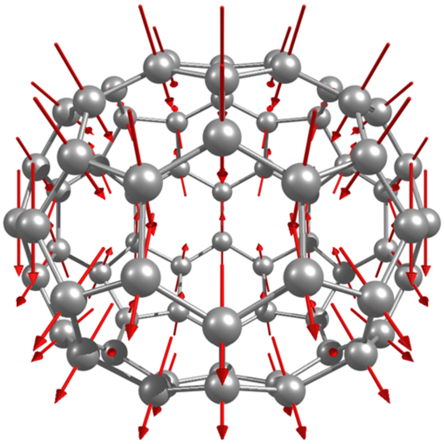


Figure S2. *Vibrational mod asociates to the* C_{70} *low frequency modes, known as cage squashing modes.*

Experimental Raman spectra in the 1150-1350 cm^{-1} range at room conditions

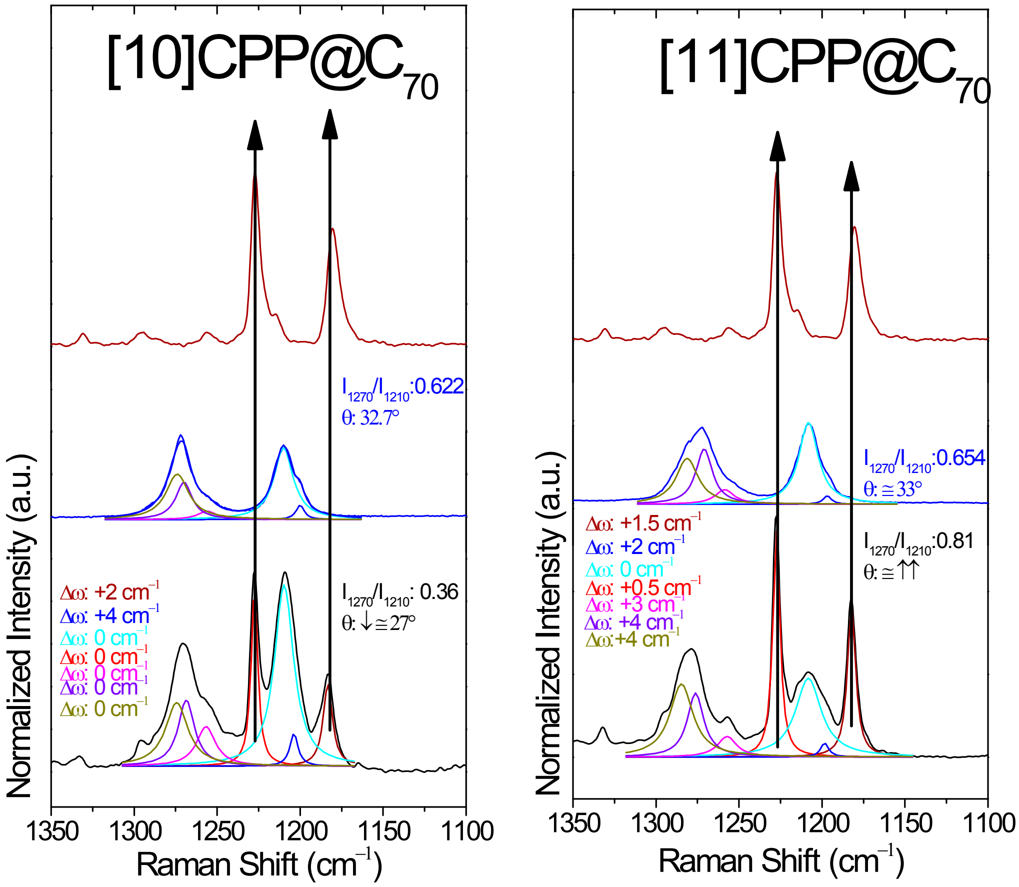


Figure S3. *785 nm experimental Raman spectra in the 1100-1350 cm^{-1} range. Left(a):[10]CPP@C_{70}; righ (b)t: [11]CPP@C_{70}. From bottom to top: pristine complex (black), pristine [n]CPP (dark blue), pristine C_{70} (dark red), all registered in solid state and ambient conditions.. These spectra have been deconvoluted into their different contributions: red lines correspond to C_{70} contributions (being the most intense ones at 1228 cm^{-1} and 1183 cm^{-1}, from the phenyl breathing mode and the C-C stretching mode, predominantly along the C_{70} short diameter direction, respectively).The remaining contributions come are originated by different CPP vibrational modes: Light blue, around 1210 cm^{-1}, A mode, C-H bending mode coupled to C-C interring stretching mode; Purple peak, around 1270 cm^{-1}, corresponds to the E mode, antisymmetric phenyl breathing mode coupled to antisymmetric C-C interring stretching mode and to antisymmetric C-H bending mode. Olive green peak, around 1280 cm^{-1}, corresponds to an A symmetry mode, from a contribution of the symmetric phenyl breathing mode coupled to C-C interring stretching mode and symmetric C-H bending mode. Dark blue and pink peaks, around 1200 and 1255 cm^{-1} respectively, may be due to the same kind of modes but from either other conformations, or from interactions between other neighboring molecules theoretically not accounted.*[1]

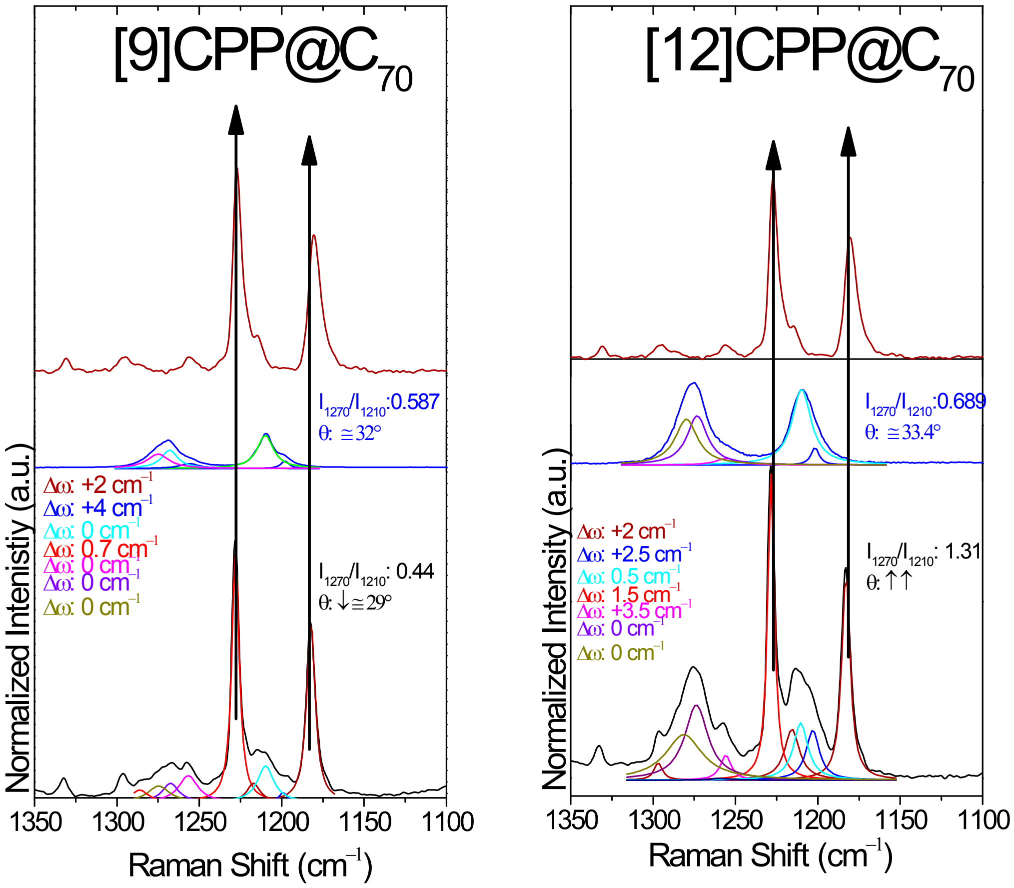


Figure S4. *785 nm experimental Raman spectra in the 1100-1350 cm^{-1} range. Lef (a)t:[9]CPP@C_{70}; right (b): [12]CPP@C_{70}. From bottom to top: pristine complex (black), pristine [n]CPP (dark blue), pristine C_{70} (dark red), all registered in solid state and ambient conditions.. These spectra have been deconvoluted into their different contributions: red lines correspond to C_{70} contributions (being the most intense ones at 1228 cm^{-1} and 1183 cm^{-1}, from the phenyl breathing mode and the C-C stretching mode, predominantly along the C_{70} short diameter direction, respectively). The remaining contributions come are originated by different CPP vibrational modes: Light blue, around 1210 cm^{-1}, A mode, C-H bending mode coupled to C-C interring stretching mode; Purple peak, around 1270 cm^{-1}, corresponds to the E mode, antisymmetric phenyl breathing mode coupled to antisymmetric C-C interring stretching mode and to antisymmetric C-H bending mode. Olive green peak, around 1280 cm^{-1}, corresponds to an A symmetry mode, from a contribution of the symmetric phenyl breathing mode coupled to C-C interring stretching mode and symmetric C-H bending mode. Dark blue and pink peaks, around 1200 and 1255 cm^{-1} respectively, may be due to the same kind of modes but from either other conformations, or from interactions between other neighboring molecules theoretically not accounted.*[1]

In linear paraphenylenes the intensity ratio between the 1280 and 1200 cm^{-1} bands, (A_g) C-C inter-ring stretching mode couples to a C-H bending mode, and breathing mode of the phenyl ring,[2] respectively, is intimately related with the torsional angle between neighboring benzenes or in other words with their conjugation along the molecule.[3] We analyze intensity of E mode around 1260-1270 cm^{-1}, corresponding to ring breathing modes (purple contribution), divided by the intensity of the 1190-1220 cm^{-1} A mode that mainly emerges from in plane CH bending modes, (light blue contribution). [1]

In the different complexes C_{70} complexes, here studied, the intensity ratio of the 1200 cm^{-1} bands behaves according to the observations already presented in the main text, for G bands of the CPPs.

- In the [10]CPP complex, this ratio significantly diminishes as result of the closing torsional angle towards a more planar conformation. As seen in the main text, this conformation favors the interaction between the CPP and the fullerene in its standing orientation, around its small diameter.
- The contrary tendency is seen on the [11] CPP complex, with lying orientation, the intensity ratio, the torsional angle, increases as a result of the complexation.
- [9]CPP@C_{70} complex, as in the [10]CPP case, there is a significant decay in the intensity ration, due to the planarization between neighboring benzenes. As explained in the main text, this is required to favor the interaction between the CPP and the fullerene in the standing orientation, although they do not precisely fit.
- [12]CPP@C_{70} complex, this ration considerably increases, meaning that an interaction between the CPP and the C70 molecule exists, even if the CPP ratio is not the most favorable.

Non important changes are observed on the Raman shifts of these bands, only the C_{70} C-C stretching mode (predominantly along the C_{70} short diameter) at about 1183 cm^{-1} seems to upshift, about 0.5 cm^{-1} more in the standing than in the lying orientation. Also the Dark blue and pink peaks, around 1200cm^{-1} band seems to be more affected by the CPP being placed in the C_{70} standing orientation than in its lying one.

Experimental Raman spectra in the 1150-1350 cm^{-1} range: High Temperature and High Pressure treatments

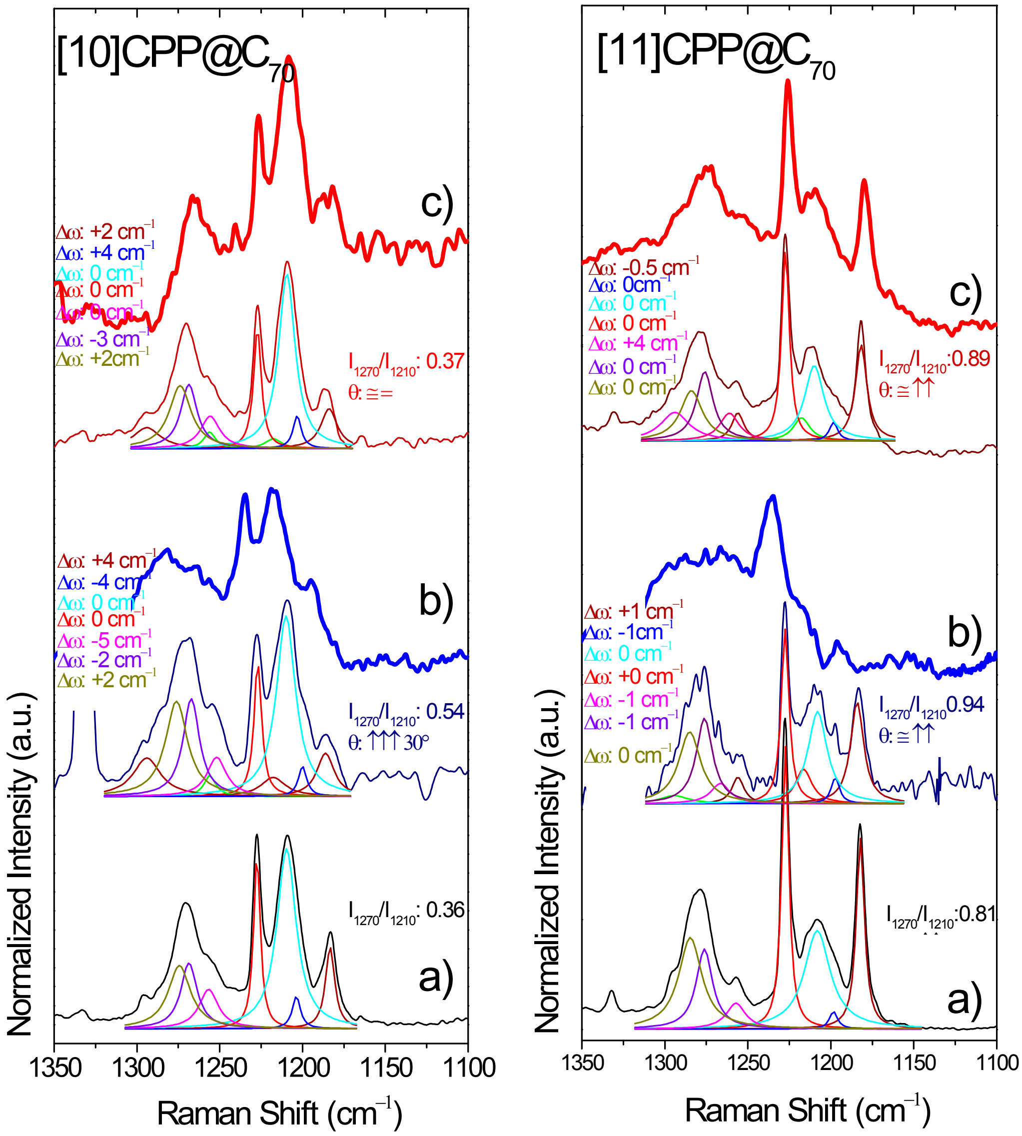


Figure S5. *785 nm experimental Raman spectra in the 1100-1350 cm^{-1} range. Lef (a)t:[10]CPP@C_{70}; right(b): [11]CPP@C_{70}. From bottom to top: (a) pristine complex (black), at room temperature and pressure; (b) thick blue line corresponds to the spectrum at high pressure (≈ 2.0 GPa) and thin dark blue line corresponds to the recovered spectrum after pressure cycle; both spectra taken at 25 °C. c) Thick red line corresponds to the spectrum at high temperature (140 °C) and thin dark red line corresponds to the recovered spectrum after thermal cycle. Both spectra are taken at room pressure These spectra have been deconvoluted into their different contributions: red lines correspond to C_{70} contributions (being the most intense ones at 1228 cm^{-1} and 1183 cm^{-1}, from the phenyl breathing mode and the C-C stretching mode, predominantly along the C_{70} short diameter direction, respectively); The remaining contributions come are originated by different CPP vibrational modes: Light blue, around 1210 cm^{-1}, A mode, C-H bending mode coupled to C-C interring stretching mode; Purple peak, around 1270 cm^{-1}, corresponds to the E mode, antisymmetric phenyl breathing mode coupled to antisymmetric C-C interring stretching mode and to antisymmetric C-H bending mode. Olive green peak, around 1280 cm^{-1}, corresponds to an A symmetry mode, from a contribution of the symmetric phenyl breathing* *mode coupled to C-C interring stretching mode and symmetric C-H bending mode. Dark blue and pink peaks, around 1200 and 1255 cm^{-1} respectively, may be due to the same kind of modes but from either other conformations, or from interactions between other neighboring molecules theoretically not accounted.*[1]

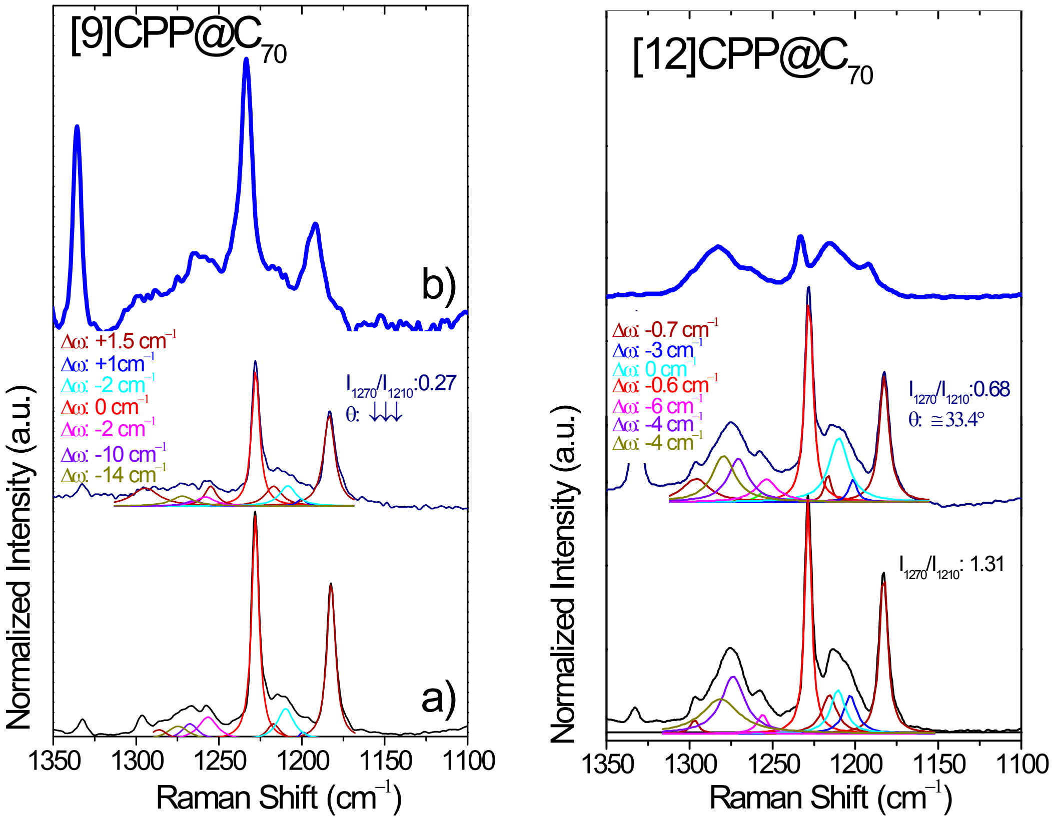


Figure S6. *785 nm experimental Raman spectra in the 1100-1350 cm^{-1} range. complexes in solid state Left (a):[9]CPP@C$_{70}$; right (b): [12]CPP@C$_{70}$. From bottom to top: (a) pristine complex (black), at room temperature and pressure; (b) thick blue line corresponds to the spectrum at high pressure (≈ 2.0 GPa) and thin dark blue line corresponds to the recovered spectrum after pressure cycle; both spectra taken at 25 °C. These spectra have been deconvoluted into their different contributions: red lines correspond to C$_{70}$ contributions (being the most intense ones at 1228 cm^{-1} and 1183 cm^{-1}, from the phenyl breathing mode and the C-C stretching mode, predominantly along the C$_{70}$ short diameter direction, respectively); The remaining contributions come are originated by different CPP vibrational modes: Light blue, around 1210 cm^{-1}, A mode, C-H bending mode coupled to C-C interring stretching mode; Purple peak, around 1270 cm^{-1}, corresponds to the E mode, antisymmetric phenyl breathing mode coupled to antisymmetric C-C interring stretching mode and to antisymmetric C-H bending mode. Olive green peak, around 1280 cm^{-1}, corresponds to an A symmetry mode, from a contribution of the symmetric phenyl breathing mode coupled to C-C interring stretching mode and symmetric C-H bending mode. Dark blue and pink peaks , around 1200 and 1255 cm^{-1} respectively, may be due to the same kind of modes but from either other conformations, or from interactions between other neighboring molecules theoretically not accounted.1*

PRRESSURE EFFECT:

- In the [10]CPP complex, the 1200 cm^{-1} bands ratio significantly increasing of the torsional angle.. this is in agreement also with the more staggered conformation required for this CPP to accommodate the C70 molecule in its standing orientation, maximizing therefore the π-π interactions between both of the systems.

- Similar tendency is seen on the [11] CPP complex, the intensity ratio slightly increases, to, as mentioned in the main text, improve the contacts between [11]CPP and C70.

- [9]CPP@C_{70} complex, in the main text we suggest that pressure further helps the formation of the supramolecular complex through a more strained [9]CPP molecule while it slightly adapts to better fit C70. This occurs by the flattening between neighboring benzenes as observed on the Figure S5.2, with the intensity ration of the 1268/1210 cm^{-1} bands.

- [12]CPP@C_{70} complex, the intensity ration of the 1200 cm^{-1} bands decreases close to the value of the pristine complex.

Non important changes are observed on the Raman shifts of these bands, but a downshift in the CPP bands, being the highest for the [9]CPP complex.

TEMPERATURE EFFECT:

- In the [10]CPP complex, the 1200 bands ratio practically remains the same than in the pristine complex, and the bands do not shift either..

- Similar tendency is seen on the [11] CPP complex, the intensity ratio slightly increases.

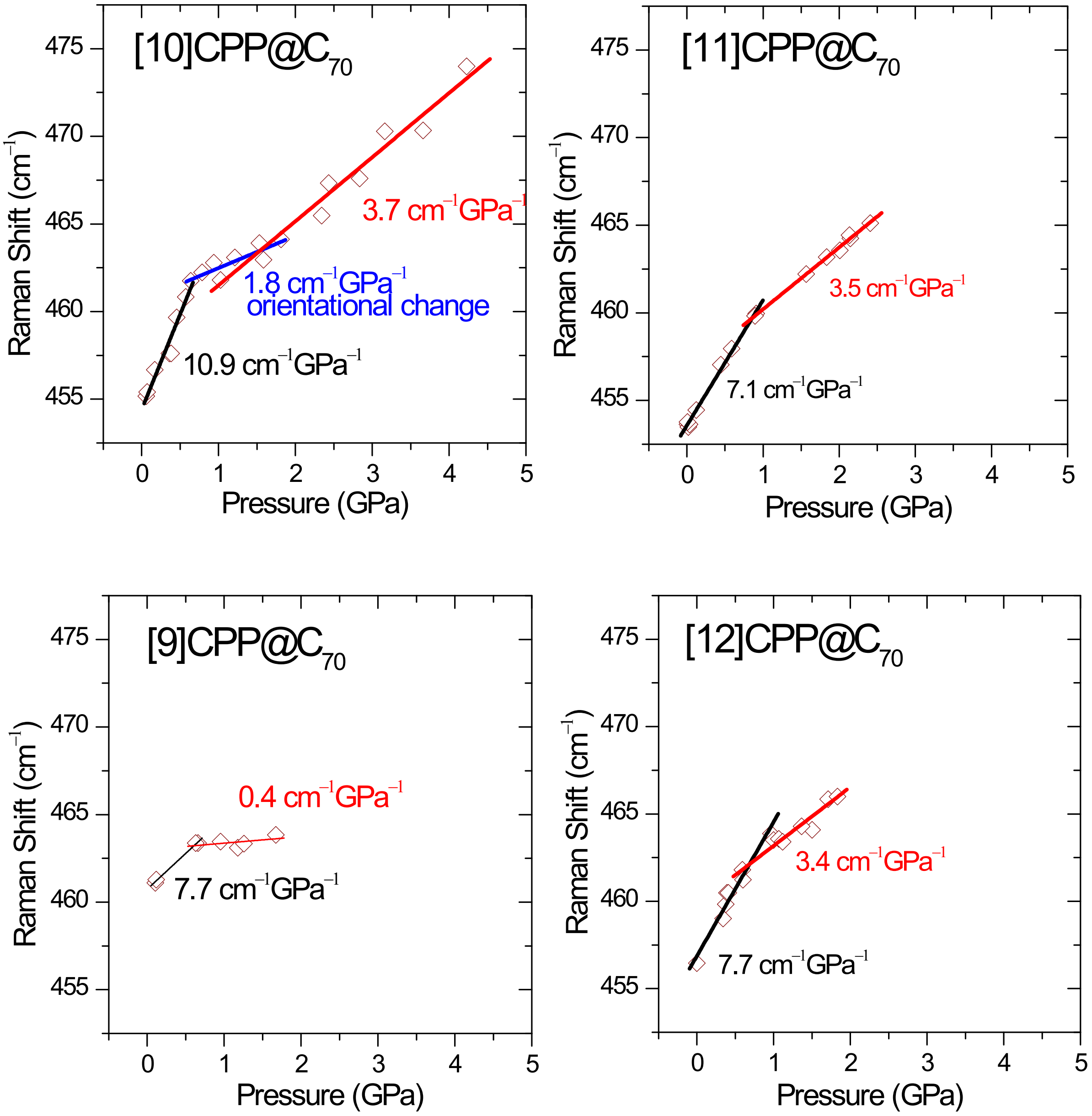


Figure 7. Raman shift pressure evolution of the C_{70} Radial breathing mode: Raman bands of top: [10]CPP@C_{70}, left, and [11]CPP@C_{70} right; bottom: [9]CPP@C_{70}, left, and [12]CPP@C_{70} right. Pressure coefficients of each linear trend are expressed in $cm^{-1}GPa^{-1}$.

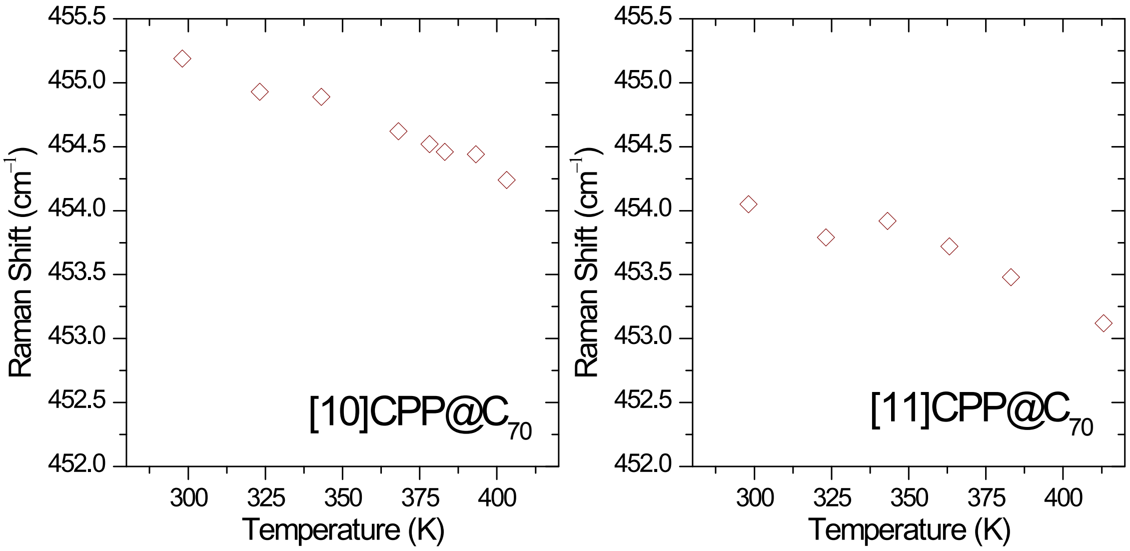


Figure S8. Raman shift temperature evolution of the C_{70} Radial breathing mode of: [10]CPP@C_{70}, left, and [11]CPP@C_{70} right.

PRRESSURE EFFECT on the fullerene Radial breathing mode:

[10]CPP@C_{70} As seen in the main text These G like modes linearly shift up to a critical pressure, 0.6 GPa, at which they stay constant with the increased pressure. As the pressure increases a second critical point at 1.6 GPa appears leading to a second linear region between their Raman shift and pressure. On the other hand, the tangential CC stretching mode of fullerene evolves with stress following two linear regimes before and after 1.6 GPa. These trends are explained by the stress induced orientational change of the C_{70} in the CPP cavity. It seems very likely that during the plateau the C_{70} is rotating towards a more standing conformation, and once that is reached stress induced the ovallization of the CPP around the C_{70}.

Accordingly, the C_{70} RBMs, which are directly affected by the C70 orientation in the ring cabvity, follow stress evolution accordingly to the G modes of the CPP, presenting also a plateau between 0.6 and 1.6 GPa.

In the [11]CPP@C_{70} case pressure induces again an overall upshift of the whole spectrum. The CPP G1 band upshifts from 1597 cm^{-1} to 1603 cm^{-1} at 2GPa, However, the whole spectra follow a different pressure trend than in the [10]CPP case. All the bands analysed depict two linear regimes separated by a critical pressure, 1.2 GPa. This change in the trend might be related with an extra flattening of the already flattened shape of [11]CPP in the standing complex, similar pressure responses have been observed in peapods.

Although is not so clear, the [9]CPP@C70 complex also have two different linear responses to stress which crosses at about 0.6 GPa. However, these seem to trend towards a similar behaviour to that presented by the [10]CPP. Unfortunately the fluorescence of this complex hinder any further observation.

Finally, as in the [11]CPP@$C_{70,}$ the RBMs of the [12]CPP@C_{70} up-shifts with stress following tow linear regimes, consequence of the probable stress induced deformation of the [12]CPP around the C_{70} and the crystalline reorganization.

Variable temperature Raman experiments.

The C70 RBMs of the [10]CPP@C_{70} and [11]CPP@C_{70} behave differently with temperature, as seen in Figure S8. While in the [11]CPP@C_{70} they follow a reversible linear trend, on the [11]CPP@C_{70} case the trend is disturbed at low temperatures, between 300 and 340 K. This supports results exposed in the main text, the change towards the lying orientation of the c70 in the complex.

References

[1] M. Peña Alvarez, P. Mayorga Burrezo, M. Kertesz, T. Iwamoto, S. Yamago, J. Xia, R. Jasti, J. T. López Navarrete, M. Taravillo, V. G. Baonza and J. Casado, *Angew. Chem. Int. Ed.* 2014, **53**, 7033.

[2] G. Zannoni, G. Zerbi, Lattice dynamics and vibrational spectra of undoped and doped polyparaphenylene, J. Chem. Phys. **1995**, *82*, 31.

[3] G. Heimel, D. Somitsch, P. Knoll, J.L Brédas, E. Zojer, Effective conjugation and Raman intensities in oligo (para-phenylenes)s: A microscopic view from first-principles calculations, J. Chem. Phys, **2005**, *122*, 114511.