Supplementary information

Vibrational spectrum and chemical imaging of cyclo[18]carbon by tip enhanced Raman spectroscopy

Shafqat Hussain,[ab] Huan Chen,[a] Zhenglong Zhang*[a] and Hairong Zheng*[a]

[a] *School of Physics and Information Technology, Shaanxi Normal University, 710119, Xi'an, China*
[b] *Nanomaterials Research group, Physics Division, PINSTECH, Islamabad, 44000, Pakistan*
Email: zlzhang@snnu.edu.cn; hrzheng@snnu.edu.cn

Computational details:

Density functional theory (DFT) calculations were performed using Gaussian 16 package[1]. First of all, isolated the cyclo[18]carbon (C_{18}) and tetrahedral silver cluster of 20-atoms (Ag_{20}) were optimized using long-range corrected hybrid exchange-correlation functional CAM-B3LYP[2,3]. The triple-ζ basis set 6-311+G(d,p) and LANL2DZ basis set were used for carbon and silver atoms respectively. In order to avoid computational complexity, Single point calculations[4] with same correlational functional and basis were performed for C_{18} with Ag_{20} located with at different positions A to L (see Fig. 1) at distance z from C_{18} ring plane and corresponding vibrational frequencies were calculated.

Time dependent DFT (TDDFT) calculation for C_{18} with silver cluster was performed using same functional and basis set as above. The charge difference density analysis was performed by using the Multiwfn.3.4.1 program.[5]

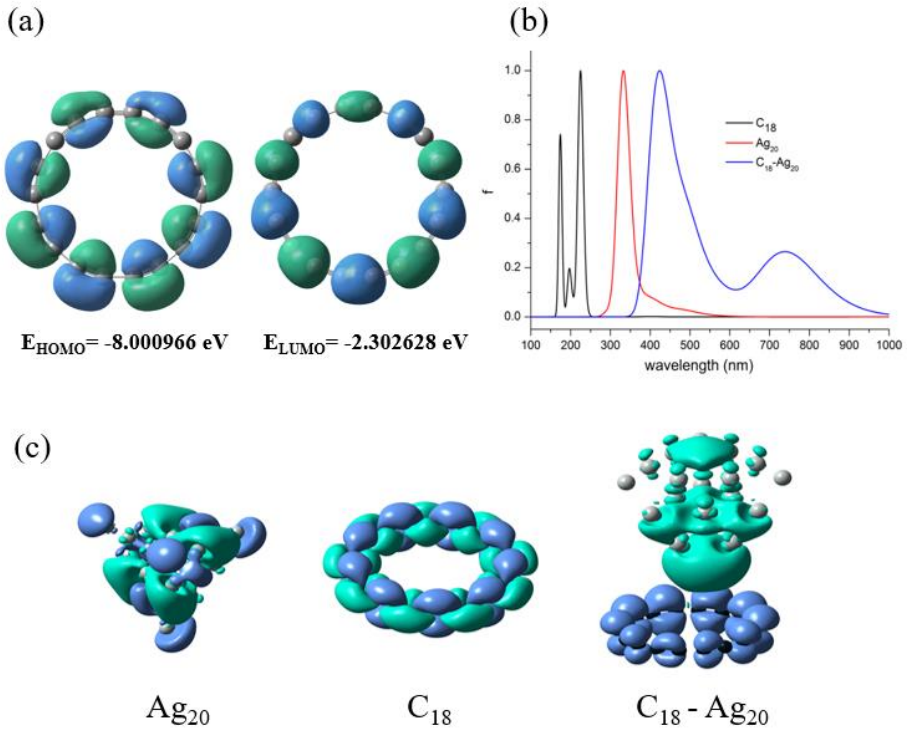

Fig S1. (a) The ground state iso-density surface plots of C_{18} for the frontier orbitals HOMO (left) and LUMO (right) calculated by CAM-B3LYP/6-311+G(d,p) functional in DFT method. (b) Normalized absorption spectra of C_{18}, Ag_{20} and C_{18} with Ag_{20} located at position H at 2.5 Å above C_{18} calculated by TDDFT/ CAM-B3LYP method for 70 lowest excited states. (c) Charge difference density analysis of first singlet excited state of Ag_{20}, C_{18} and C_{18} with Ag_{20} located at position H at 2.5 Å above C_{18}. The localization of holes (blue color) on C_{18} and electrons (green color) on Ag_{20} indicate the mutual charge transfer between metal and molecule.[6,7]

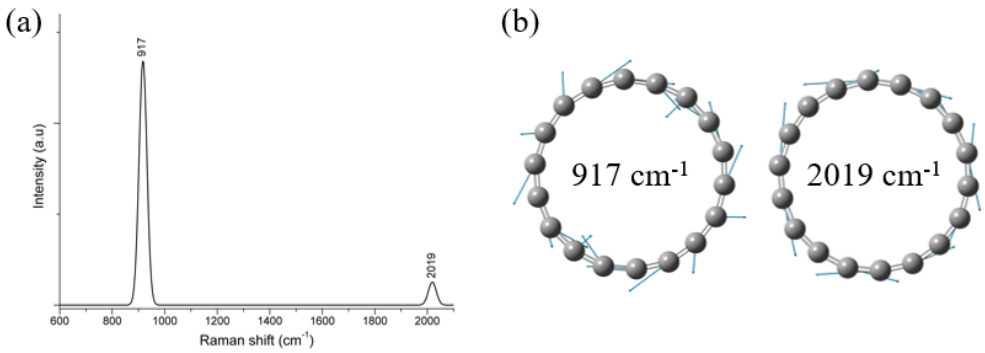

Fig S2. (a) Normal Raman spectrum of cumulenic structure of C_{18} and (b) vibrational modes of cumulenic structure of C_{18}

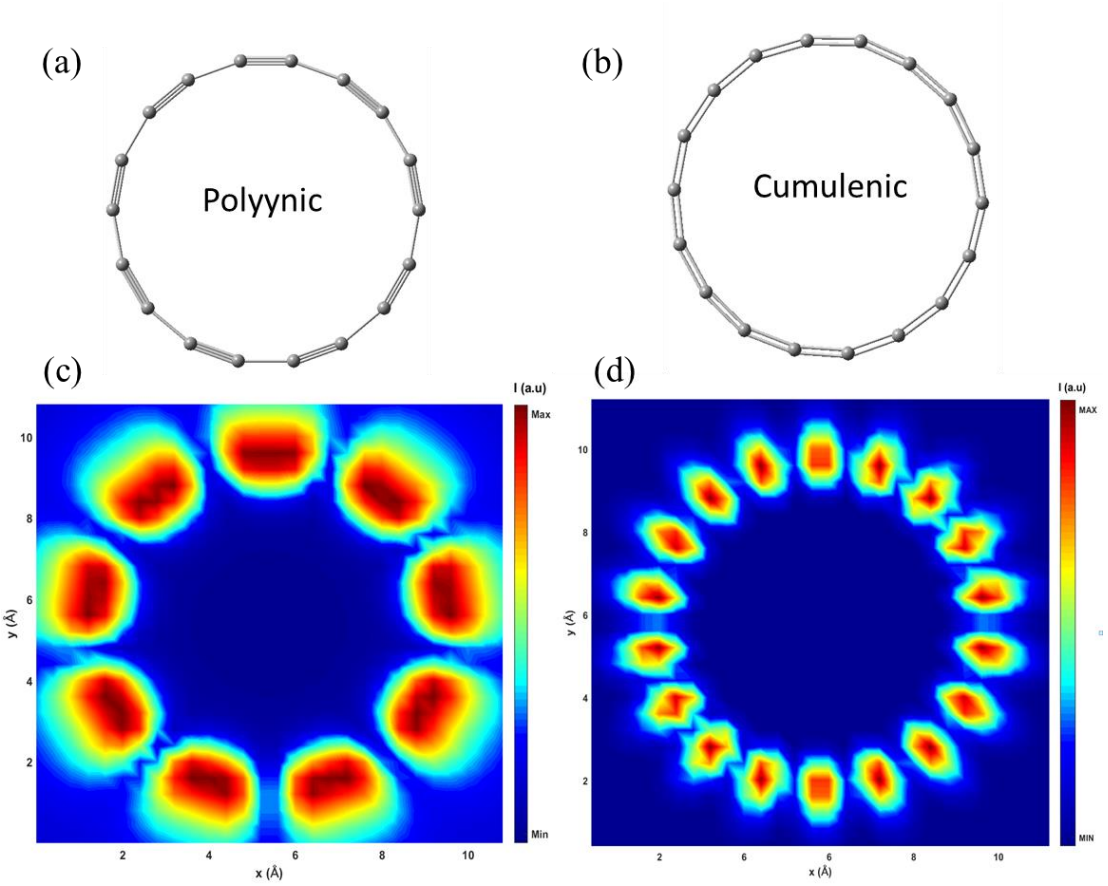

Figure S3. (a) and (b) show the optimized geometries of two structures, (c) image of vibrational mode C≡C stretching at 1760 cm^{-1} in polyynic structure and (d) image of vibrational mode C=C stretching at 1974 cm^{-1} in cumulenic structure.

References

1 X. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Petersson, G.A., Nakatsuji, H. and Li, Gaussian 16, Revision A. 03, 2016.

2 T. Yanai, D. P. Tew and N. C. Handy, Chem. Phys. Lett., 2004, 393, 51.

3 T. Tsuneda and K. Hirao, Wiley Interdiscip. Rev. Comput. Mol. Sci., 2014, 4, 375.

4 F. Latorre, S. Kupfer, T. Bocklitz, D. Kinzel, S. Trautmann, S. Gräfe and V. Deckert, Nanoscale, 2016, 8, 10229

5 Lu, T.; Chen, F. W. Multiwfn: A Multifunctional Wavefunction Analyzer. J. Comput. Chem. 2012, 33, 580−592.

6 L. Xia, M. Chen, X. Zhao, Z. Zhang, J. Xia, H. Xu and M. Sun, J. Raman Spectrosc., 2014, 45, 533.

7 M. Sun, Y. Fang, Z. Yang and H. Xu, Phys. Chem. Chem. Phys., 2009, 11, 9412.