

# Supporting information for

## *Physical Chemistry Chemical Physics*

### Identifying sp-sp<sup>2</sup> carbon materials by Raman and Infrared Spectroscopy

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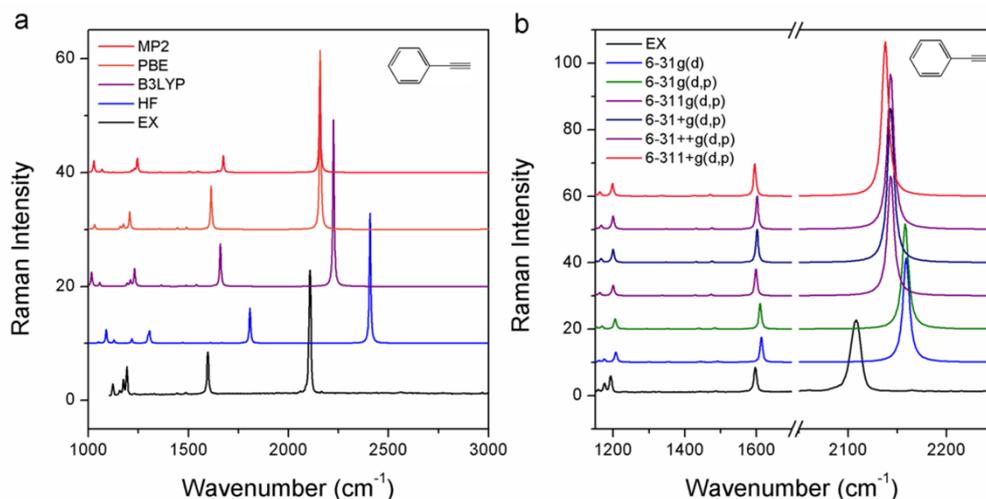
#### Testing calculations

In order to obtain a set of reasonable parameters to calculate the thermodynamic properties and vibration spectrum, we conducted a series of tests between calculations and experimental results.

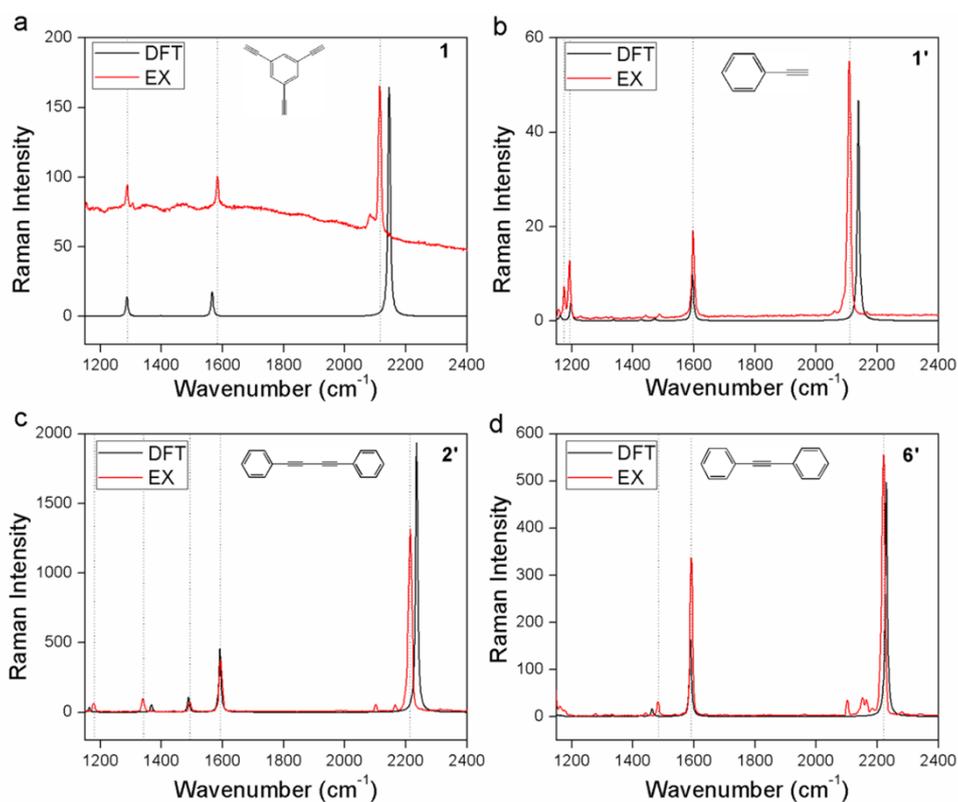
The compounds in our work are mainly composed of benzene-ring, ethenyl, and ethynyl groups. We calculated the enthalpy changes  $\Delta H$  for the reactions forming benzene and ethene from ethyne and hydrogen and the heat of formation for water, using B3LYP and PBE functionals at the basis set of 6-311+g(d,p). The comparison between calculation results and the experimental values was provided in Table S1. It shows that the B3LYP functional gives more accurate results.

**Table S1.** Theoretical and experimental<sup>1</sup> enthalpy changes  $\Delta H$  for forming water, ethene, and benzene from oxygen, hydrogen, and ethyne.

	enthalpy changes $\Delta H$ (kcal/mol)		
	PBE	B3LYP	experiment
H <sub>2</sub> O	-71.2	-72.6	-57.8
C <sub>2</sub> H <sub>4</sub>	-45.1	-42.5	-41.7
C <sub>6</sub> H <sub>6</sub>	-155.9	-142.0	-142.8



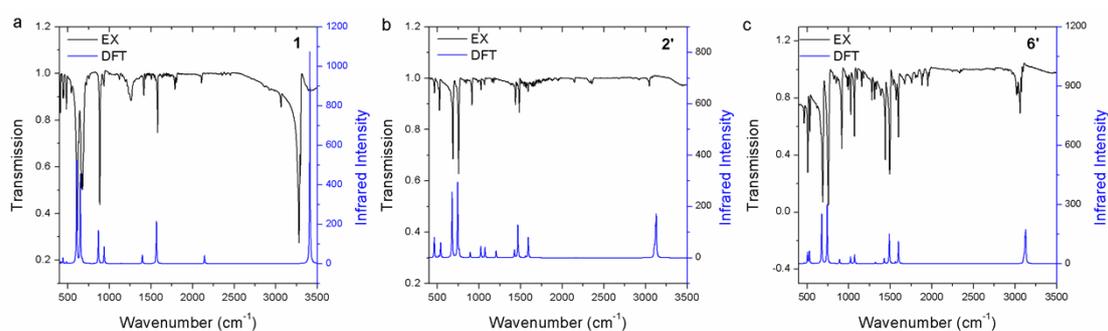
**Figure S1.** (a) Raman spectra of compound **1'** calculated using Hartree-Fock (HF), DFT with B3LYP functional, DFT with PBE functional, and MP2 methods at 6-31g(d) basis. (b) Raman spectra of compound **1'** calculated using DFT-PBE method with basis sets of 6-31g(d), 6-31g(d,p), 6-311g(d,p), 6-31+g(d,p), 6-31++g(d,p), and 6-311+g(d,p), respectively.



**Figure S2.** Experimental and theoretical Raman spectra of compound **1** (a), **1'** (b), **2'** (c), and **6'** (d). The calculation method is DFT-PBE with basis set of 6-311+g(d,p).

Raman spectra of compound **1'** were calculated using different methods and basis sets (**Figure. S1**) and were compared with the experimental values. We found that density functional theory (DFT) with PBE functional at 6-311+g(d,p) basis set gives the most accurate results. Further computation of Raman spectra for compounds **1**, **2'**, **6'** at the same level (**Figure. S2**) show consistent results with relevant experimental values, and the differences of the prominent peak positions between theory and experiment are less than 30 cm<sup>-1</sup> in the range of (1200, 2400) cm<sup>-1</sup>. It is noted that the compounds **1**, **1'**, **2'**, **6'** are obtained commercially and tested without further purification. The weak bands at 2050-2200 cm<sup>-1</sup> observed in the experiment but absent in the DFT calculations are likely to come from impurity.

Theoretical and experimental Infrared spectra of compound **1**, **2'**, and **6'** are also summarized in **Figure S3**, and give consistent results.

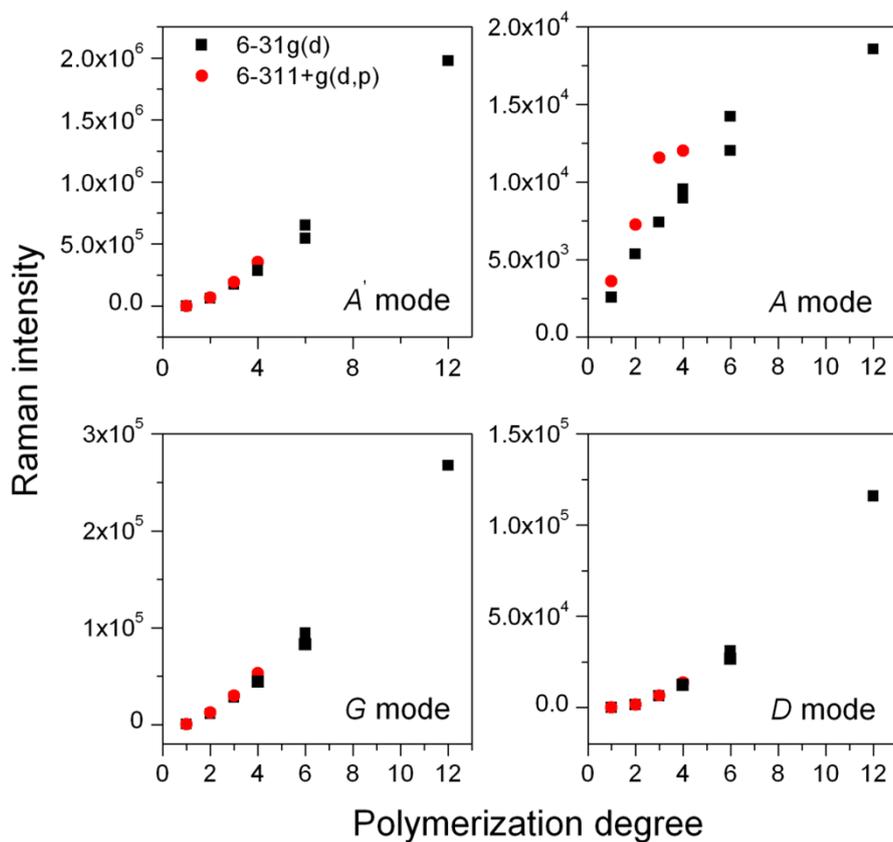


**Figure S3.** Experimental and theoretical Infrared spectra of compound **1** (a), **2'** (b), and **6'** (c).

The calculation method is DFT-PBE with basis set of 6-311+g(d,p).

### Raman spectra of TEB oligomers

We calculated the Raman spectra of the TEB oligomers at the basis sets of 6-311+g(d,p) and 6-31g(d) using DFT method with functional PBE. Both calculations showed that the Raman intensities of *A'*, *G*, and *D'* modes increase with polymerization degree *n* in the similar trends (**Figure S4**). By comparing the calculated Raman peak positions at the two basis sets in **Table S2**, we demonstrated the shifts of Raman spectra caused by polymerization degree are the same. Thus, we can deduct the Raman peak position of larger oligomers at the basis set of 6-311+g(d,p) and predict the Raman spectra of 2D-TEB network according to the regular change of Raman spectra with polymerization degree.



**Figure S4.** Raman intensities of  $A'$ ,  $A$ ,  $G$ , and  $D$  modes for compounds **1-4** at a basis set of 6-311+g(d,p) (red dots) and for compounds **1-4**, **4b**, **6**, **6b**, and **12** at a basis set of 6-31g(d) (black squares).

**Table S2.** Differences of Raman peak position of compounds **2-4** calculated at two basis sets of 6-311+g(d,p) and 6-31g(d) for  $A'$ ,  $G$ , and  $D'$  modes.

compound	$\square A'$ (cm <sup>-1</sup> )	$\square G$ (cm <sup>-1</sup> )	$\square D'$ (cm <sup>-1</sup> )
2	9	14	10
3	9	13	9
4	9	13	9