

Electronic Supplementary Information – 1 for

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## Liquid Crucible Model for Aggregation of Phenylacetylene in the Gas Phase

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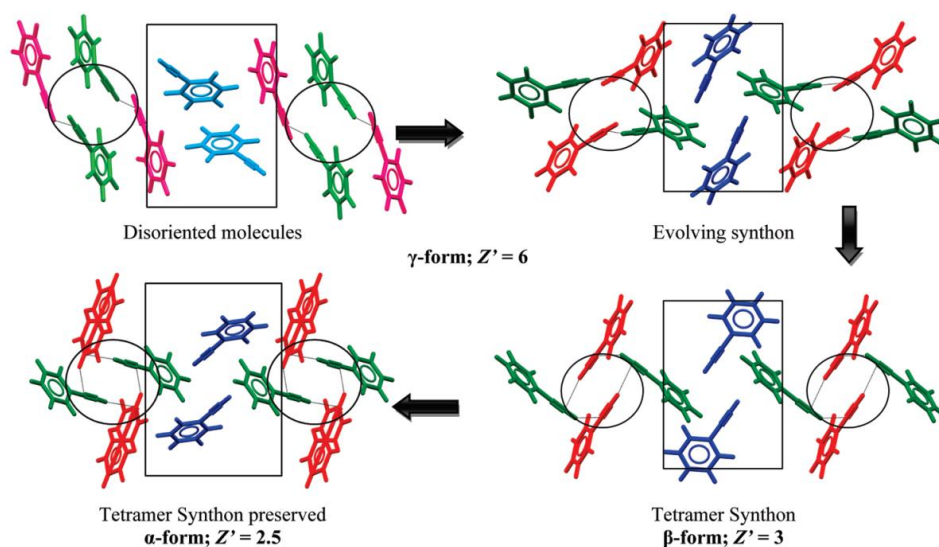
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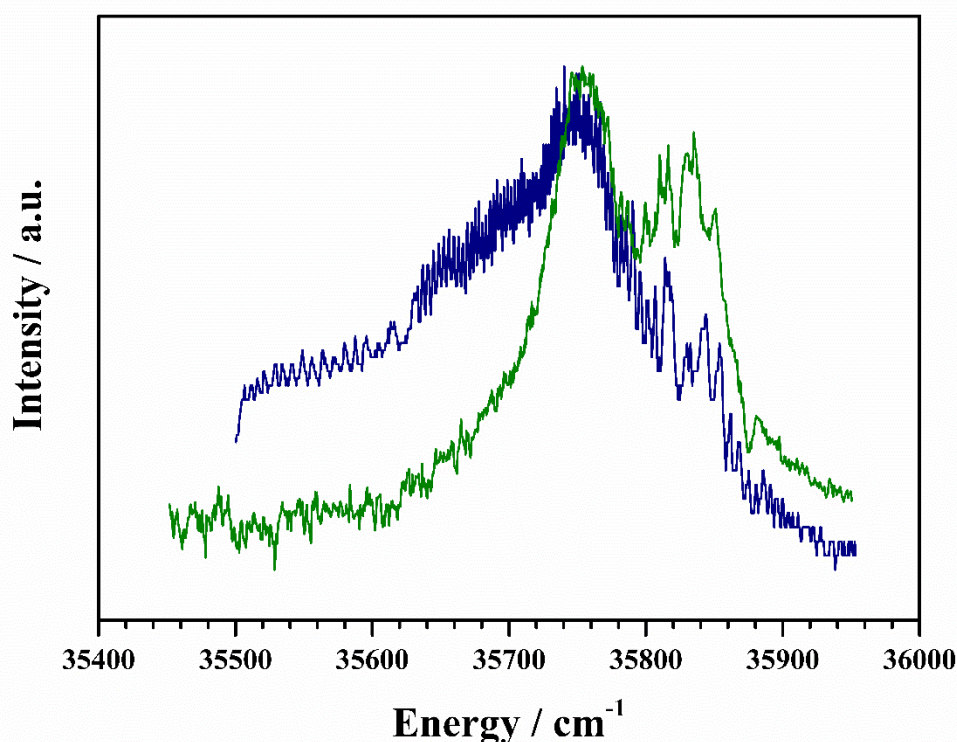
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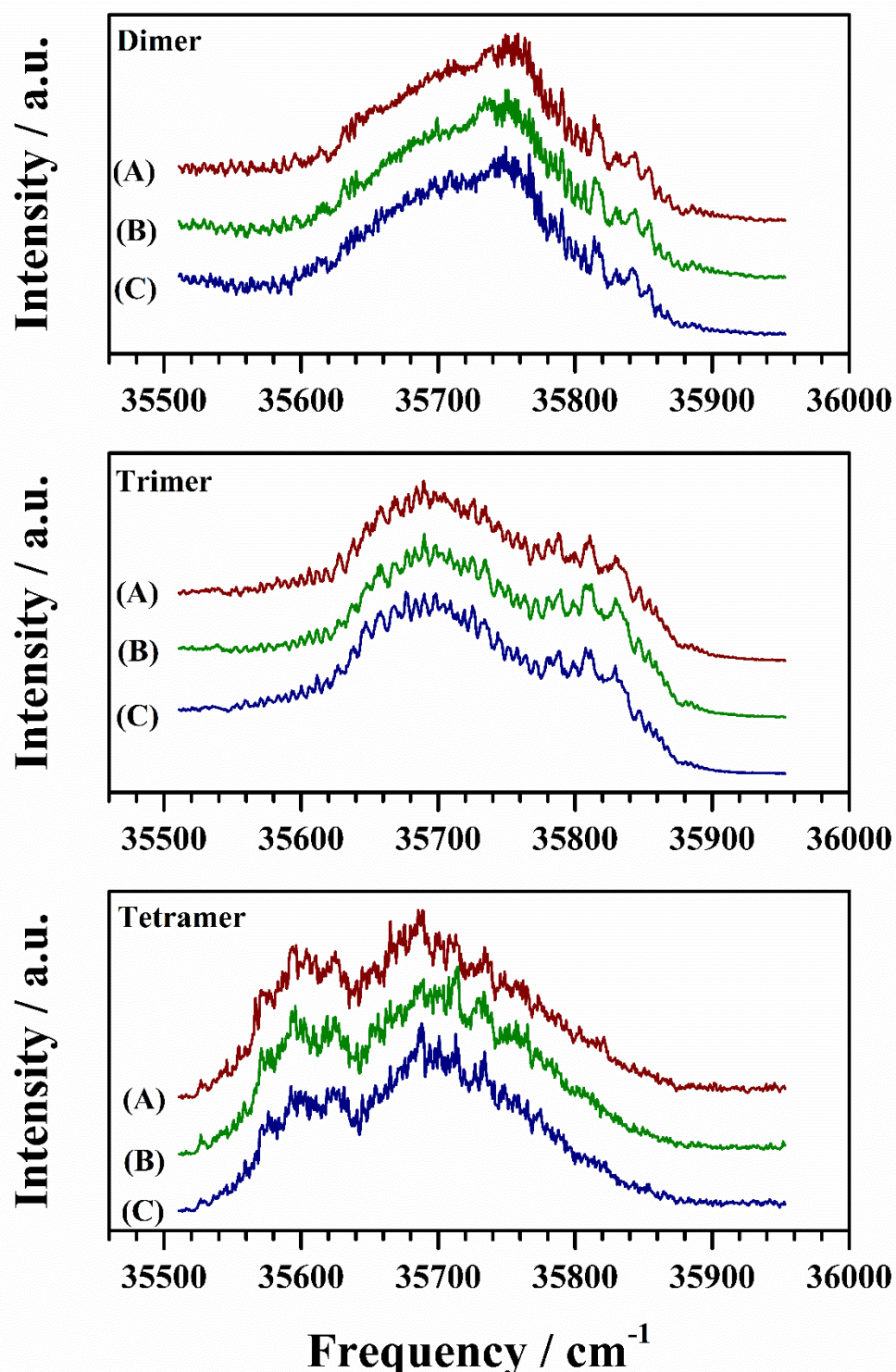
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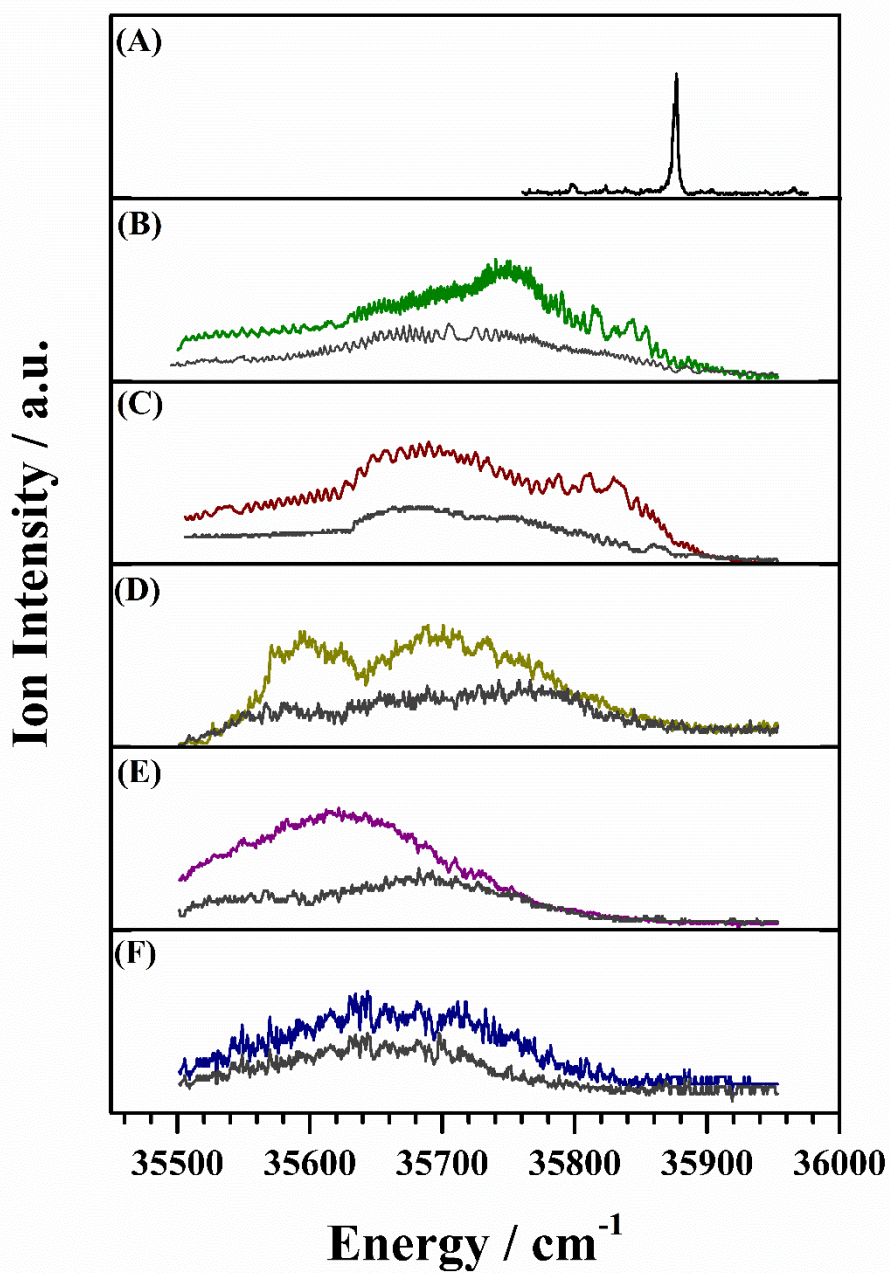
**Fig. S1.** The arrangement of phenylacetylene molecules showing the relationship between their arrangements in three different polymorphs. The evolving synthon has a tetramer as a basic unit with acetylenic C–H $\cdots\pi$  interactions as the primary interaction. Symmetry independent molecules are colour coded. Reproduced with permission from Thakur et al. *Cryst. Growth Des.*, 2010, **10**, 4246–4249.



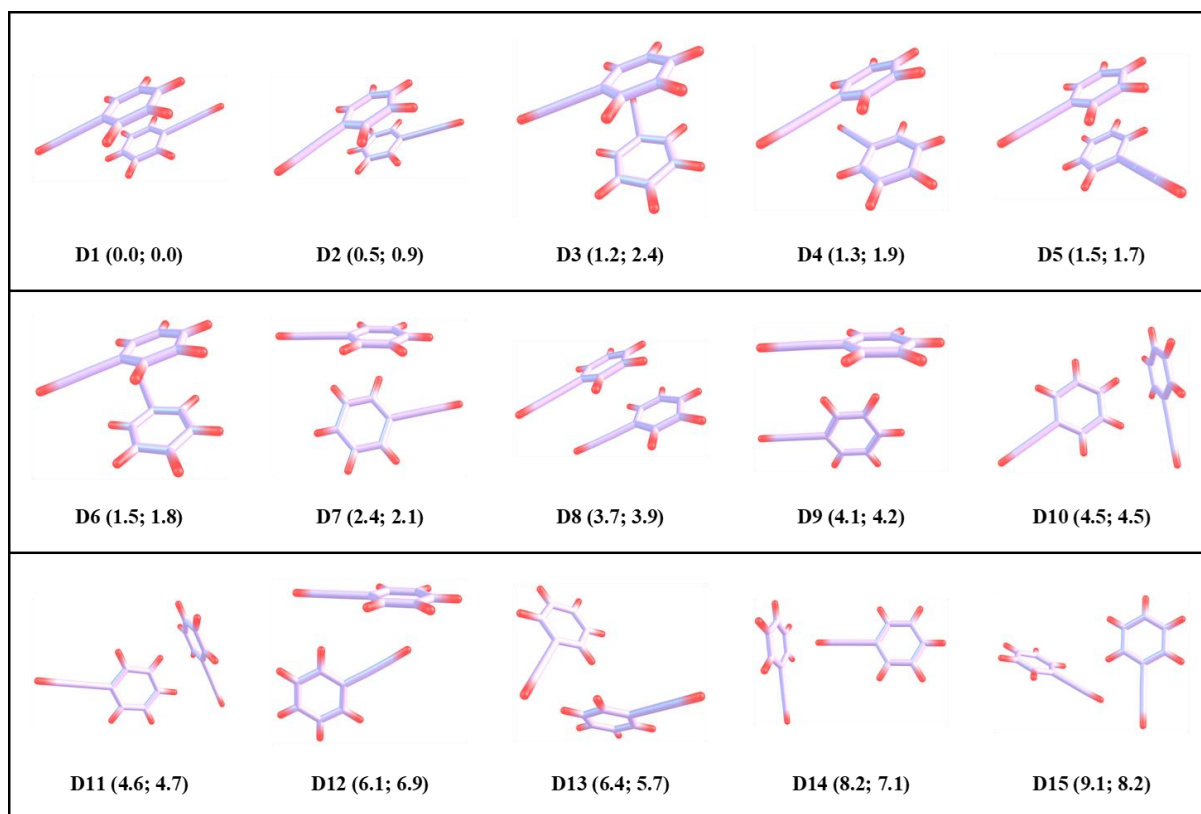
**Fig. S2.** 1C-R2PI spectra of phenylacetylene dimer. The blue curve is present work and the green curve was reported in Ref [4]. The features are essentially the same, but the shape is marginally different. This can be attributed to the difference in the tuning curve of the UV laser. Both the spectra are not corrected for the laser intensity.



**Fig. S3.** Laser power dependent 1C-R2PI spectra of phenylacetylene dimer, trimer and tetramer. In each set the traces (A), (B) and (C) were recorded with 320, 240, 180  $\mu\text{J}/\text{pulse}$  measured at 280 nm ( $\sim 35715 \text{ cm}^{-1}$ ). Typical laser power used in the experiments reported in this work is around 250  $\mu\text{J}/\text{pulse}$  at 280 nm.

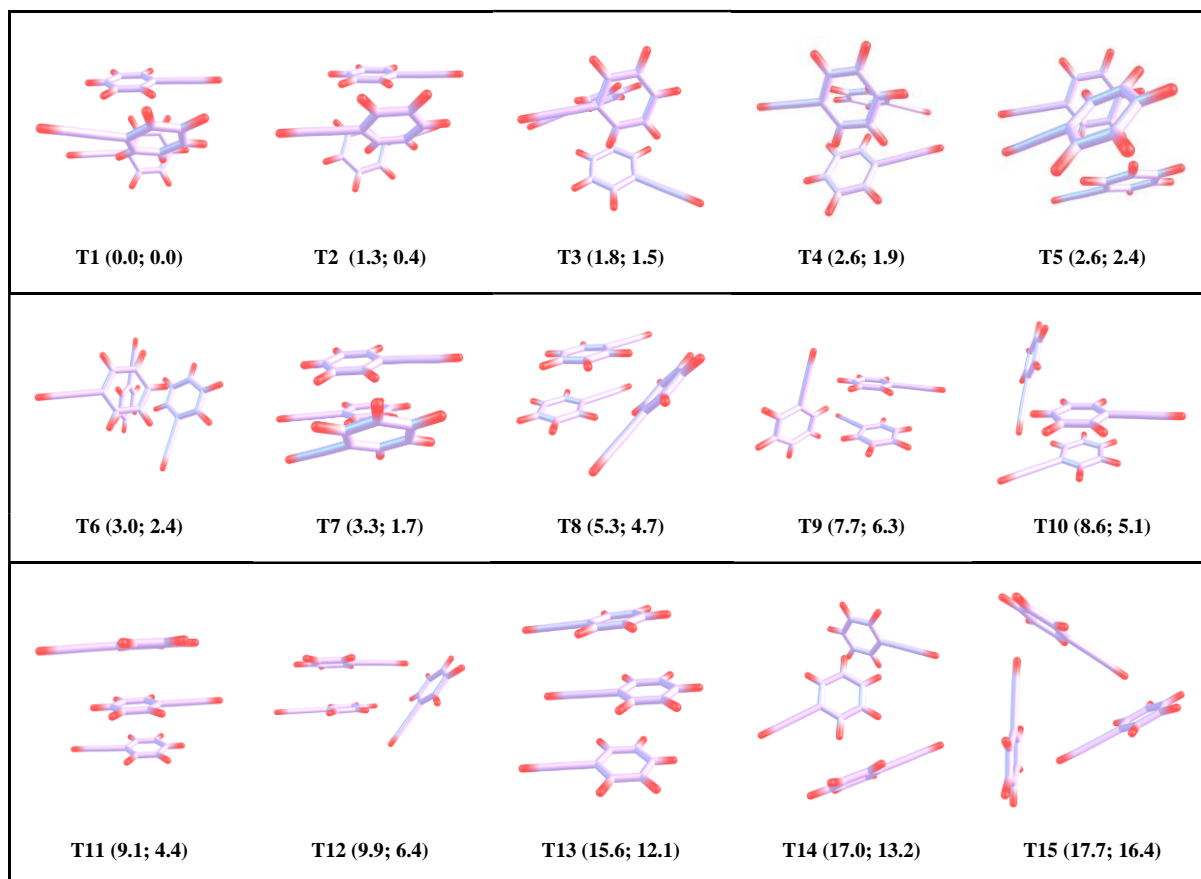


**Fig. S4.** 1C-R2PI spectra of phenylacetylene and its clusters up to six molecules. (A) monomer, (B) dimer, (C) trimer, (D) tetramer, (E) pentamer and (F) hexamer. All the spectra were recorded by monitoring the parent mass of the corresponding cluster. In each panel, the grey line represents the corresponding IR-UV hole-burnt spectrum, which was recorded by pumping the most intense band in the corresponding IR spectrum shown in Figure 4.

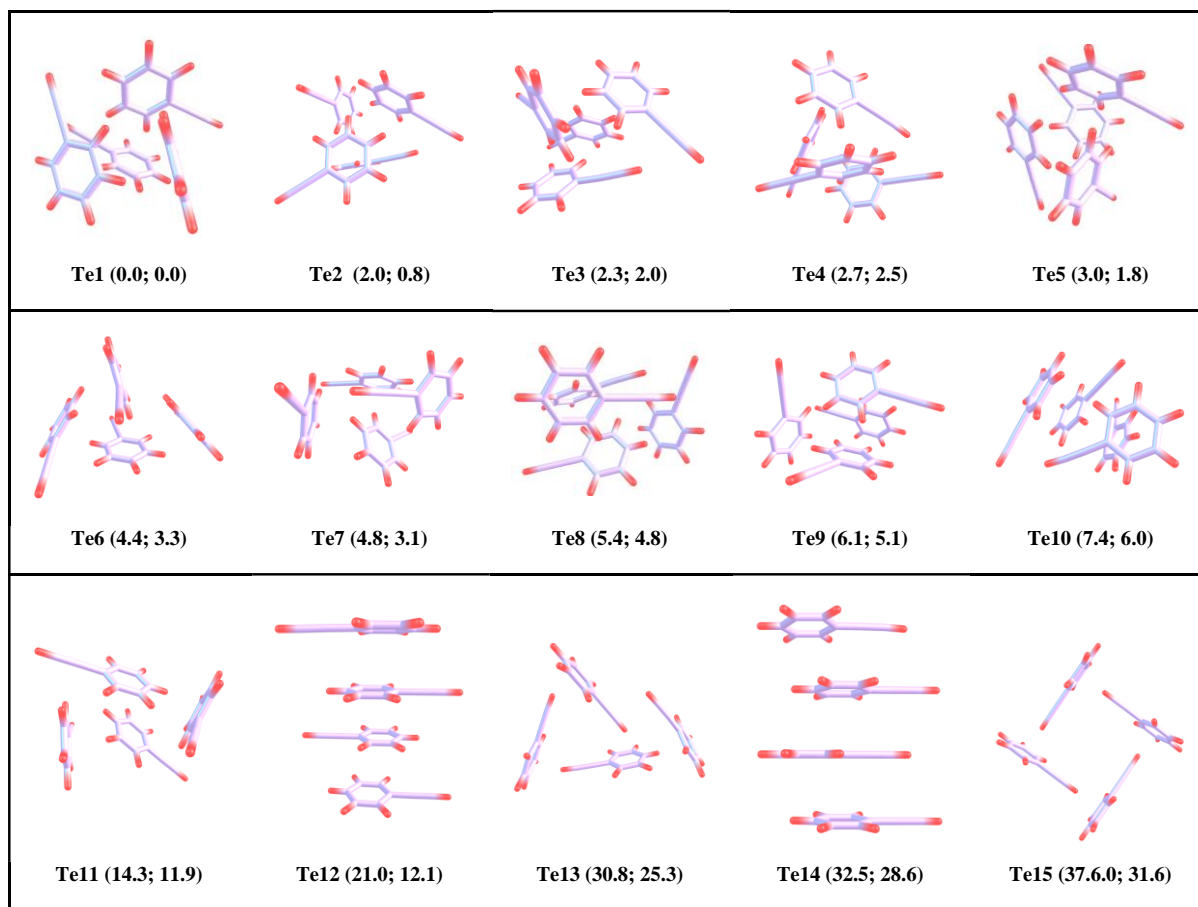


**Fig. S5.** Selected structures of phenylacetylene dimer. The relative ZPE corrected stabilization energies and relative Gibbs free energy of formation at 100K (both corrected for BSSE in the electronic energies) in  $\text{kJ mol}^{-1}$  are given against each structure. See Table S1 for more details.

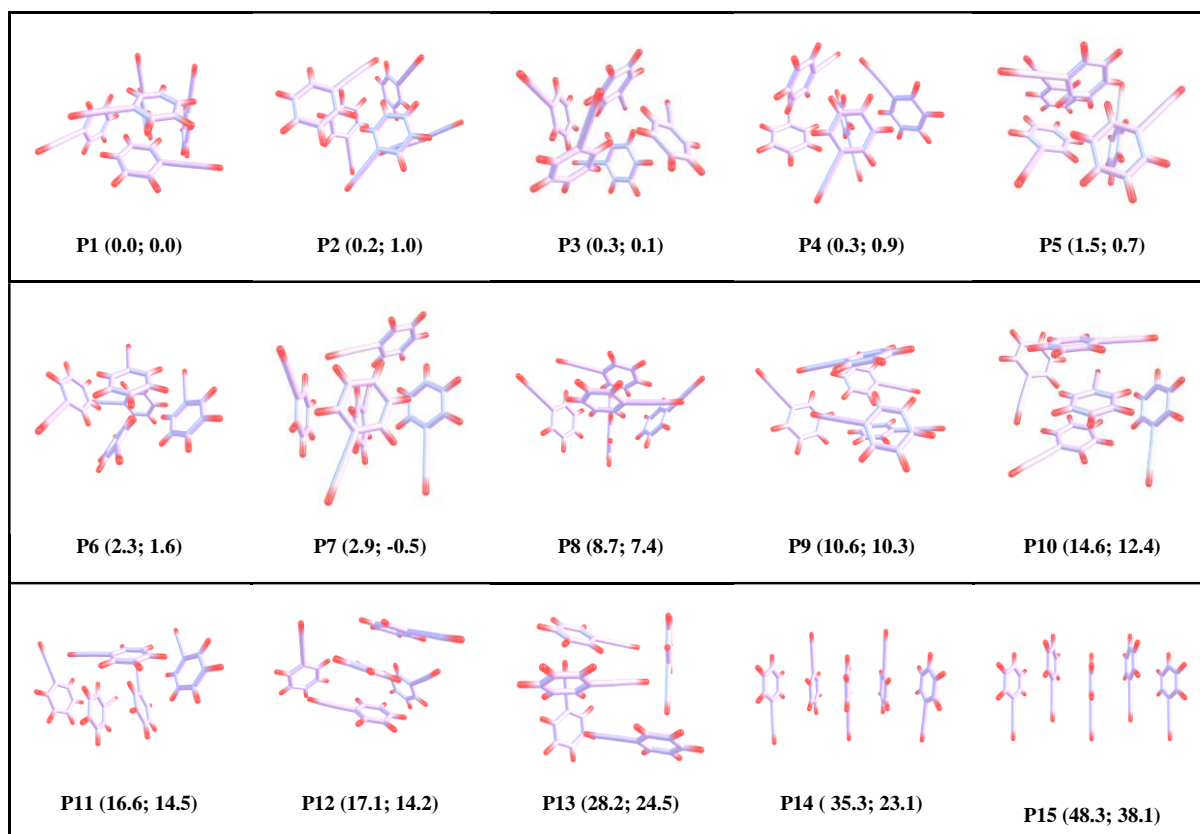




**Fig. S6.** Selected structures of phenylacetylene trimer. The relative ZPE corrected stabilization energies and relative Gibbs free energy of formation at 100K (both corrected for BSSE in the electronic energies) in  $\text{kJ mol}^{-1}$  are given against each structure. See Table S1 for more details.

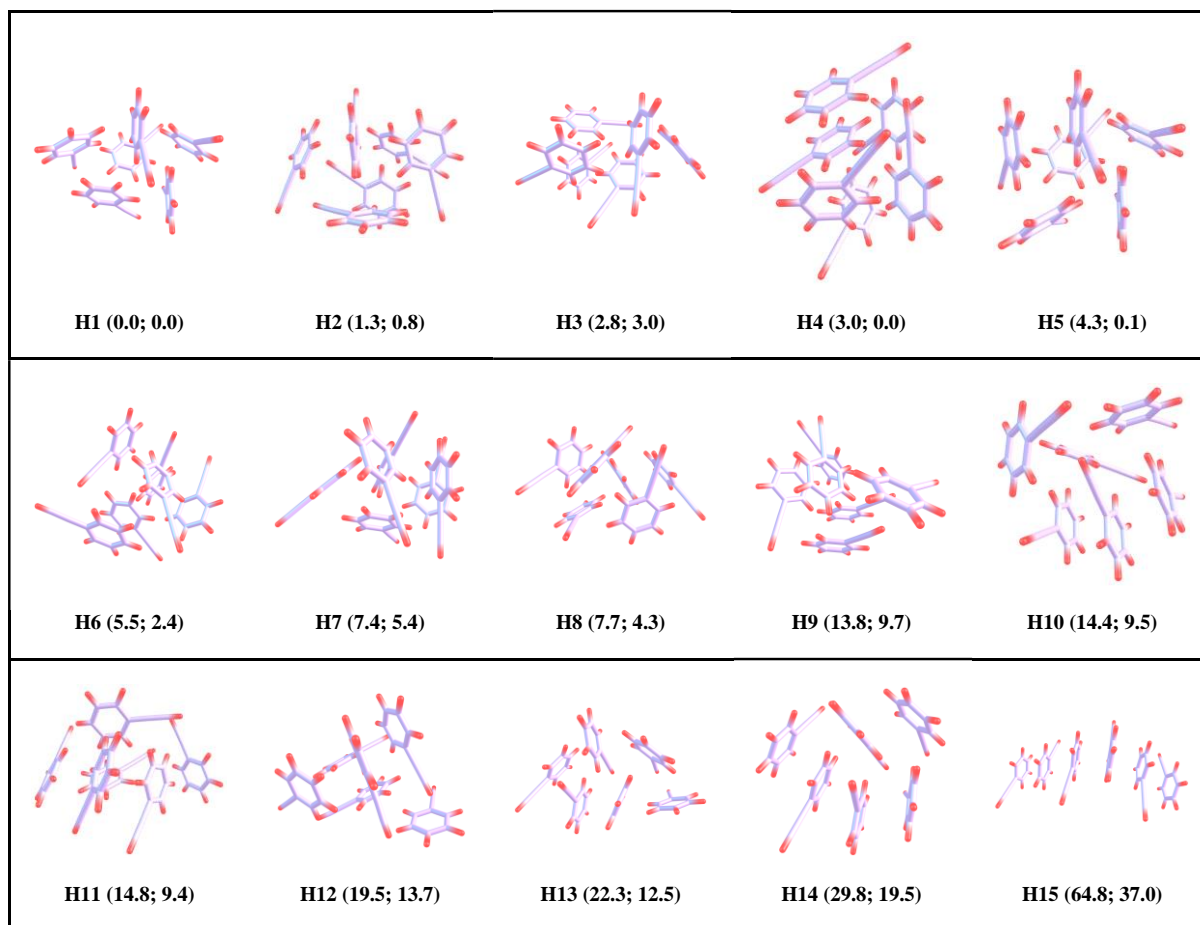


**Fig. S7.** Selected structures of phenylacetylene tetramer. The relative ZPE corrected stabilization energies and relative Gibbs free energy of formation at 100K (both corrected for BSSE in the electronic energies) in  $\text{kJ mol}^{-1}$  are given against each structure. See Table S1 for more details.

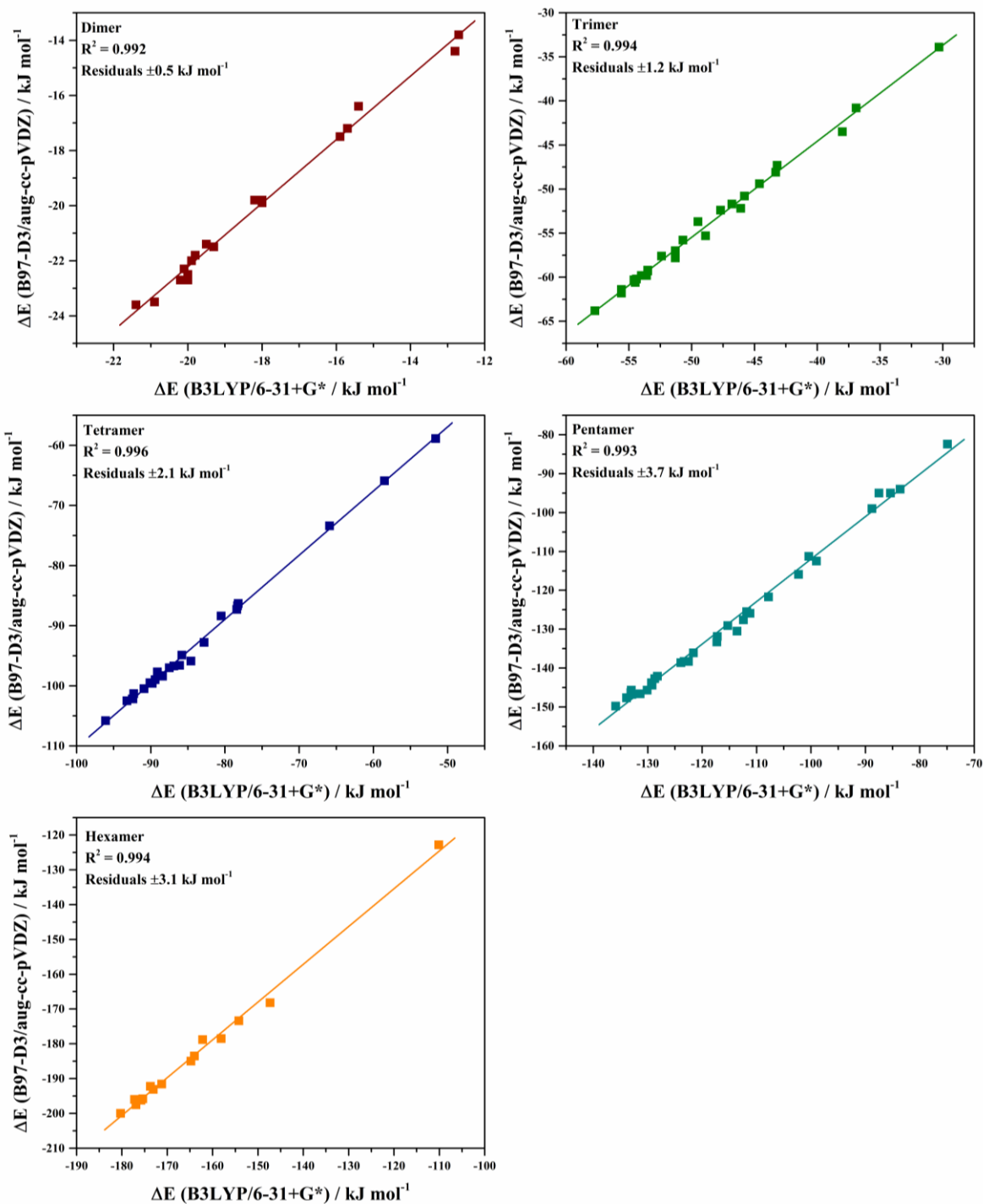


**Fig. S8.** Selected structures of phenylacetylene pentamer. The relative ZPE corrected stabilization energies and relative Gibbs free energy of formation at 100K (both corrected for BSSE in the electronic energies) in  $\text{kJ mol}^{-1}$  are given against each structure. See Table S5 for more details.

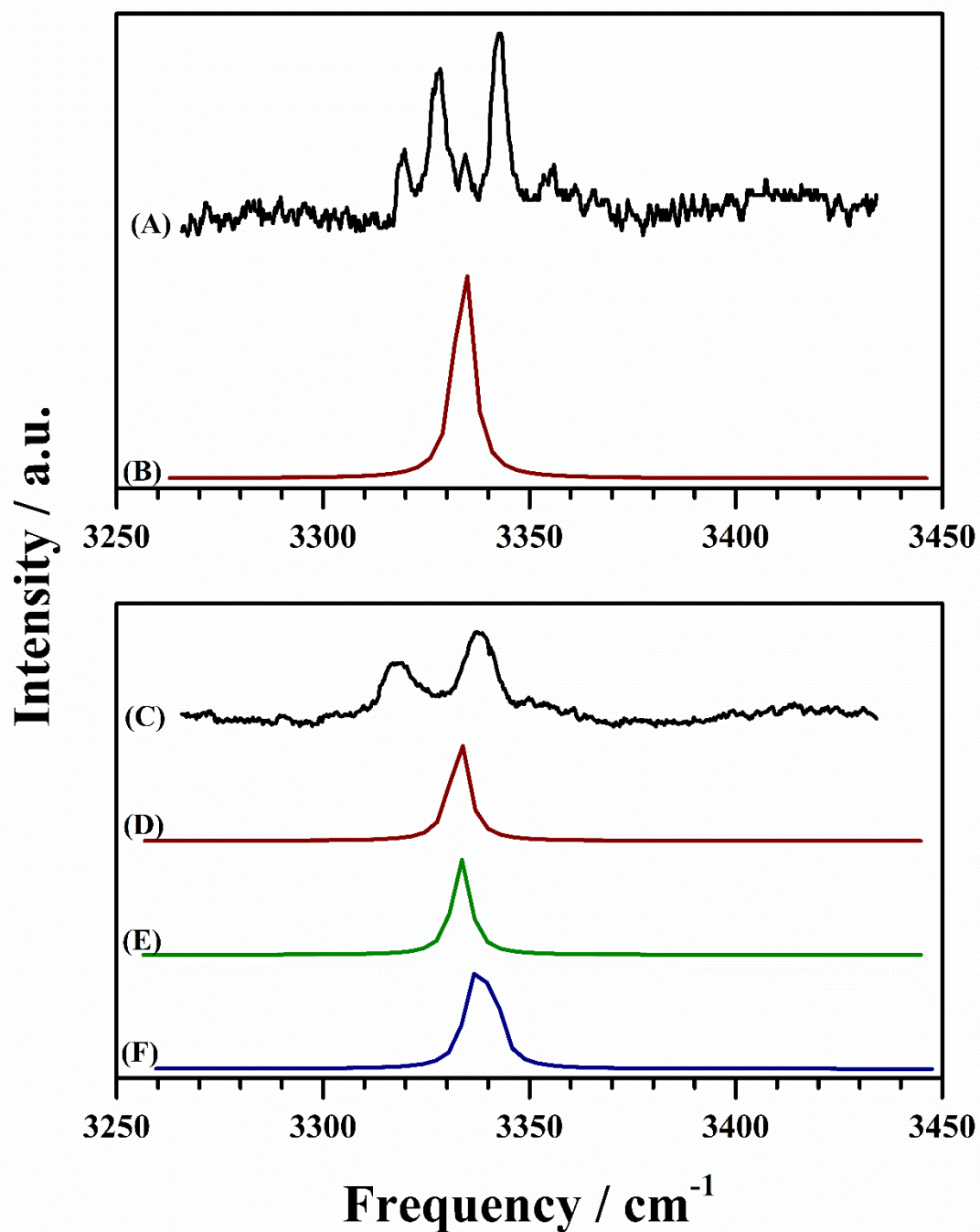




**Fig. S9.** Selected structures of phenylacetylene hexamer. The relative ZPE corrected stabilization energies and relative Gibbs free energy of formation at 100K (both corrected for BSSE in the electronic energies) in  $\text{kJ mol}^{-1}$  are given against each structure. See Table S5 for more details.



**Fig. S10.** Plots of linear-correlation in the electronic stabilization energy calculated at B97-D3/aug-cc-pVDZ and B3LYP/6-31+G\* levels of theory for phenylacetylene clusters of various sizes. In all the cases the electronic stabilization energy calculated at B97-D3/aug-cc-pVDZ level is higher than that calculated at B3LYP/6-31+G\* level. The residuals were minimum for the dimer (within  $\pm 0.5 \text{ kJ mol}^{-1}$ ) and maximum for pentamer (within  $\pm 3.7 \text{ kJ mol}^{-1}$ ).



**Fig. S11.** Comparison of experimental and computed spectra for the monomer (top panel) and the dimer (bottom panel). In the case of dimer, the three computed spectra correspond to anti-parallel  $\pi$ -stacked structure (trace D), T-shaped structure with aromatic C–H $\cdots\pi$  interactions (trace E) and parallel  $\pi$ -stacked structure (trace F). The experimental of both monomer and dimer is complicated due to anharmonic coupling, which cannot be reproduced using harmonic calculations.

**Table S1.** Electronic stabilization energies calculated at B3LYP-D3/6-31+G\* and B97-D3/aug-cc-pVDZ level, ZPE corrected stabilization energies and relative Gibbs free energy of formation at 100K (both corrected for BSSE in the electronic energies at B97-D3/aug-cc-pVDZ level) in  $\text{kJ mol}^{-1}$  for various structures of phenylacetylene dimer. The structure number given in parenthesis refers to the structure shown in Figure S5.

Structure	$\Delta E_e$ B3LYP-D3	$\Delta E_e$ B97-D3	$\Delta E$	$\Delta G$ (100K)
Dimer-01 (D1)	-21.4	-23.6	-18.2	-4.7
Dimer-02 (D2)	-20.9	-23.5	-17.8	-3.8
Dimer-03 (D4)	-20.2	-22.7	-16.9	-2.8
Dimer-04 (D3)	-20.1	-22.3	-17.1	-2.3
Dimer-05 (D6)	-20.0	-22.7	-16.7	-3.0
Dimer-06 (D5)	-20.0	-22.5	-16.8	-3.1
Dimer-07	-19.9	-22.0	-16.1	-2.8
Dimer-08 (D7)	-19.8	-21.8	-15.8	-2.6
Dimer-09	-19.5	-21.4	-15.0	-1.3
Dimer-10	-19.3	-21.5	-16.2	-2.8
Dimer-11 (D9)	-18.2	-19.8	-14.1	-0.5
Dimer-12 (D10)	-18.0	-19.8	-13.7	-0.2
Dimer-13 (D11)	-18.0	-19.9	-13.6	0.0
Dimer-14	-15.9	-17.5	-11.8	1.2
Dimer-15 (D12)	-15.7	-17.2	-12.1	2.2
Dimer-16 (D13)	-15.4	-16.4	-11.8	1.0
Dimer-17 (D14)	-12.8	-14.4	-9.1	3.5
Dimer-18 (D15)	-12.7	-13.8	-10.0	2.4
Dimer-19 (D8)	--	-19.6	-14.5	-0.8

**Table S2.** Electronic stabilization energies calculated at B3LYP-D3/6-31+G\* and B97-D3/aug-cc-pVDZ level, ZPE corrected stabilization energies and relative Gibbs free energy of formation at 100K (both corrected for BSSE in the electronic energies at B97-D3/aug-cc-pVDZ level) in kJ mol<sup>-1</sup> for various structures of phenylacetylene trimer. The structure number given in parenthesis refers to the structure shown in Figure S6.

Structure	$\Delta E_e$ B3LYP-D3	$\Delta E_e$ B97-D3	$\Delta E$	$\Delta G$ (100K)
Trimer-01 (T1)	-57.7	-63.8	-45.5	-13.7
Trimer-02 (T2)	-55.6	-61.8	-44.1	-13.3
Trimer-03 (T3)	-55.6	-61.4	-43.6	-12.2
Trimer-04 (T6)	-54.6	-60.3	-42.4	-11.3
Trimer-05 (T4)	-54.5	-60.6	-42.9	-11.9
Trimer-06 (T5)	-54.4	-60.2	-42.9	-11.3
Trimer-07	-54.0	-59.8	-42.4	-11.4
Trimer-08	-53.6	-59.8	-42.6	-11.9
Trimer-09	-53.5	-59.3	-42.3	-11.9
Trimer-10	-53.5	-59.2	-41.1	-9.7
Trimer-11	-52.4	-57.6	-42.3	-10.9
Trimer-12	-51.3	-57.0	-39.9	-8.4
Trimer-13 (T7)	-51.3	-57.8	-42.2	-12.0
Trimer-14 (T8)	-50.7	-55.8	-40.2	-10.3
Trimer-15	-49.5	-53.7	-38.1	-6.6
Trimer-16	-48.9	-55.3	-40.2	-9.0
Trimer-17 (T9)	-47.7	-52.4	-37.7	-7.4
Trimer-18	-46.8	-51.7	-37.0	-6.7
Trimer-19	-46.1	-52.2	-37.3	-7.9
Trimer-20	-45.8	-50.8	-36.7	-7.0
Trimer-21 (T10)	-44.6	-49.4	-36.8	-8.6
Trimer-22 (T11)	-43.3	-48.1	-36.3	-9.3
Trimer-23 (T12)	-43.2	-47.3	-35.6	-7.3
Trimer-24	-38.0	-43.5	-27.7	2.7
Trimer-25 (T14)	-36.9	-40.8	-28.4	-0.5
Trimer-26 (T15)	-30.3	-33.9	-22.7	4.1
Trimer-27 (T13)		-41.8	-29.9	-1.6

**Table S3.** Electronic stabilization energies calculated at B3LYP-D3/6-31+G\* and B97-D3/aug-cc-pVDZ level, ZPE corrected stabilization energies and relative Gibbs free energy of formation at 100K (both corrected for BSSE in the electronic energies at B97-D3/aug-cc-pVDZ level) in  $\text{kJ mol}^{-1}$  for various structures of phenylacetylene tetramer. The structure number given in parenthesis refers to the structure shown in Figure S7.

Structure	$\Delta E_e$ B3LYP-D3	$\Delta E_e$ B97-D3	$\Delta E$	$\Delta G$ (100K)
Tetramer-01 (Te1)	-96.1	-105.8	-75.3	-26.5
Tetramer -02 (Te2)	-93.2	-102.5	-73.3	-25.8
Tetramer -03 (Te5)	-92.5	-102.2	-72.3	-24.8
Tetramer-04 (Te3)	-92.4	-102.2	-73.0	-24.6
Tetramer-05 (Te4)	-92.3	-101.3	-72.6	-24.1
Tetramer-06	-90.9	-100.5	-70.9	-23.0
Tetramer-07 (Te6)	-90.1	-99.5	-70.9	-23.2
Tetramer-08	-89.8	-99.6	-70.5	-23.4
Tetramer-09	-89.4	-99.0	-70.4	-22.2
Tetramer-10	-89.4	-99.0	-70.3	-23.5
Tetramer-11 (Te9)	-89.1	-97.7	-69.2	-21.4
Tetramer-12	-88.5	-98.3	-70.1	-23.0
Tetramer-13	-88.4	-98.4	-69.9	-23.8
Tetramer-14 (Te7)	-87.5	-97.0	-70.5	-23.4
Tetramer-15 (Te8)	-86.9	-96.7	-69.9	-21.7
Tetramer-16	-86.1	-96.6	-67.6	-19.3
Tetramer-17	-85.8	-94.9	-67.2	-19.5
Tetramer-18 (Te10)	-84.6	-95.9	-67.9	-20.5
Tetramer-19	-82.8	-92.8	-67.2	-21.9
Tetramer-20	-80.5	-88.4	-64.8	-19.5
Tetramer-21	-78.4	-87.3	-61.9	-17.0
Tetramer-22 (Te11)	-78.3	-86.7	-61.0	-14.6
Tetramer-23	-78.2	-86.3	-63.0	-18.8
Tetramer-24 (Te12)	-65.9	-73.4	-54.3	-14.4
Tetramer-25 (Te13)	-58.5	-65.9	-44.5	-1.3
Tetramer-26 (Te15)	-51.6	-58.9	-37.7	5.1
Tetramer-27 (Te14)		-62.7	-42.8	2.1



**Table S4.** Electronic stabilization energies calculated at B3LYP-D3/6-31+G\* and B97-D3/aug-cc-pVDZ level, ZPE corrected stabilization energies and relative Gibbs free energy of formation at 100K (both corrected for BSSE in the electronic energies at B97-D3/aug-cc-pVDZ level) in kJ mol<sup>-1</sup> for various structures of phenylacetylene pentamer. The structure number given in parenthesis refers to the structure shown in Figure S8.

Structure <sup>(a)</sup>	$\Delta E_e$ B3LYP-D3	$\Delta E_e$ B97-D3	$\Delta E$	$\Delta G$ (100K)
Pentamer-01 (P1)	-130.1	-145.7	-106.9	-41.1
Pentamer-02 (P2)	-133.9	-147.7	-106.7	-40.1
Pentamer-03 (P3)	-133.9	-147.6	-106.6	-40.2
Pentamer-04 (P4)	-135.9	-149.8	-106.5	-40.1
Pentamer-05 (P5)	-132.9	-146.8	-105.4	-40.4
Pentamer-06 (P6)	-133.0	-145.7	-104.6	-39.5
Pentamer-07	-133.1	-146.3	-104.5	-40.3
Pentamer-08	-133.1	-146.4	-104.4	-39.9
Pentamer-09	-131.4	-146.6	-104.1	-38.8
Pentamer-10 (P7)	-129.2	-144.4	-104.0	-41.6
Pentamer-11	-129.3	-143.8	-103.0	-37.1
Pentamer-12	-128.7	-142.7	-102.2	-37.7
Pentamer-13	-128.2	-142.1	-100.3	-35.0
Pentamer-14	-128.2	-142.1	-100.2	-34.9
Pentamer-15 (P8)	-123.9	-138.6	-98.2	-33.7
Pentamer-16	-123.3	-138.3	-97.6	-34.3
Pentamer-17	-121.6	-136.1	-97.2	-31.9
Pentamer-18 (P9)	-122.5	-138.3	-96.3	-30.8
Pentamer-19	-117.3	-133.3	-94.1	-30.3
Pentamer-20	-117.2	-131.9	-93.3	-31.8
Pentamer-21 (P10)	-113.6	-130.5	-92.3	-28.7
Pentamer-22 (P11)	-115.3	-129.1	-90.3	-26.6
Pentamer-23 (P12)	-111.2	-125.9	-89.8	-26.9
Pentamer-24	-111.8	-125.5	-88.9	-26.8
Pentamer-25	-112.4	-127.6	-87.2	-24.1
Pentamer-26	-107.8	-121.7	-85.9	-21.8
Pentamer-27	-102.3	-115.9	-83.1	-22.1
Pentamer-28 (P13)	-99.0	-112.5	-78.7	-16.6
Pentamer-29	-100.4	-111.3	-78.2	-15.5
Pentamer-30 (P14)	-88.8	-99.0	-71.6	-18.0
Pentamer-31	-85.4	-95.0	-68.2	-12.4
Pentamer-32	-87.5	-95.0	-68.1	-12.5
Pentamer-33	-83.6	-94.0	-63.0	-2.7
Pentamer-34 (P15)	-74.9	-82.4	-58.6	-3.0

**Table S5.** Electronic stabilization energies calculated at B3LYP-D3/6-31+G\* and B97-D3/aug-cc-pVDZ level, ZPE corrected stabilization energies and relative Gibbs free energy of formation at 100K (both corrected for BSSE in the electronic energies at B97-D3/aug-cc-pVDZ level) in  $\text{kJ mol}^{-1}$  for various structures of phenylacetylene hexamer. The structure number given in parenthesis refers to the structure shown in Figure S9.

<b>Structure<sup>(a)</sup></b>	<b><math>\Delta E_e</math> B3LYP-D3</b>	<b><math>\Delta E_e</math> B97-D3</b>	<b><math>\Delta E</math></b>	<b><math>\Delta G</math> (100K)</b>
Hexamer-01 (H1)	-180.3	-200.0	-160.4	-56.6
Hexamer-02 (H5)	-177.2	-196.0	-156.1	-56.5
Hexamer-03 (H2)	-176.9	-197.5	-159.1	-55.8
Hexamer-04 (H4)	-175.8	-196.2	-157.4	-56.6
Hexamer-05 (H3)	-175.4	-195.8	-157.6	-53.6
Hexamer-06 (H7)	-173.7	-192.2	-153.0	-51.2
Hexamer-07 (H6)	-173.1	-193.1	-154.9	-54.2
Hexamer-08 (H8)	-171.2	-191.6	-152.7	-52.3
Hexamer-09 (H9)	-164.8	-185.0	-146.6	-46.9
Hexamer-10 (H10)	-164.0	-183.5	-146.0	-47.1
Hexamer-11 (H11)	-162.2	-178.8	-145.6	-47.2
Hexamer- (H12)	-158.1	-178.5	-140.9	-42.9
Hexamer-13 (H13)	-154.2	-173.4	-138.1	-44.1
Hexamer-14 (H14)	-147.3	-168.2	-130.6	-37.1
Hexamer-15 (H15)	-110.1	-122.8	-95.6	-19.6