Supporting Information

Vibrational Sum Frequency Generation Study of the Interference Effect on a Thin Film of 4,4′-Bis(N-carbazolyl)-1,1'-biphenyl (CBP) and Its Interfacial Orientation

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A. Calculation of α and μ for 140^0 dihedral angle conformer

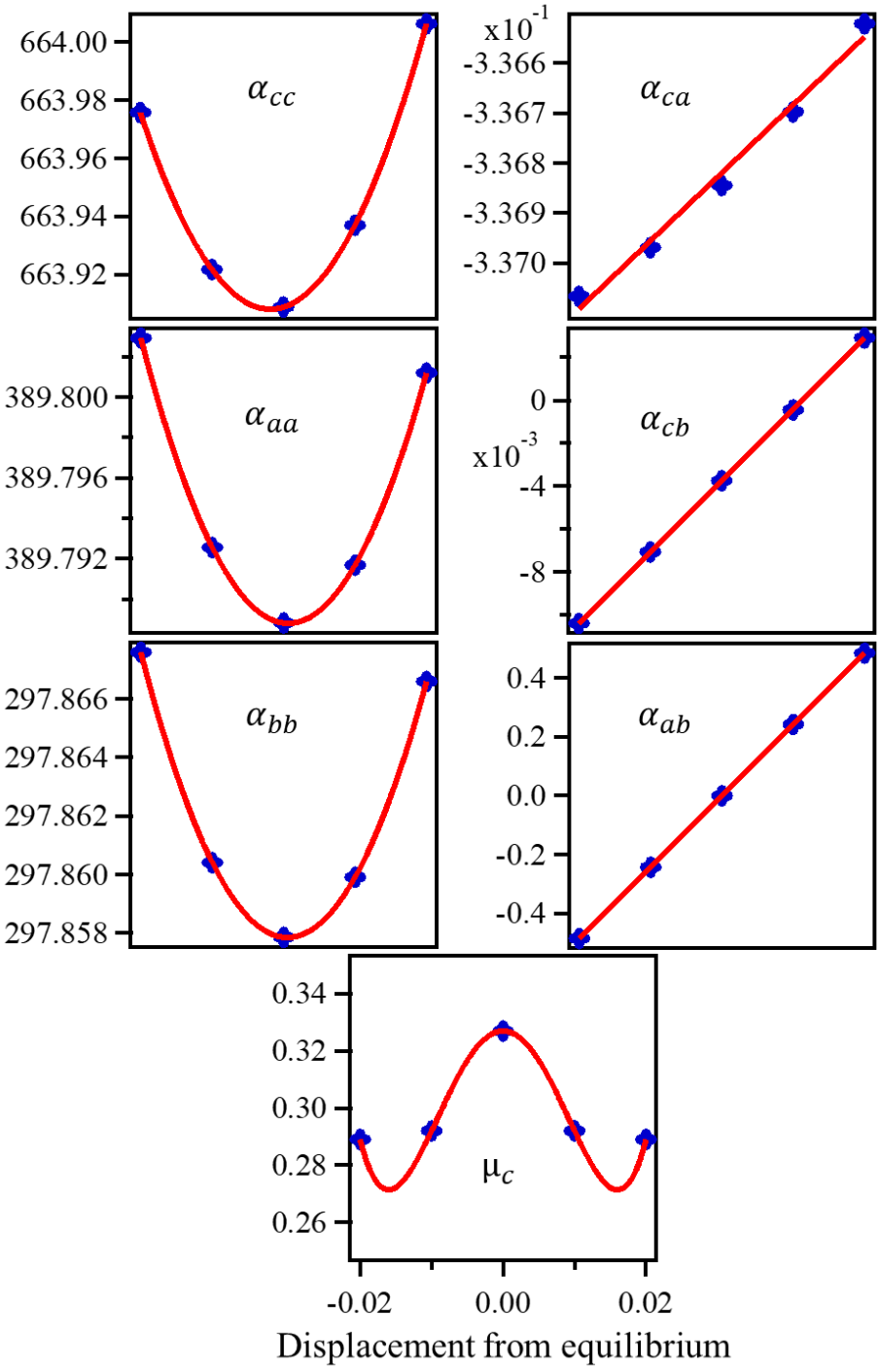

Figure S1. Plots of polarizability (α) and IR transition dipole moment (μ) with respect to nuclear displacement for the 140^0 dihedral angle conformer of CBP. Six polarizability elements are shown, as $\alpha_{ca} = \alpha_{ac}$; $\alpha_{cb} = \alpha_{bc}$; $\alpha_{ab} = \alpha_{ba}$.The blue markers and the red lines represent the calculated numbers and the polynomial fits respectively. Derivatives are calculated from the fitted equation at the zero nuclear displacement.

The orientation plots for different conformers of CBP molecule are shown in the following. χ_{PPP}/χ_{SSP} is plotted with respect to the orientation angle of the transition dipole of the 1600 cm^{-1} vibrational mode of CBP from the laboratory Z axis; for both air/CBP ($\chi^{I}_{PPP}/\chi^{I}_{SSP}$) and CBP/$CaF_2$ ($\chi^{II}_{PPP}/\chi^{II}_{SSP}$) interfaces. The horizontal dotted black lines represent the PPP/SSP amplitude ratio of the Lorentzians for air/CBP and CBP/CaF_2 interface; as obtained from the global fitting procedure. For the air/CBP interface, the interfacial refractive index is varied between $1.0 \leq n'_{CBP/air} \leq 1.7$; whereas for CBP/ CaF_2 interface, it is varied in between $1.4 \leq n'_{CBP/\mathrm{CaF2}} \leq 1.7$; with n' = 1.7 (green), n' = 1.6 (black), n' = 1.5 (blue), n' = 1.4 (red), n' = 1.3 (grey), n' = 1.2 (pink), n' = 1.1 (nude), n' = 1.0 (brown).

B. Orientation plot for 140^0 dihedral angle conformer of CBP

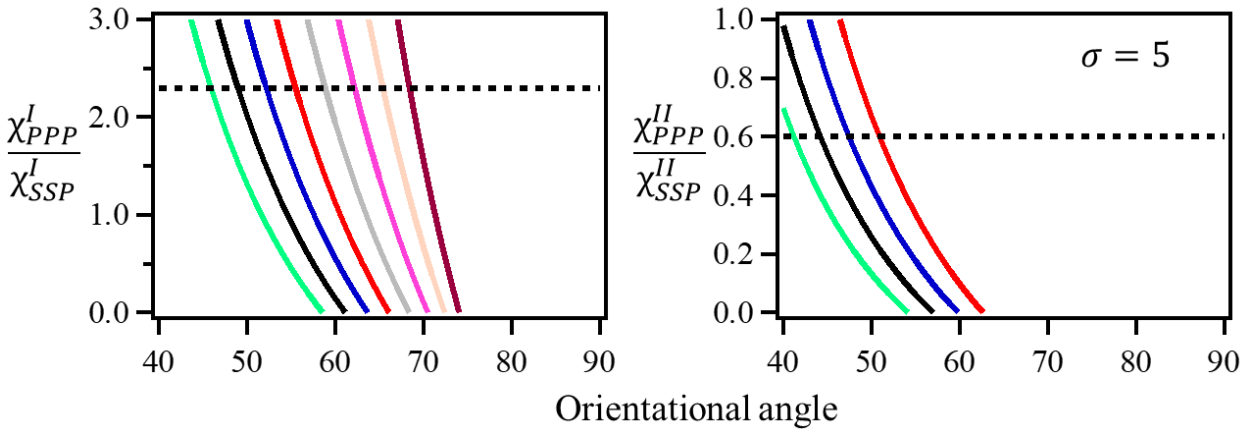

Figure S2: Plots of (left panel) $\chi^{I}_{PPP}/\chi^{I}_{SSP}$ and (right panel) $\chi^{II}_{PPP}/\chi^{II}_{SSP}$ as a function of orientation angle. Distribution width of the tilt angle is taken $\sigma = 20^0$

C. Orientation plot for 150^0 dihedral angle conformer of CBP

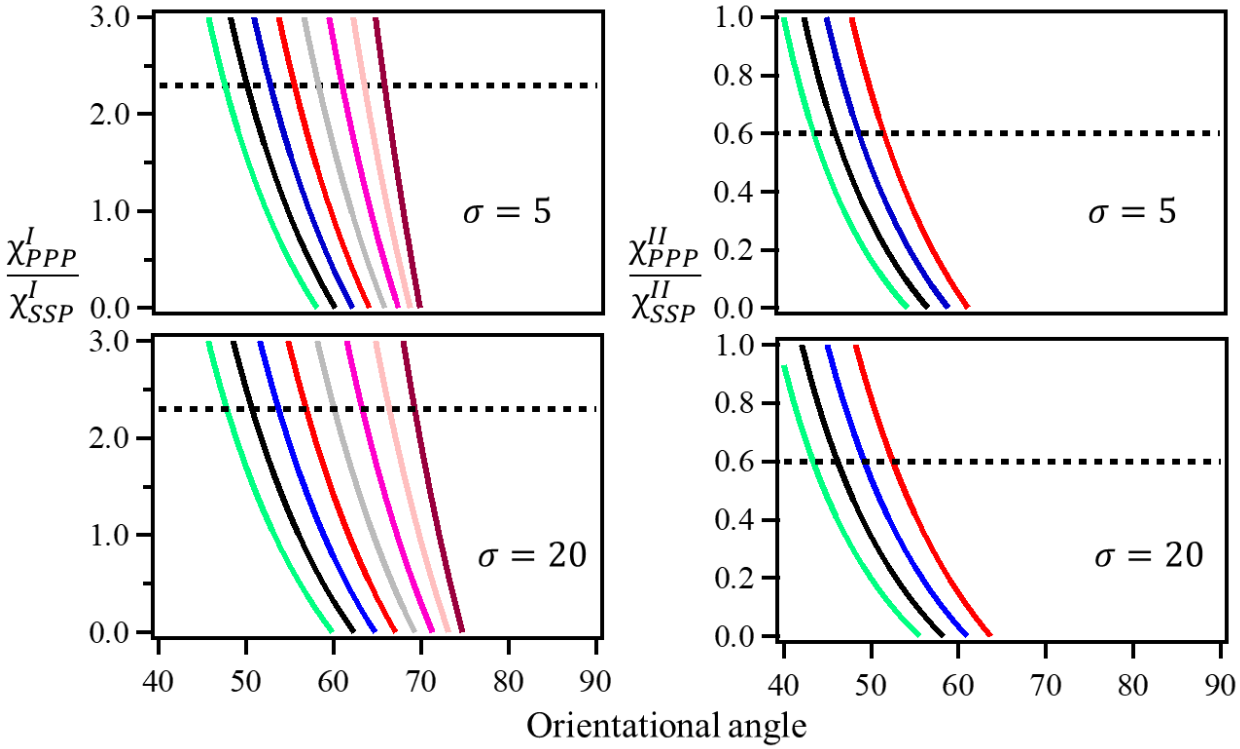

Figure S3: Plots of (left panel) $\chi^I_{PPP}/\chi^I_{SSP}$ and (right panel) $\chi^{II}_{PPP}/\chi^{II}_{SSP}$ as a function of orientation angle. The top and the bottom panels represent the distribution width of the tilt angle to be $\sigma = 5^0$ and $\sigma = 20^0$ respectively.

D. Orientation plot for 130^0 dihedral angle conformer of CBP

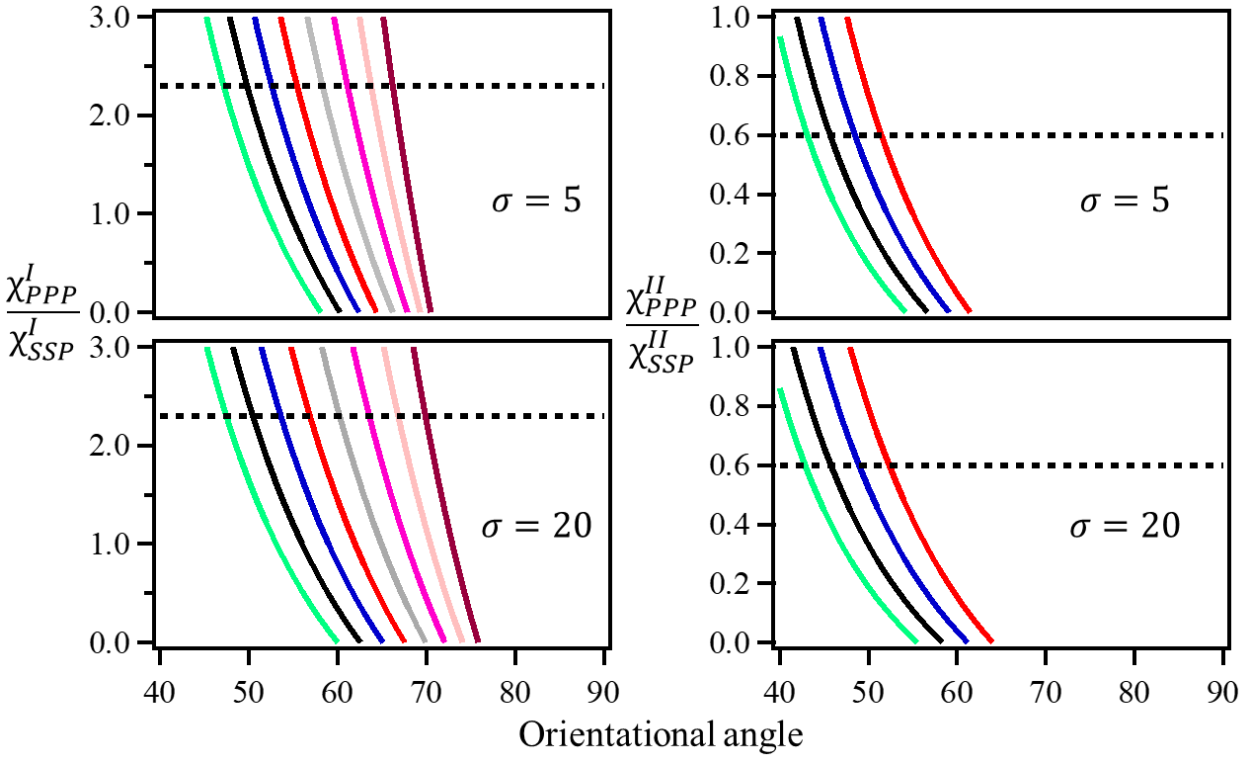

Figure S4: Plots of (left panel) $\chi^I_{PPP}/\chi^I_{SSP}$ and (right panel) $\chi^{II}_{PPP}/\chi^{II}_{SSP}$ as a function of orientation angle. The top and the bottom panels represent the distribution width of the tilt angle to be $\sigma = 5^0$ and $\sigma = 20^0$ respectively.

E. No in-plane azimuthal anisotropy observed for the CBP molecule.

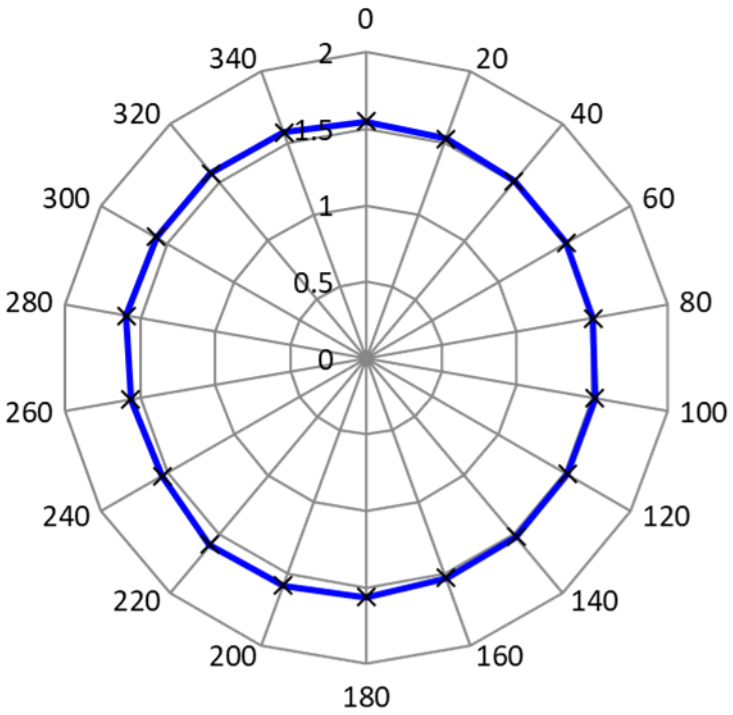

Figure S5: Azimuthal anisotropy study of the CBP film. The CBP film was kept on a rotational stage and VSFG spectra were measured changing the azimuthal angle of the film by 20^0. The black crosses correspond to the normalized VSFG intensity. The blue line connecting the black crosses traces a circle, suggesting that the VSFG intensity doesn't change with the azimuthal angle.

F. Spectral fitting using two interfering Lorentzians and eliminating the third Lorentzian centered ~1630 cm^{-1}.

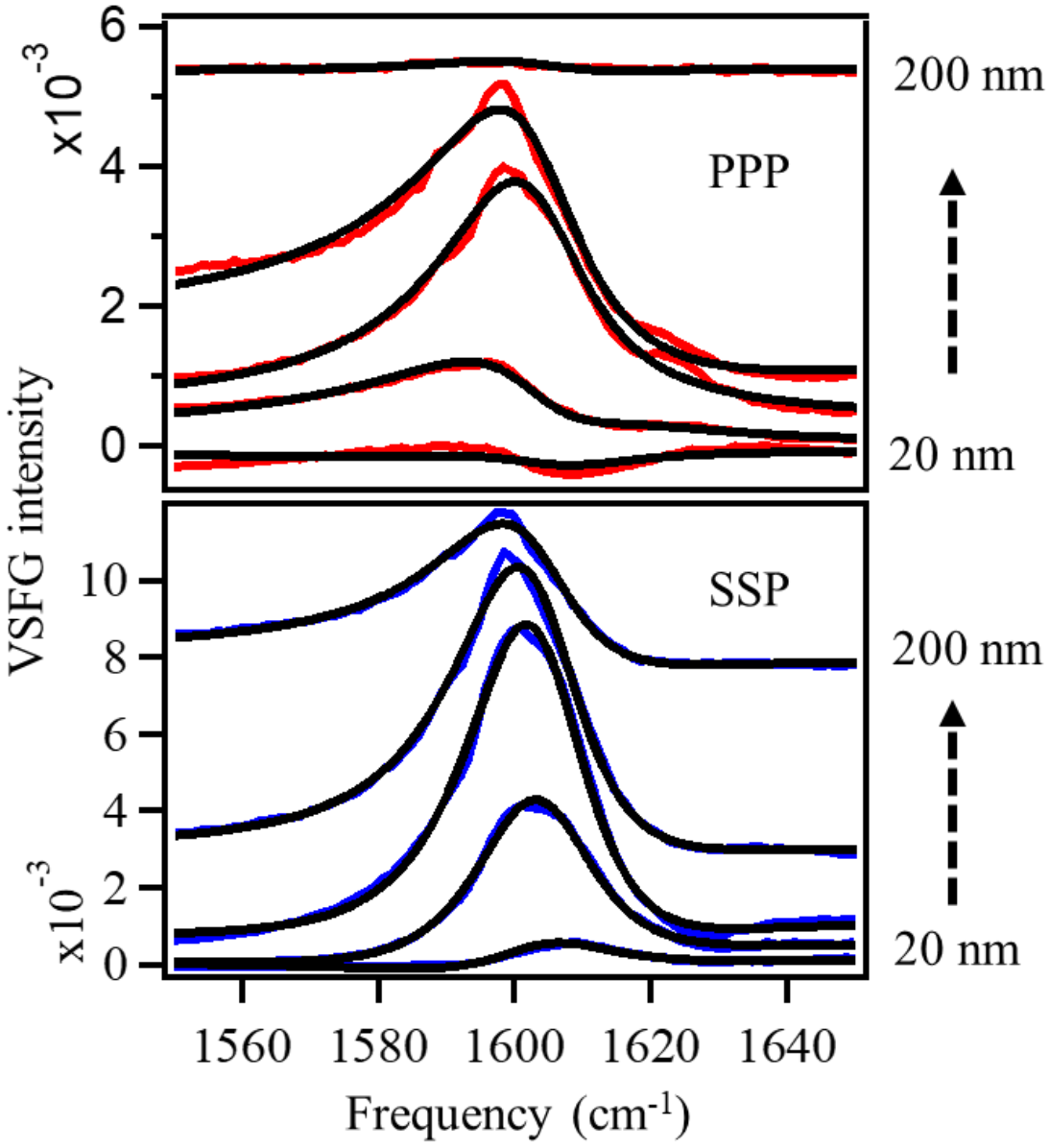

Figure S6: VSFG spectra at PPP and SSP polarization combinations as a function of film thickness. Spectra of 20 nm, 50 nm, 100 nm, 150 nm and 200 nm films are reported. The black lines correspond to the fits of the spectra. The spectral fitting is done using two interfering Lorentzians and eliminating the third Lorentzian centered ~1630 cm^{-1}.

G. Table S1. Global fitting parameters obtained by using only two interfering Lorentzians.

	20 nm		50 nm		100 nm		150 nm		200 nm	
	PPP	SSP	PPP	SSP	PPP	SSP	PPP	SSP	PPP	SSP
y_0	-0.03	-0.02	-0.03	-0.04	-0.02	0.0003	-0.02	0	-0.002	-0.0002
A	-0.18	0.15	0.18	-0.19	-0.16	0.01	0.14	0.005	0.04	0.02
φ	23.6	26.6	45.6	4.51	64.4	60.7	48.8	50.0	42.6	52.9
b_1	0.35	0.28	0.37	0.3	-0.27	-0.22	-0.25	-0.2	-0.07	-0.06
b_2	0.005	0.03	-0.02	-0.11	0.05	0.27	0.05	0.27	0.02	0.11
Γ_1	20.4	These parameters are kept constant during the global fitting.								
Γ_2	13.6									
ω_1	1606.6									
ω_2	1603.2									
Φ_2	13.7	11.1	17.2	14.7	22.2	18.8	28.7	24.9	29.2	31.2

H. Normal mode vector for 1600 cm^{-1} band (showing maximum displacement)

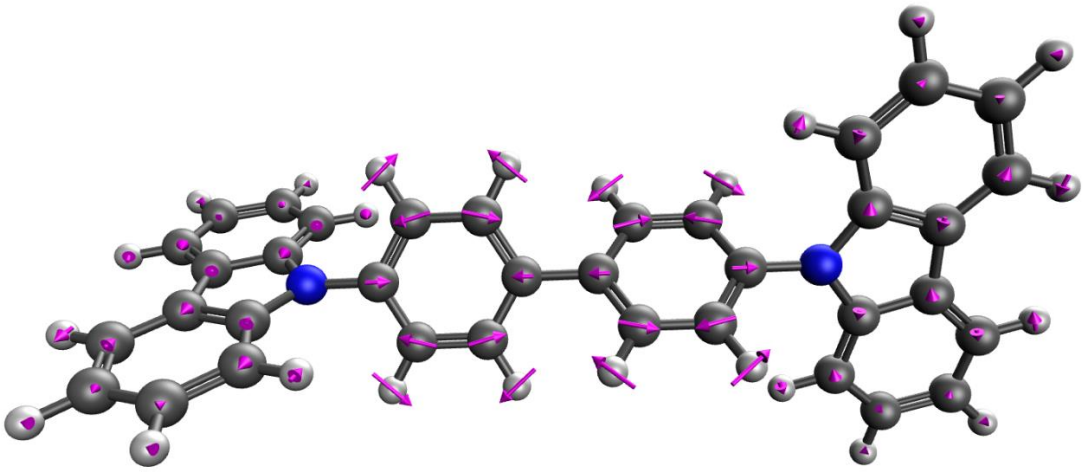

Figure S7: CBP molecule exported from iqmol visualization software in QChem. The pink arrows in this graphic represent the normal mode vectors corresponding to the ~1600 cm^{-1} band of CBP. This normal mode is mainly localized on the biphenyl portion and has negligible contribution from the carbazole moiety of the molecule.

I. Normal mode vector for 1630 cm^{-1} band (showing maximum displacement)

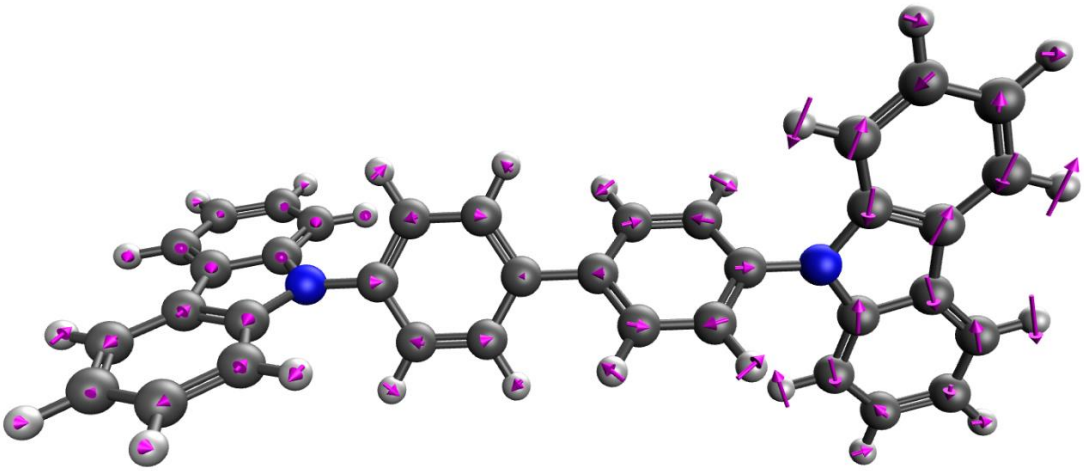

Figure S8: CBP molecule exported from iqmol visualization software in QChem. The pink arrows in this graphic represent the normal mode vectors corresponding to the ~1630 cm^{-1} band of CBP. This normal mode is predominantly localized on the carbazole part of the molecule.