Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for:

"*The Covalently Bound Diazo Group as an Infrared Probe for Hydrogen Bonding Environments*"

Table S1. Population relaxation dynamics of diazo asymmetric stretching modes at two selected frequencies.

Position (cm^{-1})	a_1	τ_1, ps	a_2	τ_2, ps
2097.5	4.26	0.25	3.43	1.28
2127.4	-8.06	0.33	-5.63	1.47

Table S2. Position (ω_0) of the diazo asymmetric stretching vibration determined from linear IR experiments and parameters of spectral diffusion obtained from 2D-IR measurements.

Diazo group	ω_0, cm^{-1}	A	τ, ps	B
DON in water	2097.5	0.20	1.01	0.23

Fig. S1 C=N=N asymmetric stretching vibration band of DOBAEE in different solvents, as indicated. The solid line in each case is the fit of the data to a Voigt profile.

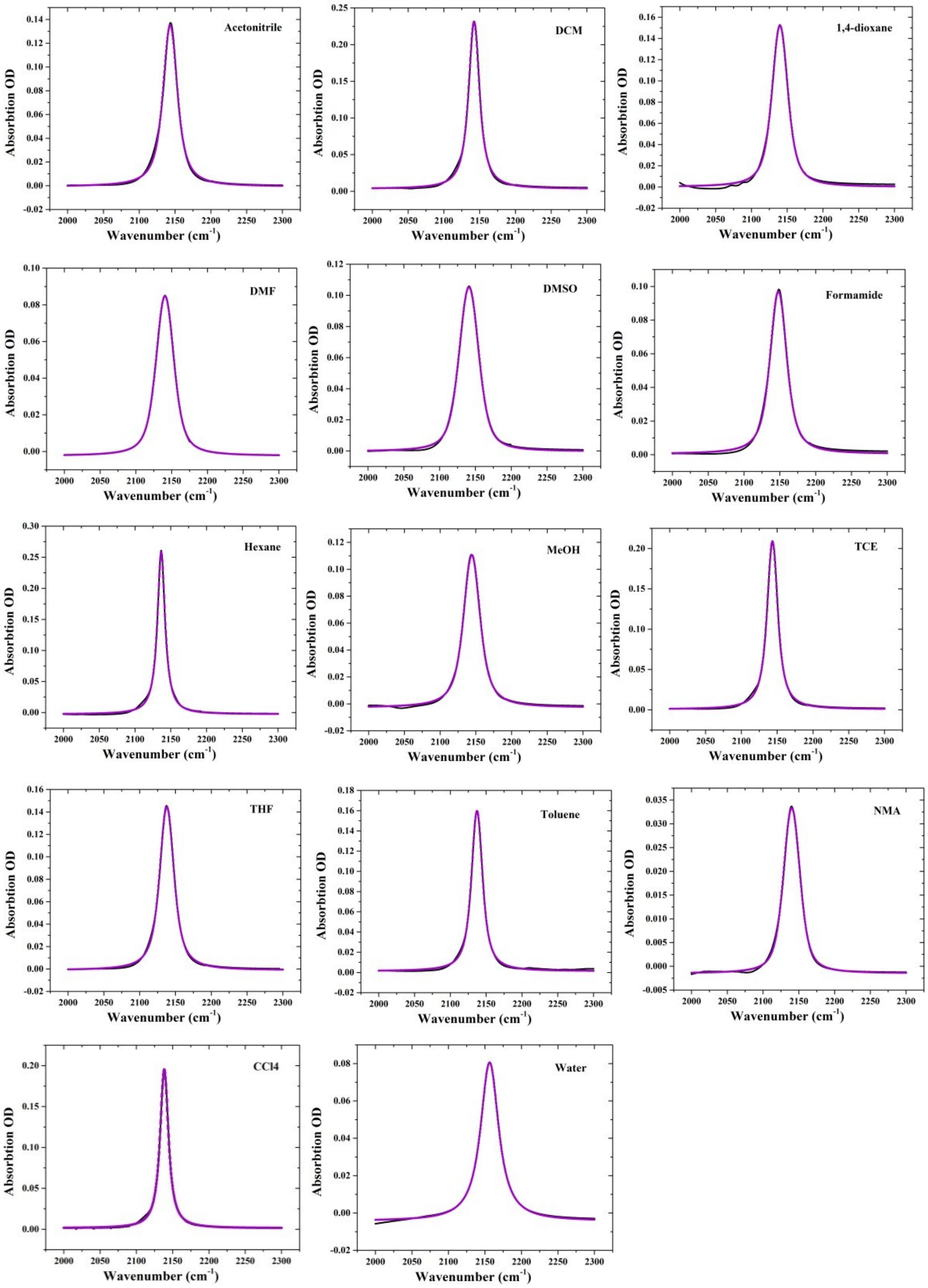


Fig. S2 Position (ω_0) and FWHM of C=N=N asymmetric stretching vibration band of DOBAEE versus the solvent parameter α in protic solvents (top) and all studied solvents (bottom).

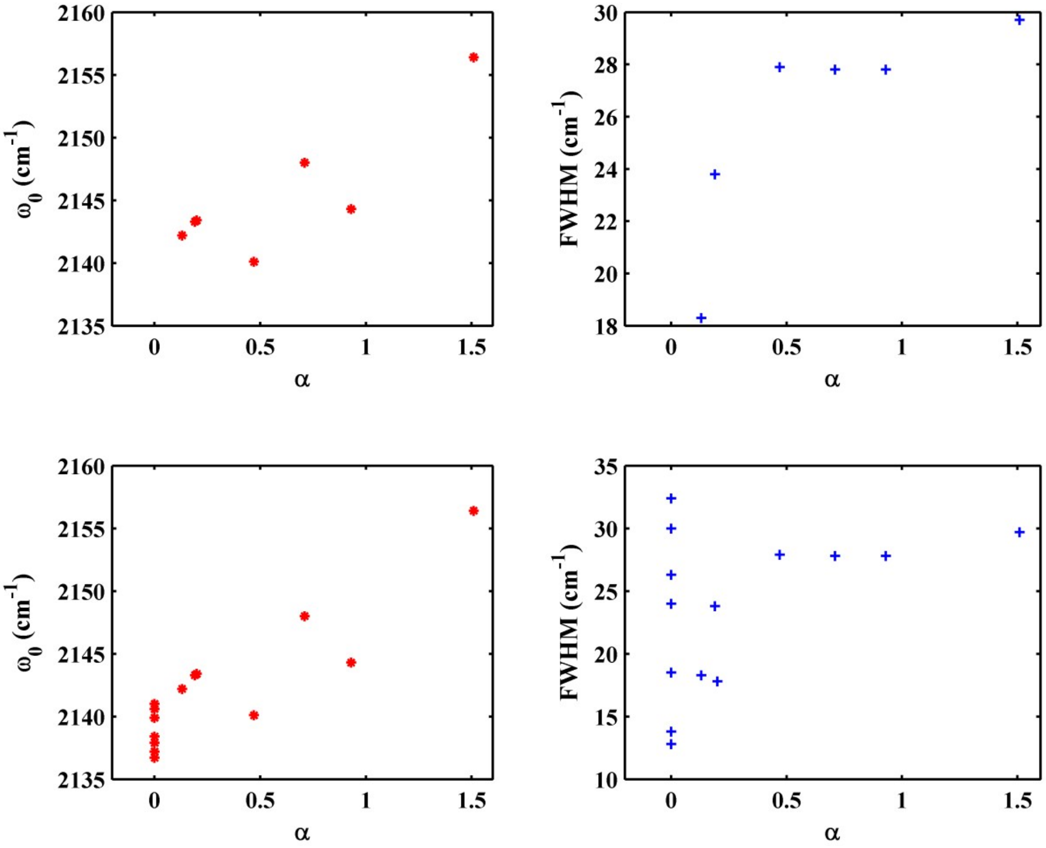
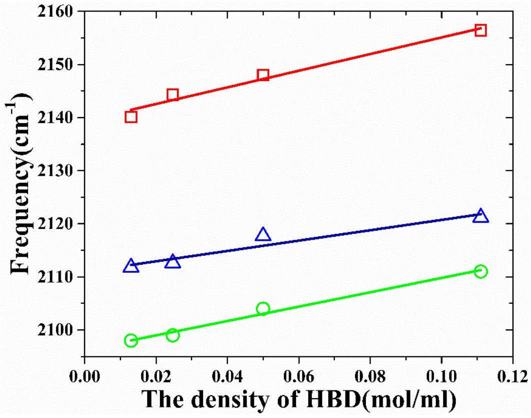


Fig. S3 Position of C=N=N and N=N=N asymmetric stretching vibration (v_{as}) versus the density of hydrogen-bond donor (HBD) groups in solvents. Red line: C=N=N v_{as} of DOBAEE in HBD solvents; Blue line: N=N=N v_{as} of 3-(p-azidophenyl)-1-propanoic acid in HBD solvents; Green line: N=N=N v_{as} of 5-azido-1-pentanoic acid in HBD solvents.



To further validate the relationship between FWHM and Kamlet–Taft parameters, we analyzed the results of other probes in literatures using these methods[1, 2]. For nitrile ν_{as} of either 5-cyanoindole (shown in Fig. S4 and S5) or N=N=N stretch of 3-(pazidophenyl)-1-propanoic acid (shown in Fig. S6 and S7), there is no linear correlation between FWHM and any single Kamlet–Taft parameters (π^* and β) or combination ($\pi^*+\beta$, $\pi^*-\beta$) was observed. However, as shown in Fig. S8, there is a strong linear correlation between FWHM of N=N=N ν_{as} of 5-azido-1-pentanoic acid and $\pi^*-\beta$ in aprotic solvents but this no longer valid in all studied solvents as shown in Fig. S9 based on the results in Ref. 2. Despite this success, we have to admit that this linear relationship is obtained based on empirical solvent parameters. Hence, it is difficult to yield a precise interpretation of the environment of the specific C=N=N residue in proteins. Nonetheless, this relationship validates the notion that the C=N=N ν_{as} bandwidths can sense both the polarizability and HBA of solvent.

Fig. S4 FWHM of nitrile asymmetric stretching vibration band of 5-cyanoindole in aprotic solvents versus the solvent parameters π^*, β, $\pi^*+\beta$ and $\pi^*-\beta$.

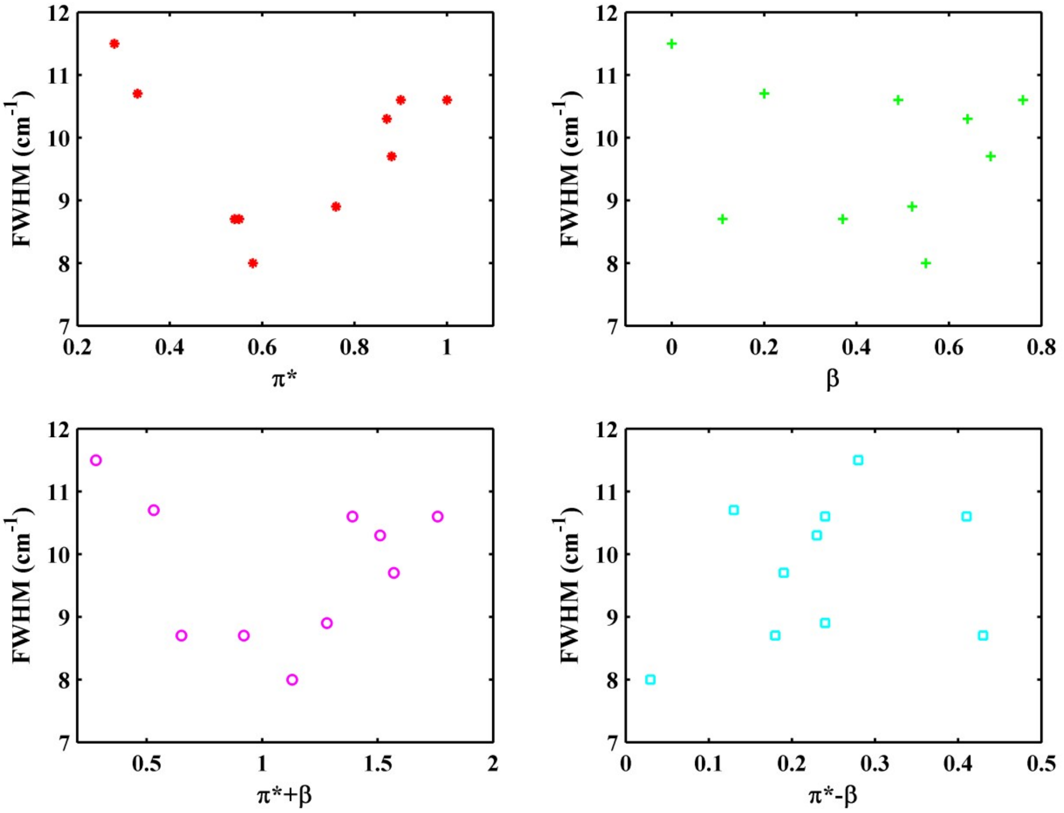


Fig. S5 FWHM of nitrile asymmetric stretching vibration band of 5-cyanoindole in all studied solvents versus the solvent parameters π^*, β, π^*+β and π^*- β.

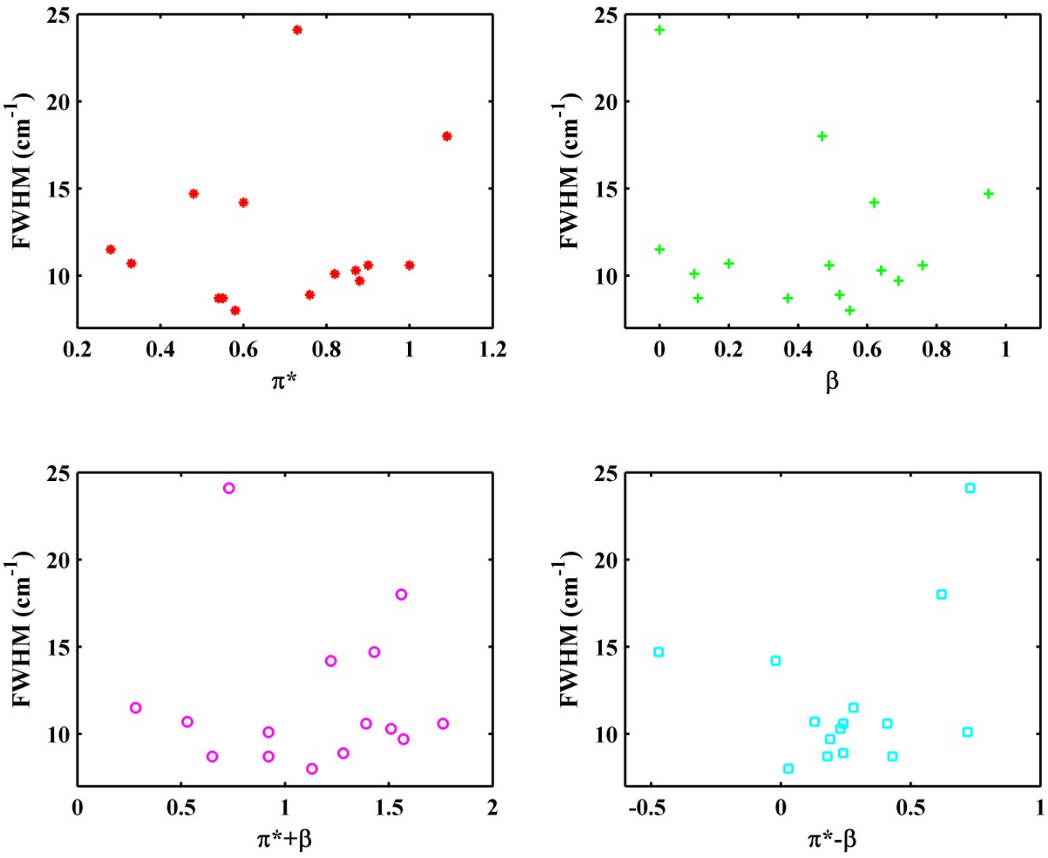


Fig. S6 FWHM of N=N=N asymmetric stretching vibration band of 3-(pazidophenyl)-1-propanoic acid in aprotic solvents versus the solvent parameters π^*, β, π^* + β and π*-β.

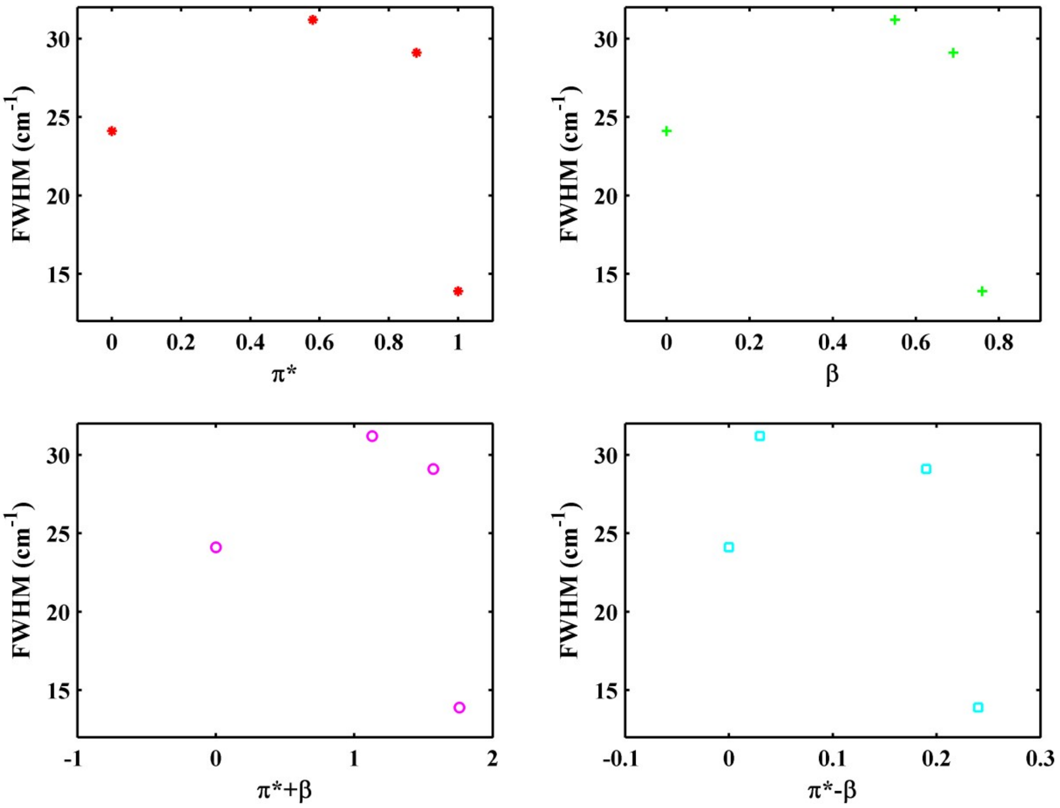


Fig. S7 FWHM of N=N=N asymmetric stretching vibration band of 3-(pazidophenyl)-1-propanoic acid in all studied solvents versus the solvent parameters π^*, β, π^* + β and π*-β.

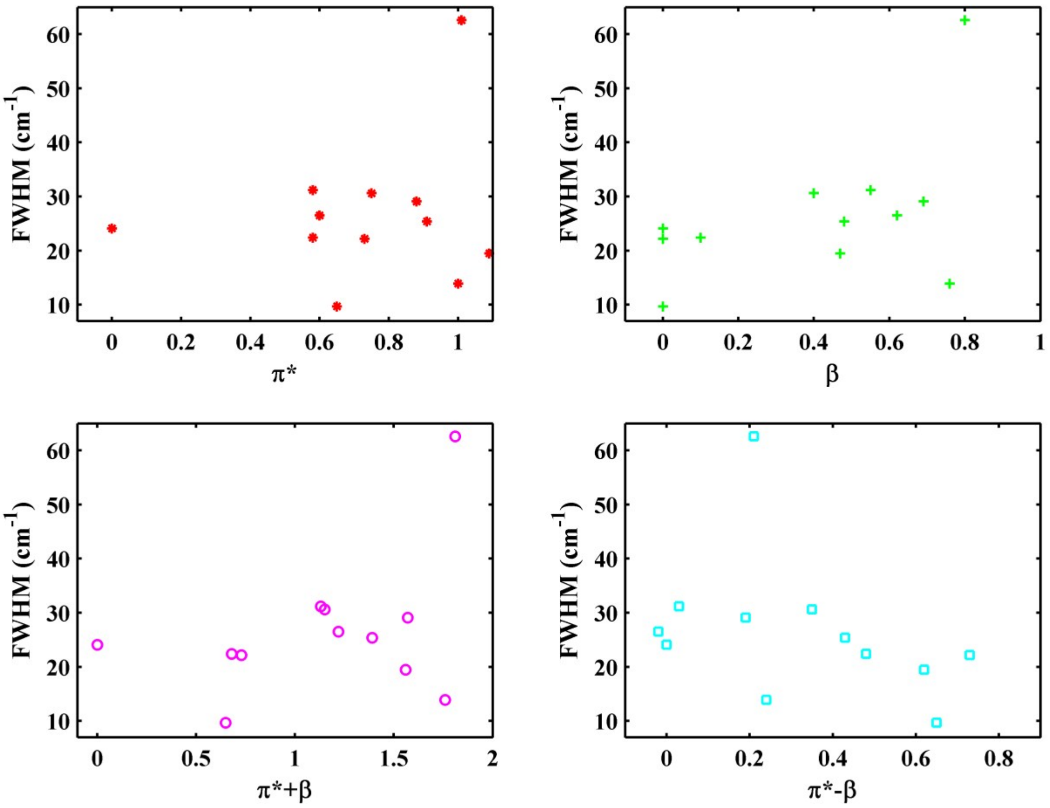


Fig. S8 FWHM of N=N=N asymmetric stretching vibration band of 5-azido-1-pentanoic acid in aprotic solvents versus the solvent parameters π^*, β, $\pi^* + \beta$ and $\pi^* - \beta$.

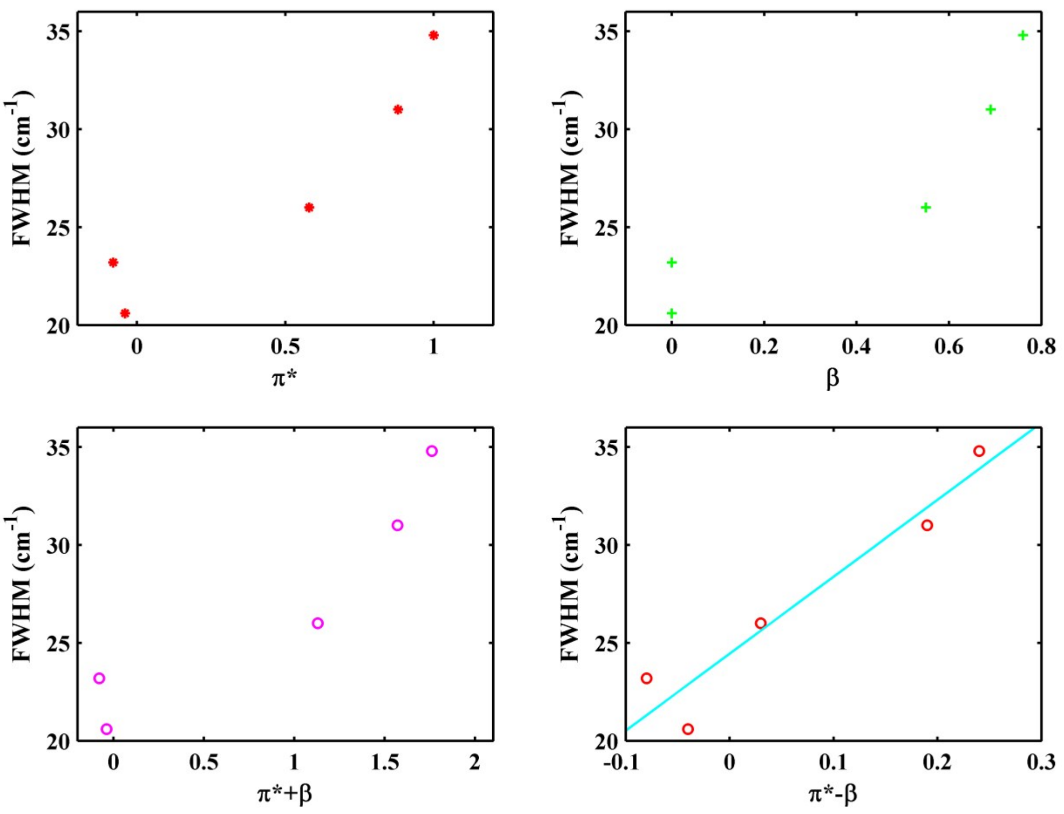
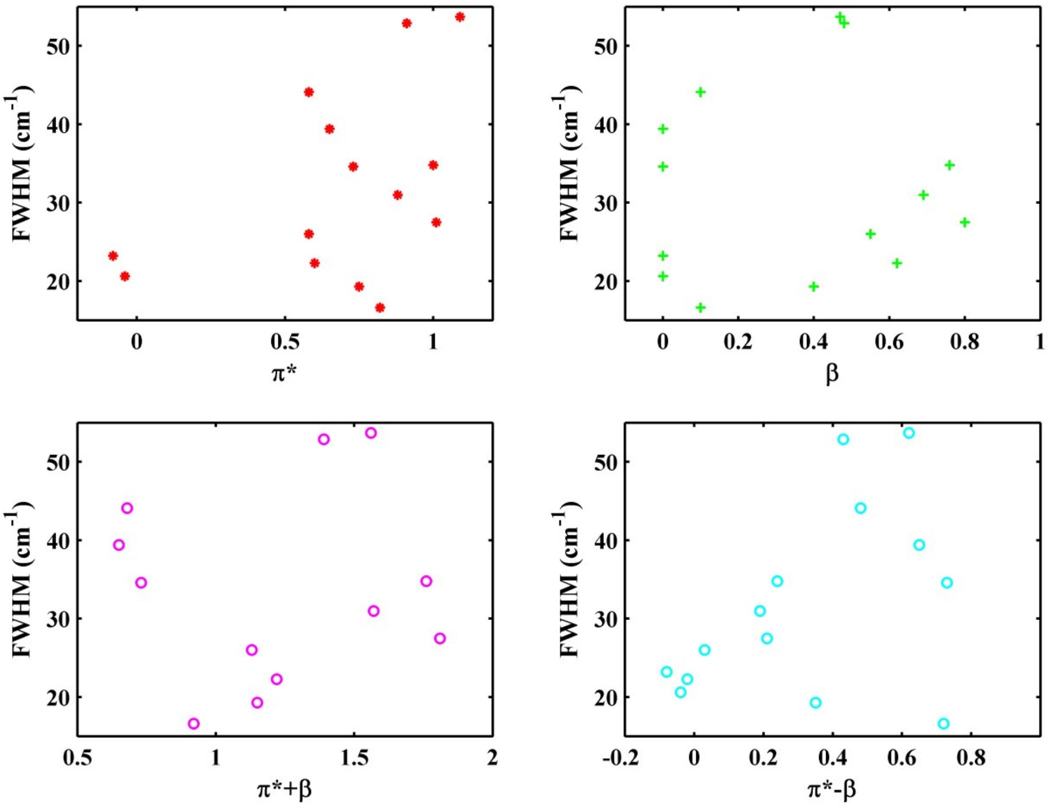


Fig. S9 FWHM of N=N=N asymmetric stretching vibration band of 5-azido-1-pentanoic acid in all studied solvents versus the solvent parameters π*, β, π* + β and π*- β.



References

1. W. Zhang, B. N. Markiewicz, R. S. Doerksen, A. B. Smith Iii and F. Gai, *Physical Chemistry Chemical Physics*, 2016, 18, 7027-7034.
2. M. P. Wolfshorndl, R. Baskin, I. Dhawan and C. H. Londergan, *The Journal of Physical Chemistry B*, 2012, 116, 1172-1179.