

Supporting Information

THz spectra and dynamics of aqueous solutions studied by the ultrafast optical Kerr effect

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(a) Time Domain Data The time domain data recorded through OHD-OKE experiment was normalized at the electronic response ($t = 0$) are shown here on a longer timescale than Figure 2.

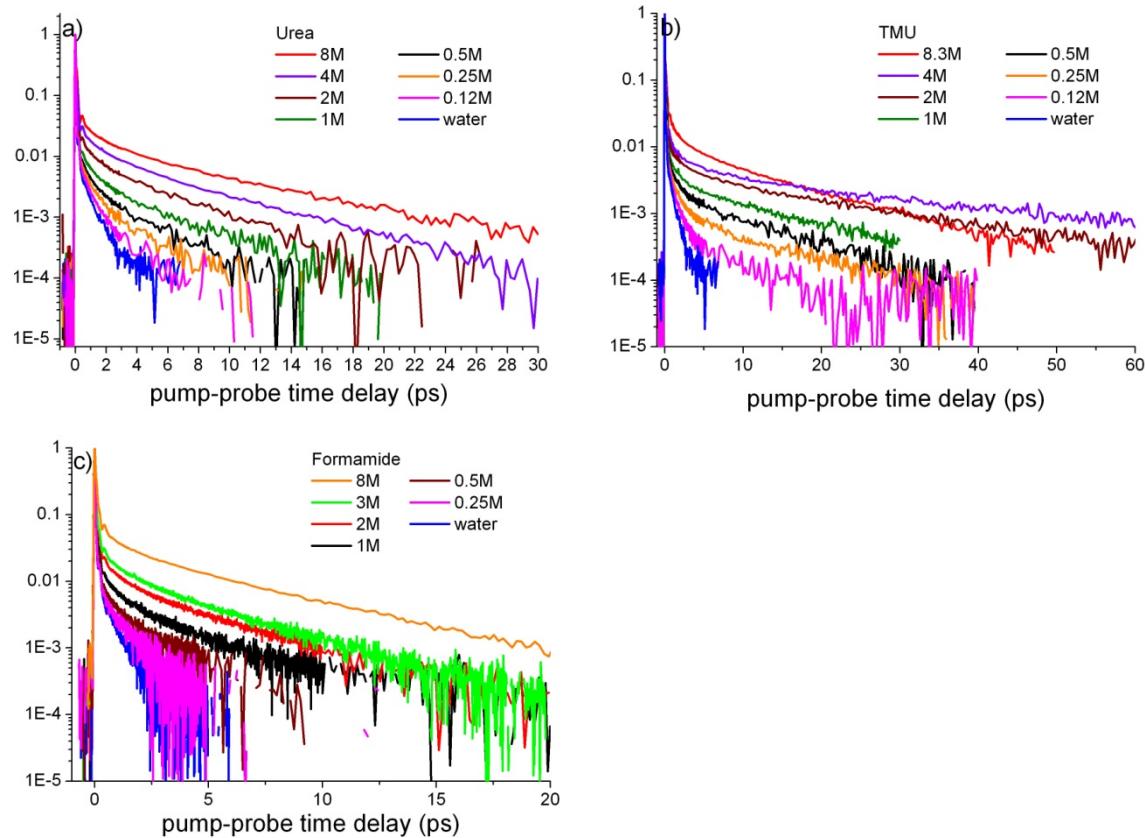


Figure S1. Time domain data of urea, tetramethylurea and formamide.

(b) Fiting data for the sum of exponentials analysis of the solution relaxation time (fits to $t > 1$ ps)

Urea

Concentration /mol	a ₁	τ ₁	a ₂	τ ₂
0	0.008	0.46	0.0018	1.55
0.06	0.010	0.50	0.0016	1.98
0.12	0.009	0.51	0.0019	2.03
0.25	0.011	0.54	0.0020	2.89
0.5	0.008	0.81	0.0020	4.10
1	0.009	0.94	0.0030	5.05
2	0.012	1.17	0.0060	5.50
4	0.017	1.33	0.0100	6.36
8	0.022	1.71	0.0130	8.81

Formamide

Concentration /mol	a ₁	τ ₁	a ₂	τ ₂
0	0.008	0.46	0.0018	1.55
0.06	0.010	0.50	0.0019	2.03
0.12	0.010	0.54	0.0019	2.08
0.25	0.008	0.60	0.0016	2.60
0.5	0.009	0.70	0.0023	3.90
1	0.012	0.95	0.0034	5.00
2	0.015	1.28	0.0061	5.58
3	0.019	1.40	0.0080	5.70
6	0.028	1.38	0.0180	5.81
8	0.035	1.40	0.0260	5.87
25	0.030	1.48	0.0210	14.11

TMU

Concentration /mol	a ₁	τ ₁	a ₂	τ ₂	a ₃	τ ₃
0	0.008	0.46	0.0018	1.55		
0.06	0.009	0.49	0.0016	1.70	0.0003	3.16
0.12	0.007	0.59	0.0010	1.74	0.0006	7.21
0.25	0.006	0.62	0.0017	1.99	0.0009	12.25
0.5	0.005	0.85	0.0014	2.30	0.0017	12.65
1	0.005	1.19	0.0010	3.10	0.0025	15.55
2	0.005	1.38	0.0030	5.56	0.0028	29.27
4	0.006	1.30	0.0043	6.64	0.0030	46.90
6	0.007	1.70	0.0040	7.20	0.0030	47.90
8.3	0.026	1.06	0.0050	7.66	0.0058	15.74

TMAO

Concentration /mol	a ₁	τ ₁	a ₂	τ ₂
0	0.008	0.46	0.0018	1.55
0.25	0.006	0.71	0.0010	1.95
0.5	0.005	0.80	0.0009	2.31
1	0.004	0.90	0.0009	3.03
2	0.003	1.10	0.0010	5.44
4	0.002	1.20	0.0019	6.36

Table S1. The amplitudes and relaxation times obtained from fitting the time domain data to Eq.3.

(c) Calculating the hydration number

The molar volumes obtained from the DFT calculations were 45.62 cm³/mol, 30.54 cm³/mol, 108.08 cm³/mol and 82.61 cm³/mol for UA, FA, TMU and TMAO, respectively. The molecular volumes were calculated from above molar volumes: 75.76 Å³, 50.72 Å³, 179.47 Å³ and 137.18 Å³ for UA, FA, TMU and TMAO, respectively. The volume of water molecule was calculated to be 22 Å³. Knowing the volume of each molecule and assuming spherical shape, the number of water molecules adjacent to the solute, was obtained on the basis of simple geometrical calculations: 21, 17, 32, 28 for UA, FA, TMU, TMAO, respectively.

(d) Calculating the solute rotational time

Weighted mean relaxation time, if only bulk water relaxation and solute rotation is observed might be written in the form:

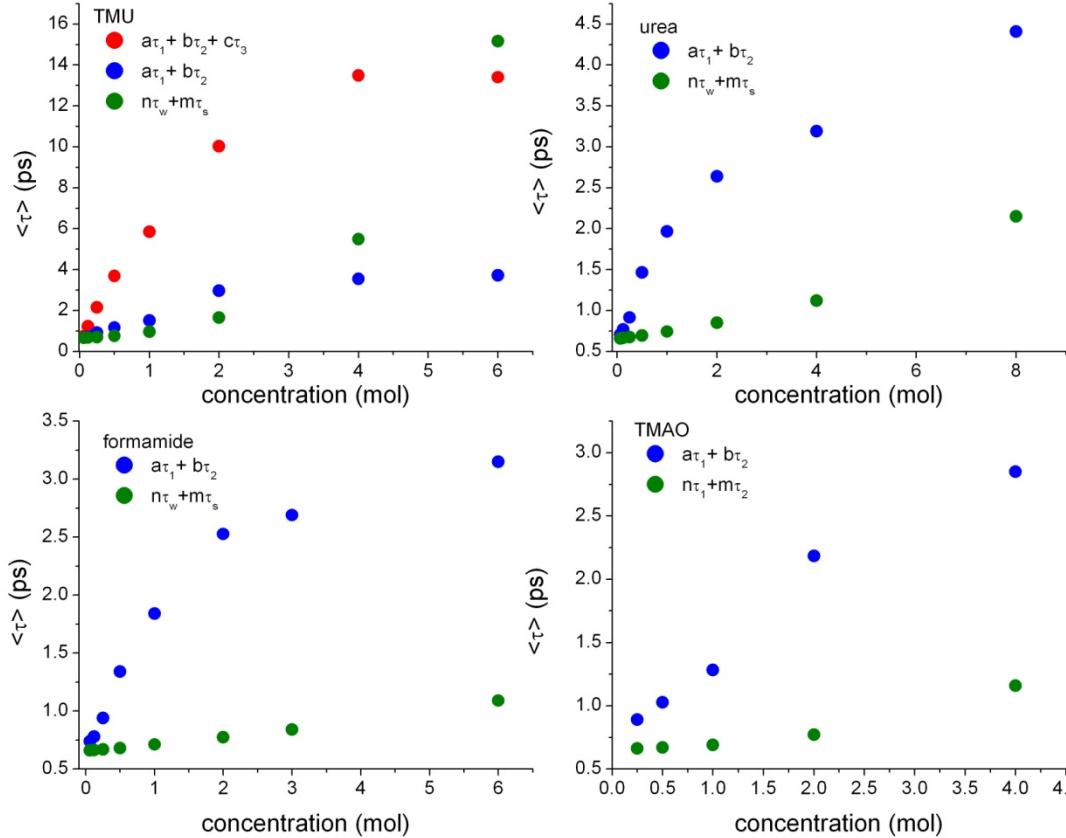
$$\langle \tau_x \rangle = n_w \tau_w + n_s \tau_s \quad (1)$$

Where n_w and n_s is molar fraction of bulk water and solute, respectively. τ_w and τ_s are relaxation time of water and rotational time of solute, respectively.

Rotational time of each solute, τ_s was calculated from:

$$\tau_s = \tau_\infty / \left(\frac{\eta_\infty}{\eta_x} \right) \quad (2)$$

τ_∞ is the time observed for the highest concentration, η_∞ is the viscosity at the highest concentration, and η_x is the viscosity at the concentration studied.



Figu

re S2. Comparison of the weighted mean lifetime (blue dot) with time calculated from Equation S1 (green dot) for four molecules studied. The red dots denote weighted mean lifetime of TMU calculated from three exponential functions.

Values obtained from the Eq. 1 are lower from the ones obtained experimentally, suggesting that an additional contribution must be taken into consideration. We assumed this contribution is slow relaxation of hydration water.

(e) Comparison of entire spectrum with the RSD spectrum

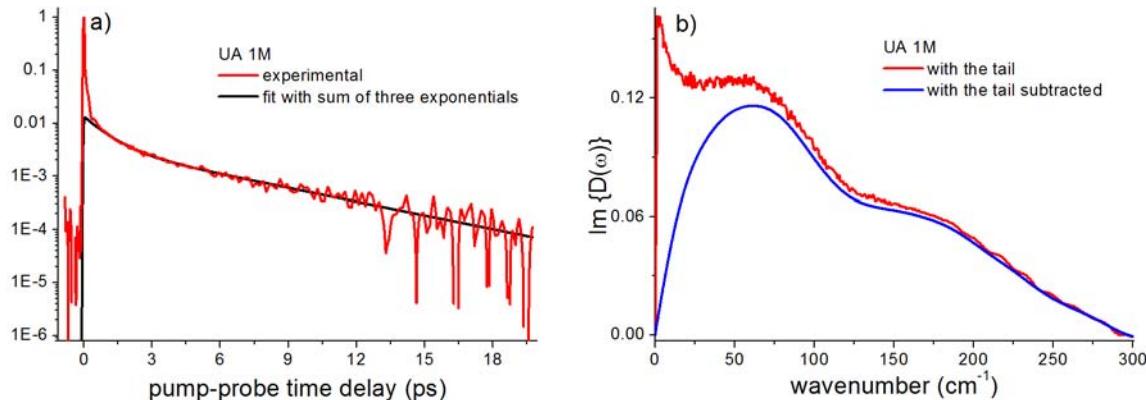


Figure S3. a) Fit by a sum of two exponentials to the urea 1M, b) Fourier transform spectra for UA 1M. The red line denotes the entire spectrum with all contributions included, the blue one is the RSD spectrum (with reorientational picosecond contribution subtracted).

(f) Analysing the Reduced Raman Spectral Densities

The RSD spectra of peptides were fit with two or three functions depending on the concentration.

1. Bucaro-Litovitz (BL) associated with interaction-induced contributions:

$$I_{BL} = A_{BL} \omega^\alpha \exp[-(\omega / \omega_{BL})]$$

where α, A_{BL} are the fitting parameters, ω_{BL} is a characteristic frequency.

2. Gaussian (G)

$$I_G = A_G \exp\left[-\frac{\omega - \omega_G}{\Delta\omega_G}\right]^2$$

3. Antisymmetrized Gaussian (AG)

$$I_{ASG} = A_{ASG} \left[\exp\left[-\frac{\omega - \omega_{ASG}}{\Delta\omega_{ASG}}\right]^2 - \exp\left[-\frac{\omega + \omega_{ASG}}{\Delta\omega_{ASG}}\right]^2 \right]$$

where ω_G, ω_{ASG} denote the centre frequency and $\Delta\omega_G, \Delta\omega_{ASG}$ are the full width at half maximum (FWHM) of fitted components. The A_G, A_{ASG} indicate amplitudes.

The full details of the fitting results to all spectral densities are listed in Tables S1.

concentration (mol)	formamide								
	A_{BL}	α	ω_{BL} (cm ⁻¹)	A_G	ω_G (cm ⁻¹)	$\Delta\omega_G$ (cm ⁻¹)	A_{ASG}	ω_{ASG} (cm ⁻¹)	$\Delta\omega_{ASG}$ (cm ⁻¹)
0.06	0.05	1.54	30.54	-	-	-	0.040	174.3	132.6
0.12	0.06	1.43	31.59	-	-	-	0.044	175.0	127.9
0.25	0.06	1.41	33.96	-	-	-	0.044	175.0	132.6
0.5	0.07	1.32	35.54	0.016	76.1	92.3	0.046	175.8	111.9
1	0.07	1.36	25.00	0.046	77.0	81.5	0.063	169.6	117.0
2	0.12	1.32	27.20	0.055	81.5	65.6	0.089	163.0	121.2
3	0.14	1.29	23.32	0.10	82.0	70.0	0.118	164.0	117.9
6	0.24	1.20	27.72	0.16	84.62	66.8	0.182	164.8	116.1
8	0.33	1.29	25.34	0.25	86.43	65.9	0.25	164.8	110.8
25	0.42	1.21	25.53	0.53	96.03	76.6	0.43	183.8	99.7

concentration (mol)	urea								
	A_{BL}	α	ω_{BL} (cm ⁻¹)	A_G	ω_G (cm ⁻¹)	$\Delta\omega_G$ (cm ⁻¹)	A_{ASG}	ω_{ASG} (cm ⁻¹)	$\Delta\omega_{ASG}$ (cm ⁻¹)
0.06	0.06	1.74	26.45	-	-	-	0.045	171.6	123.6
0.12	0.06	1.5	32.35	-	-	-	0.041	175.0	110.0
0.25	0.07	1.52	33.00	-	-	-	0.042	179.4	118.1
0.5	0.06	1.27	36.10	0.02	63.77	78.3	0.045	173.2	126.9
1	0.08	1.18	31.44	0.04	74.64	66.5	0.050	167.9	129.0
2	0.10	1.35	20.98	0.10	75.15	72.2	0.06	159.1	131.1
4	0.14	1.21	23.10	0.18	77.19	74.6	0.08	157.5	125.6
8	0.21	1.28	19.87	0.32	80.00	77.1	0.11	150.0	126.7

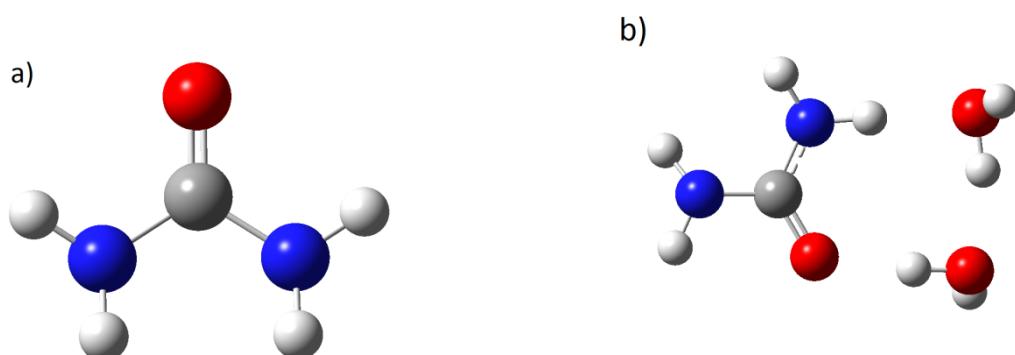
concentration (mol)	TMAO								
	A_{BL}	α	ω_{BL} (cm ⁻¹)	A_G	ω_G (cm ⁻¹)	$\Delta\omega_G$ (cm ⁻¹)	A_{ASG}	ω_{ASG} (cm ⁻¹)	$\Delta\omega_{ASG}$ (cm ⁻¹)
0.25	0.05	2.20	21.0	-	-	-	0.04	172.2	148.0
0.5	0.05	2.21	21.0	-	-	-	0.05	174.0	142.7

1	0.05	2.20	22.0	-	-	-	0.04	174.0	130.0
2	0.04	2.20	22.0	-	-	-	0.05	176.0	140.0
4	0.05	2.20	22.0	-	-	-	0.04	171.5	132.6

concentration (mol)	TMU											
	A_{BL}	α	ω_{BL} (cm ⁻¹)	A_{G2}	ω_{G2} (cm ⁻¹)	$\Delta\omega_{G2}$ (cm ⁻¹)	A_{G3}	ω_{G3} (cm ⁻¹)	$\Delta\omega_{G3}$ (cm ⁻¹)	A_{ASG}	ω_{ASG} (cm ⁻¹)	$\Delta\omega_{ASG}$ (cm ⁻¹)
0.06	0.05	1.52	30.0	-	-	-	-	-	-	0.04	177.0	129.6
0.12	0.06	2.0	23.2	-	-	-	-	-	-	0.04	175.0	130.0
0.25	0.07	2.0	21.5	-	-	-	-	-	-	0.04	171.9	130.0
0.5	0.09	1.65	23.4	-	-	-	-	-	-	0.05	172.5	139.9
1	0.09	1.52	19.5	0.44	56.3	54.2	0.01	133.3	78.1	0.05	173.3	180.1
2	0.19	1.37	23.73	0.036	47.6	58.0	0.01	136.0	29.4	0.07	172.0	140.0
4	0.22	1.33	20.53	0.143	54.4	60.0	0.03	132.0	60.0	0.08	169.0	148.8
6	0.30	1.05	28.54	0.11	52.9	57.6	0.02	130.2	48.15	0.08	172.0	140.0
8.3	0.30	1.05	28.54	0.11	51.4	50.7	0.05	106.7	70.1	0.05	172.3	145.3

Table S2. Fit parameters of Fourier Transform Kerr Spectra of formamide, urea, TMAO and TMU. BL denotes Bucaro-Litovitz, G Gaussian and ASG antisymmetrized Gaussian.

(g) DFT calculations



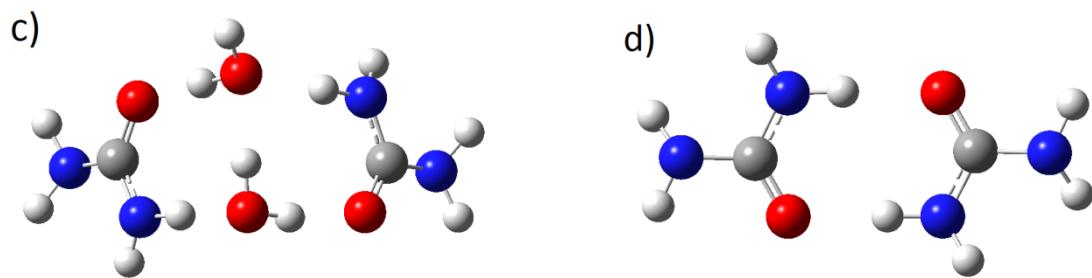


Figure S4. Optimized structure of a) urea monomer b) urea monomer with two water molecules c) urea dimer separated by two water molecules, d) urea dimer

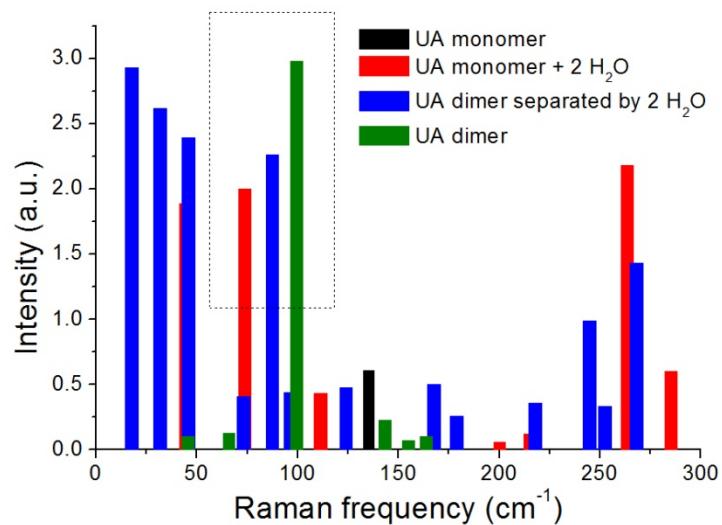
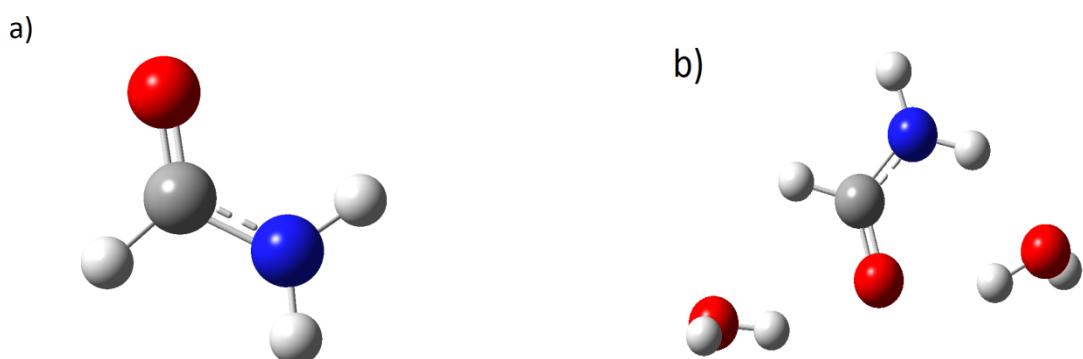


Figure S5. Raman frequencies obtained from DFT calculations. The G mode is marked with the frame.



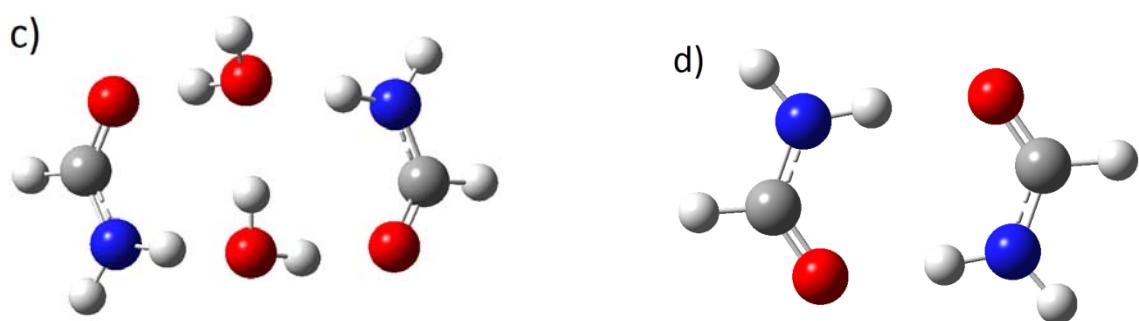


Figure S6. Optimized structures of a) formamide monomer, b) formamide monomer with two water molecules, c) formamide dimer separated by two water molecules, d) formamide dimer

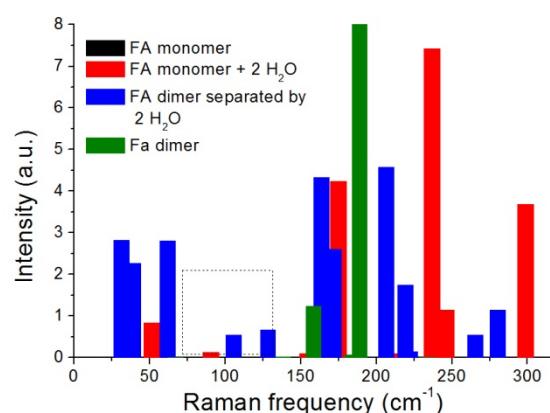


Figure S7. Raman frequencies obtained from DFT calculations. The G mode is marked with the frame.

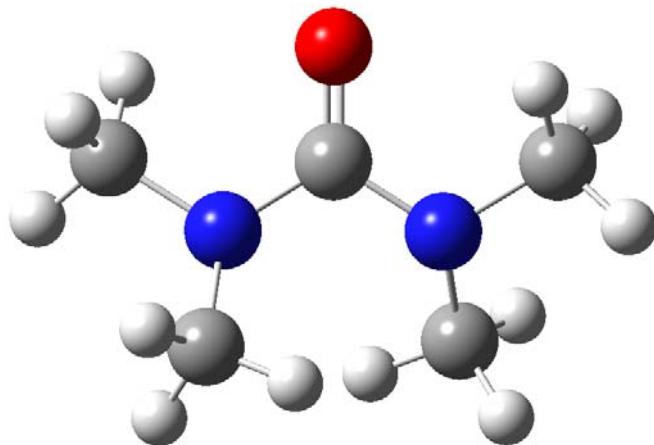


Figure S8. TMU structure

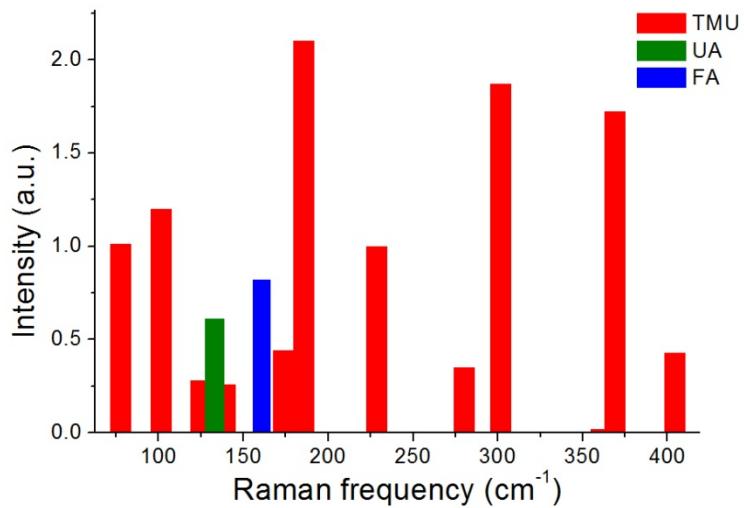


Figure S9. Comparison of DFT spectra for UA, FA and TMU monomers. Multiply modes were obtained for TMU and single modes for UA and FA.