Electronic Supplementary Information (ESI):

Solvatochromism in Urea/Water and Urea-Derivative/Water Solutions

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Solvent polarizability has been obtained from the Lorentz-Lorenz equation $f(n^2)$, and from the refraction indexes measured herein. Catalan and Hopf (European J Org Chem. 2004 Nov;(22):4694–5702) demonstrated that there exists a linear correlation between the SP scale and the Lorentz-Lorenz equation; $SP = -9115.7\ f(n^2) + 23791$. The SdP values were estimated from the results given by Catalán (J Phys Chem B. 2009 Apr 30;113(17), 5951–5960) from the equation which relates the SdP paramer with the Δf function, which depends on the Kirkwood relationship $f(\varepsilon)$ minus the $f(n^2)$ Lorentz-Lorenz relationship ($\Delta f = f(\varepsilon) - f(n^2)$), that is: $SdP = -2.549\ \Delta f + 3.913\ \Delta f^2 + 0.655$. (For instance, $f(\varepsilon) = (\varepsilon-1)/(\varepsilon+2)$; $f(n^2) = (n^2-1)/(n^2+2)$.)

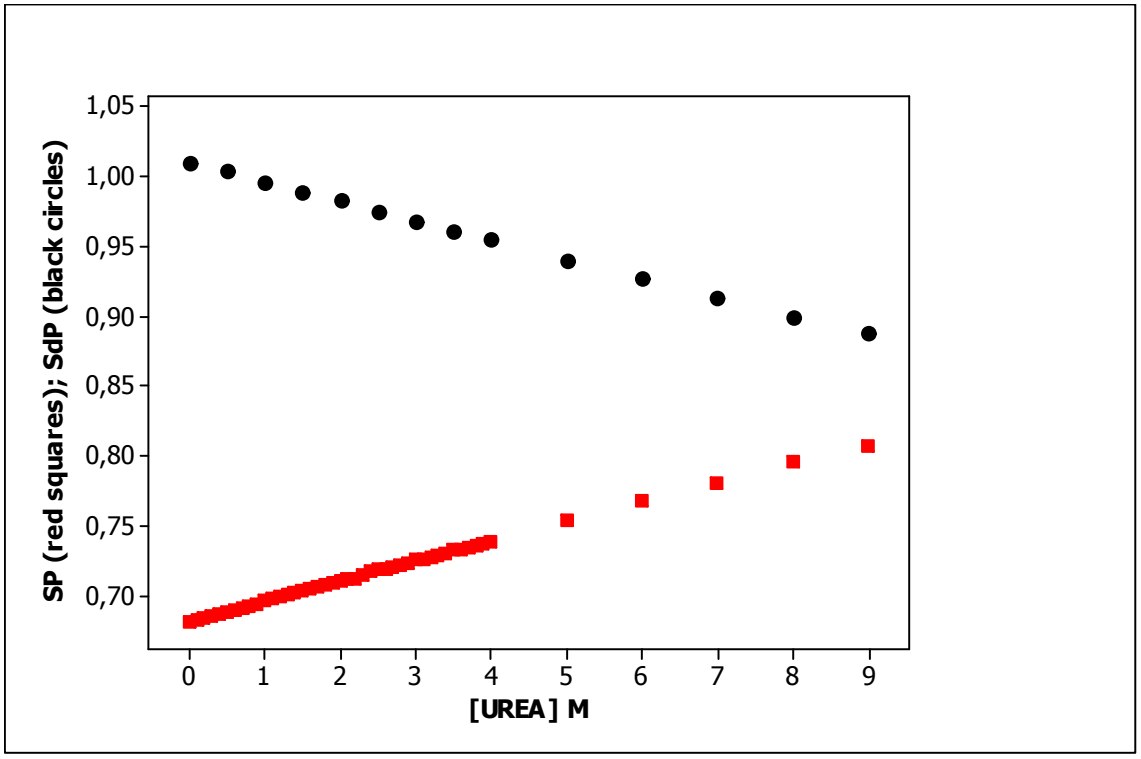

Figure 1. Relationship of the SP (red squares) and SdP (black circles) values for the Urea/Water (U/W) solutions against urea molar concentration.

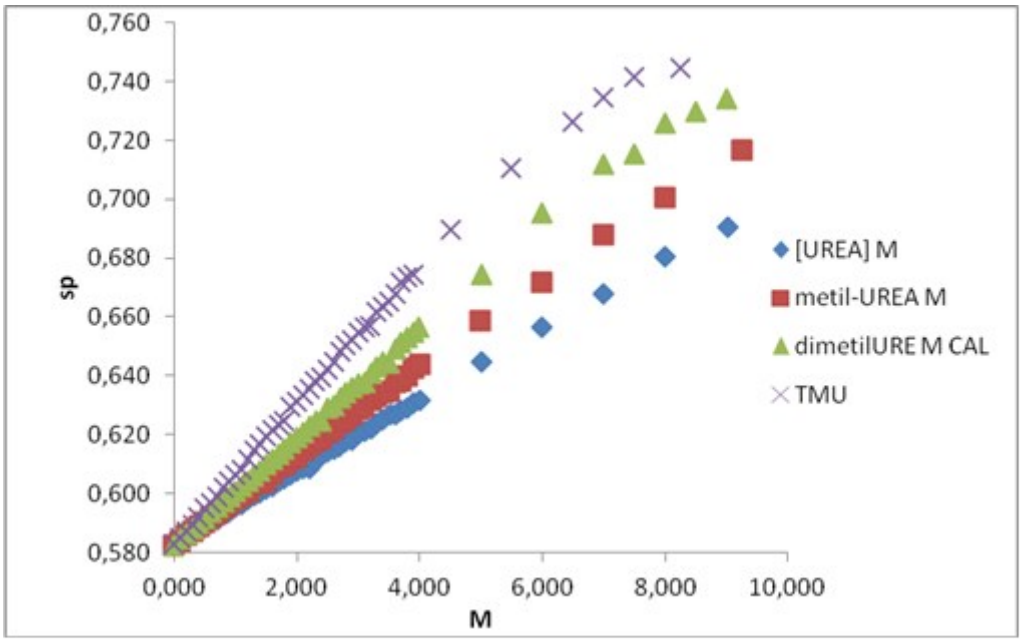

Figure 2. SP values for the solutions of Urea/Water (U/W), Methylurea/Water (MU/W), Dimethylurea/Water (DMU), and Tetramethylurea/Water (TMU/W) against molar concentration of the corresponding denaturant. All of them show quite a linear relationship up to 9 M sample concentration.

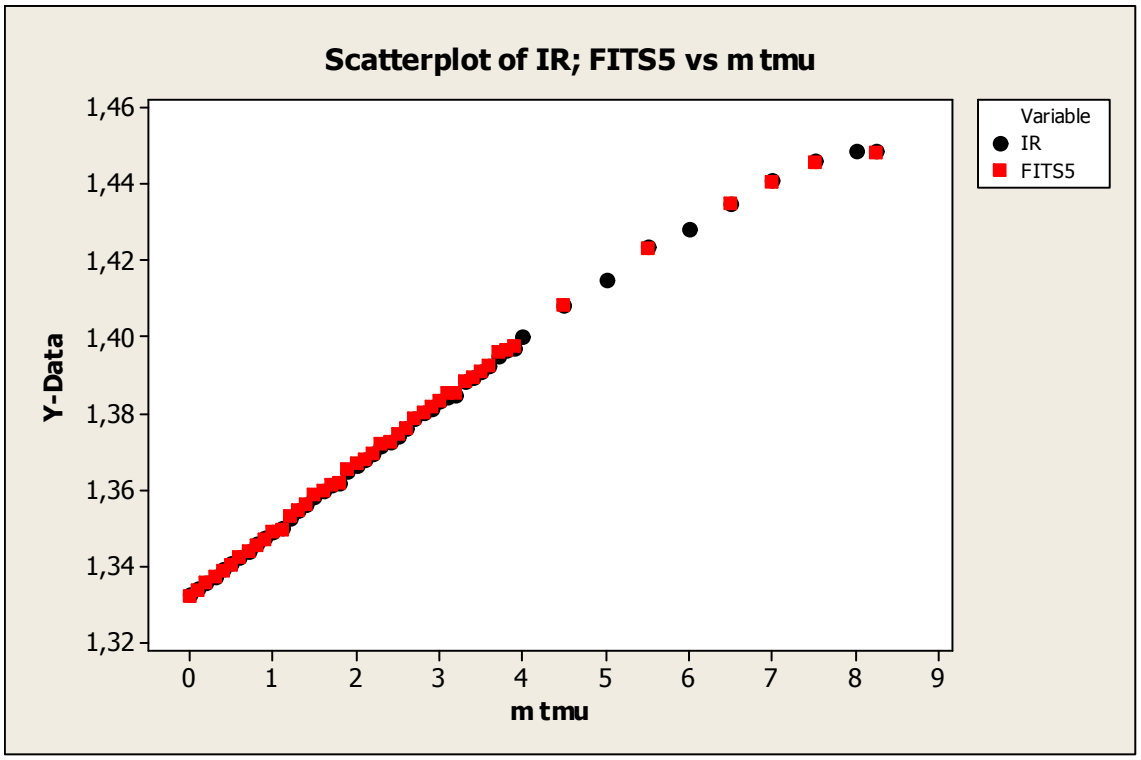

Figure 3. Refraction indexes for the molecule tetramethylurea (TMU) in water solution aginst TMU molar concentration up to 8 M. The fit in red is compared with the

experimental value in black. See also Table 1, n_{tmu} = 0.767 + 0.829 SP, S = 0.000393192 and R^2 = 1.00.

Table S1. Solvatochromic parameters SA, SB and SPP for urea in water solutions.

Molarity	Urea SA	Urea SB	Urea SPP
0.0	1.062	0.025	0.9620
0.5	1.050	0.022	0.962
1.0	1.040	0.017	0.962
2.0	1.026	0.075	0.9620
3.0	1.004	0.078	0.9610
4.0	1.001	0.075	0.9605
5.0	0.985	0.124	0.9585
6.0	0.969	0.114	0.9570
7.0	0.966	0.132	0.9510
8.0	0.965	0.131	0.949

Table S2. Solvatochromic parameters SP and SdP for urea in water solutions.

M Urea in water	SP	SdP
0	0.681	0.997
0.1	0.682	1.008
0.2	0.684	1.008
0.5	0.688	1.000
1.0	0.696	1.000
2.0	0.710	0.992
3.0	0.725	0.978
4.0	0.738	0.964
5.0	0.754	0.946
6.0	0.767	0.937
7.0	0.780	0.920
8.0	0.795	0.895
9.0	0.807	0.874

Table S3. Solvatochromic parameters SA and SB for urea and its derivatives methylurea (MU), dimethylurea (DMU) and tetramethylurea (TMU) in water solutions.

Molarity	Urea SA	Urea SB	DMU SA	DMU SB	TMU SA	TMU SB	MU SA	MU SB
0.0	1.062	0.025	1.062	0.025	1.062	0.025	1.062	0.025
0.5	1.050	0.022	1.038	0.080	1.056	0.102	1.044	0.050
1.0	1.040	0.017	1.013	0.132	1.023	0.174	1.030	0.076
2.0	1.026	0.075	0.974	0.191	0.972	0.248	0.999	0.126
3.0	1.004	0.078	0.947	0.225	0.911	0.285	0.977	0.163

4.0	1.001	0.075	0.914	0.253	0.852	0.323	0.950	0.184
5.0	0.985	0.124	0.882	0.278	0.834	0.339	0.933	0.204
6.0	0.969	0.114	0.860	0.298	0.794	0.350	0.911	0.215
7.0	0.966	0.132	0.838	0.310	0.760	0.370	0.894	0.228
8.0	0.965	0.131	0.814	0.327	0.724	0.406	0.875	0.243

Table S4. Solvatochromic parameters SP. SdP and SPP for the urea (U) derivatives methylurea (MU), dimethylurea (DMU) and tetramethylurea (TMU) in water solutions.

M	MU SP	MU SdP	MU SPP	DMU SP	DMU SdP	DMU SPP	TMU SP	TMU SdP	TMU SPP
0	0.681	0.997	0.962	0.681	0.997	0.962	0.681	0.997	0.962
0.5	0.617	0.996		0.614			0.695	0.977	0.945
1	0.699	0.999	0.960	0.724	0.944	0.957	0.701	0.958	0.950
2	0.716	0.969	0.958	0.742	0.918	0.956	0.737	0.869	0.940
3	0.735	0.938	0.954	0.758	0.893	0.957	0.765	0.801	0.932
4	0.752	0.914	0.961	0.776	0.853	0.958	0.795	0.73	0.925
5	0.770	0.879	0.959	0.791	0.816	0.959	0.818	0.673	0.923
6	0.785	0.860	0.955	0.809	0.785	0.960	0.839	0.617	0.924
7	0.805	0.819	0.962	0.825	0.750	0.961	0.857	0.573	0.927
8	0.819	0.800	0.960	0.837	0.722	0.961			0.927

Absorption spectra of some of the molecular probes employed in this work.

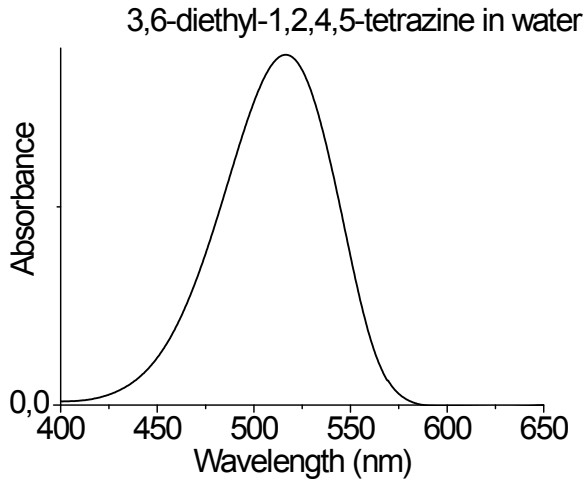

Figure 4 Absorption spectrum of 3,6-diethyl-1,2,4,5-tetrazine in water solution.

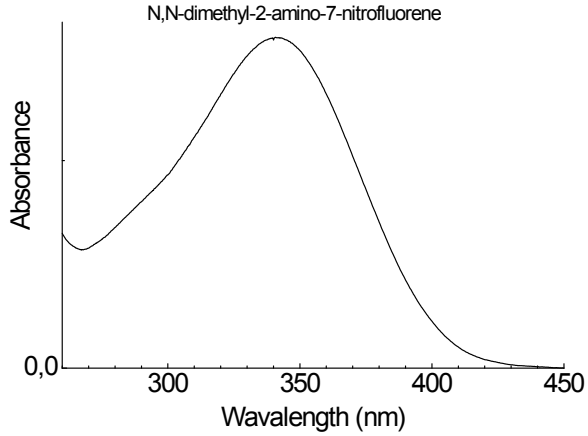

Figure 5 Absorption spectrum of N,N-dimethyl-2-amino-7-nitrofluorene in water solution.

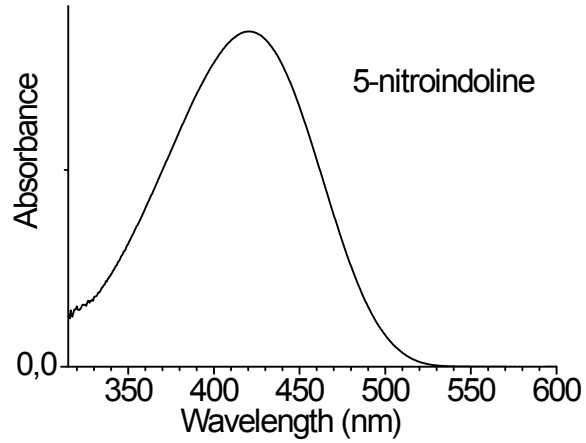

Figure 6 Absorption spectrum of the 5-nitroindoline molecule in water.

The UV-Vis absorption spectrum of the molecular probe 1-methyl-5-nitroindoline is reported in ACS Omega, 2018, 3, 18930-18934 (J. Catalán and J.C. del Valle). The UV-Vis absorption spectrum of the 3,6-diethyl-1,2,4,5-tetrazine molecule is reported in Eur. J. Org. Chem. 1999, 885-891 (J. Catalán, C. Díaz –c.f. reference 50 in the paper).