Supplementary Material (ESI) for New Journal of Chemistry

Table S1 Geometrical parameters (bond length, in Å, bond angle, in deg) and vibrational stretching frequencies(cm^{-1}) [a] for formamide in the isolated monomer (I) and in the monohydrated complex (II) in gas phase and in six kinds of solvents, calculated at B3LYP/6-311++G(d,p) level of theory and some corresponding experimental values [b]

Solvents / Parameters	GAS			CCl4			THF		ETH		ACN			DMSO		WAT	
	I	II	Exp	I	II	Exp	I	II	I	II	I	II	Exp	I	II	I	II
R_{N1-H2}	1.010	1.017	1.0016[c]	1.011	1.017		1.013	1.016	1.014	1.016	1.014	1.016		1.014	1.016	1.014	1.016
R_{N1-H9}	1.007	1.006	1.0015[c]	1.009	1.008		1.011	1.011	1.012	1.012	1.012	1.012		1.012	1.012	1.012	1.012
R_{C3-H4}	1.106	1.103	1.098[c]	1.105	1.102		1.104	1.101	1.104	1.101	1.104	1.101		1.104	1.101	1.103	1.101
$R_{C3=O5}$	1.212	1.223	1.219[c]	1.218	1.228		1.223	1.232	1.226	1.234	1.226	1.234		1.226	1.234	1.227	1.234
R_{C3-N1}	1.361	1.349	1.352[c]	1.354	1.346		1.348	1.342	1.346	1.340	1.345	1.340		1.345	1.340	1.345	1.340
$\alpha_{H2-N1-C3}$	119.4	119.1	118.5[c]	119.9	119.3		120.3	119.6	120.6	119.7	120.6	119.8		120.6	119.8	120.6	119.8
$\alpha_{N1-C3=O5}$	124.9	125.0	124.7[c]	125.0	124.9		125.1	124.8	125.2	124.8	125.2	124.8		125.1	124.8	125.1	124.8
$\alpha_{N1-C3-H4}$	112.4	113.6	112.7[c]	112.6	113.7		112.8	113.8	112.9	113.9	112.9	113.9		112.9	113.9	112.9	113.9
$\tau_{H7O6H8H2}$	–	-143.5		–	-137.1		–	-131.3	–	-128.1	–	-127.5		–	-127.2	–	-127.1
υ_{asN-H}	3577.1	3553.4	3570[d]	3543.8	3524.0	3533[e]	3505.3	3493.9	3490.6	3482.7	3488.0	3480.5	3471[f]	3487.1	3479.7	3485.4	3477.8
υ_{sN-H}	3445.1	3348.2	3448[d]	3415.9	3349.3	3411[e]	3382.3	3350.3	3370.3	3349.5	3368.0	3349.2	3357[f]	3367.2	3349.0	3365.7	3348.0
υ_{C3-H4}	2833.5	2868.8	2855[d]	2847.2	2877.7		2856.3	2884.4	2859.3	2886.9	2859.8	2886.9		2859.7	2887.0	2860.4	2887.4
$\upsilon_{C3=O5}$	1725.1	1695.1	1754[d]	1688.8	1669.1		1657.1	1644.5	1644.4	1634.6	1642.5	1633.3		1641.5	1632.7	1639.9	1630.9
υ_{C3-N1}	1216.5	1265.5	1255[d]	1225.4	1266.2		1234.1	1266.4	1237.1	1266.6	1237.6	1266.4		1238.0	1266.5	1238.1	1266.1

[a] Frequencies scaled by 0.963.[9] I denotes the monomer; II denotes the complex. [b] Experimental values correspond to isolated formamide. [c] From ref.2. [d] From ref.10. [e] From ref.11. [f] From ref.12.

Table S2 GIAO B3LYP/aug-cc-pVTZ calculated ^{1}H NMR chemical shifts (δ_H, in ppm) and variations of ^{1}H chemical shifts upon solvation ($\Delta\delta_H$(sol-gas), in ppm) [a] and upon complexation ($\Delta\delta_H$(II-I), in ppm) [b] in gas phase and in the six selected solvents within the framework of the IEF-PCM model for formamide in the isolated monomer (I) and in the complex (II) [c], using the geometries optimized at the B3LYP/6-311++G(d,p) level.

Solvent	δ_{H9}		$\Delta\delta_{H9}$(sol-gas)		$\Delta\delta_{H9}$(II-I)	δ_{H4}		$\Delta\delta_{H4}$(sol-gas)		$\Delta\delta_{H4}$(II-I)	δ_{H2}		$\Delta\delta_{H2}$(sol-gas)		$\Delta\delta_{H2}$(II-I)
	I	II	I	II	II-I	I	II	I	II	II-I	I	II	I	II	II-I
GAS	4.81	4.99	0.00	0.00	0.18	8.53	8.48	0.00	0.00	-0.05	4.79	7.47	0.00	0.00	2.68
CCl4	5.27	5.45	0.46	0.46	0.18	8.55	8.52	0.02	0.03	-0.03	5.14	7.39	0.35	-0.08	2.25
THF	5.72	5.89	0.91	0.90	0.17	8.57	8.55	0.03	0.07	-0.02	5.45	7.23	0.66	-0.24	1.78
ETH	5.89	6.06	1.07	1.07	0.18	8.58	8.56	0.05	0.08	-0.01	5.56	7.14	0.78	-0.33	1.58
ACN	5.91	6.09	1.10	1.10	0.18	8.58	8.57	0.05	0.08	-0.01	5.58	7.13	0.79	-0.35	1.54
DMSO	5.93	6.10	1.12	1.11	0.18	8.58	8.57	0.05	0.09	-0.01	5.59	7.13	0.80	-0.34	1.54
WAT	5.95	6.12	1.14	1.13	0.17	8.59	8.57	0.05	0.09	-0.01	5.61	7.11	0.82	-0.37	1.50

[a] $\Delta\delta_H$(sol-gas) = δ_H (in a given solution) - δ_H (in gas phase).

[b] $\Delta\delta_H$(II-I) = δ_H (in the complex) - δ_H (in the monomer).

[c] Chemical shifts calculated are referred to TMS.

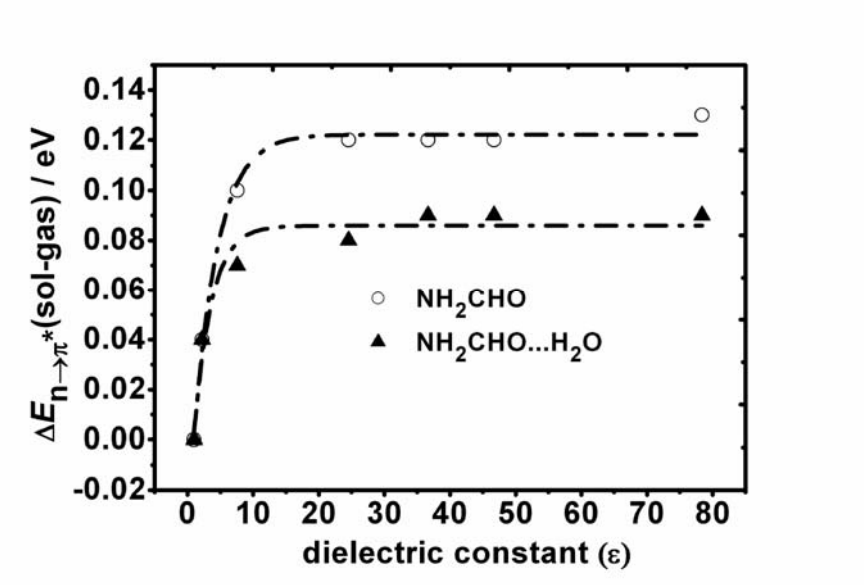

Fig. S1 Dependences of variations in n→π* transition energies of formamide upon solvation ($\Delta E_{n\to\pi^*}(sol-gas)$) on dielectric constants of solvents (ε) in the monomer and the complex, derived from TDDFT calculations.