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

Evolution of microstructures and hydrogen bond interactions within choline amino acid ionic liquid and water mixtures

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Electronic Supplementary Information

1. *Effect of temperature on the viscosity of [Cho][AA]-water mixtures with different ratios*

The viscosity changes of [Cho][AA]-water mixtures with increased temperature are shown in Fig.S1. It can be seen that the viscosity values of all [Cho][AA]-water mixtures decreased with the increase of temperature. The motion capacities of cations and anions were continuously enhanced by heat energy. As results, intermolecular interactions between [Cho][AA] ions were weakened by heating, and the viscosity values decreased.

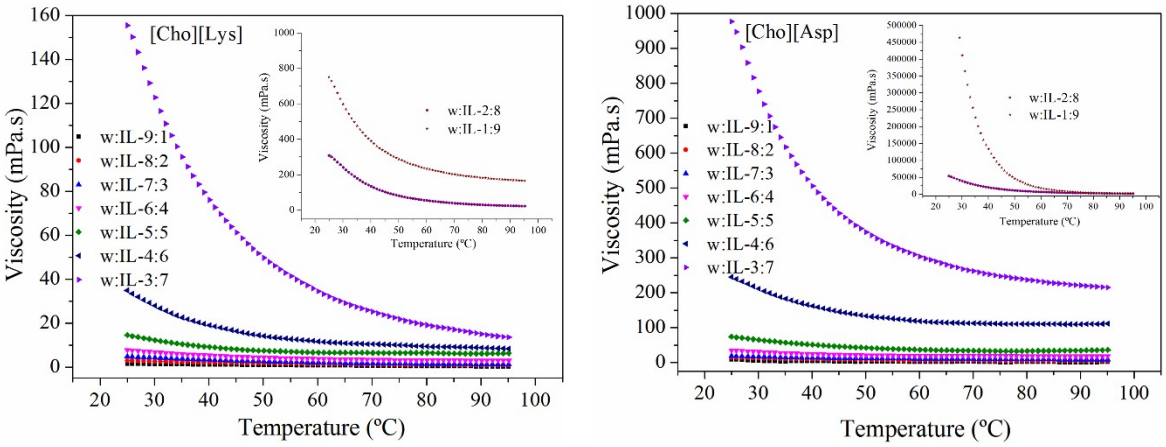

Fig.S1 The effect of temperature on the viscosity of [Cho][AA]-water mixtures with different ratios.

2. The spectral assignments of vibration modes of [Cho][AA] ionic liquid (IL)

A pre-request to analyse the vibration frequency shifts of functional groups ($-COO^-$, $-NH_2$ and -COOH) is the correct assignment of vibration modes of [Cho][AA] IL. Here, [Cho][AA] dimer that resembles the real three-dimensional network structure of IL was chosen to make a correct assignment. By calculating the harmony frequency (Table S1-S2), the vibration modes were associated with $-NH_2$, -OH, $-CH_3$, $-CH_2$, $-N-(CH_3)_3$, -COOH and $-COO^-$ groups of [Cho][AA] IL in ATR-FTIR spectra (Fig.S2). It can be seen from Fig.S2 that asymmetric (3351 cm^{-1}, $\nu_{as}NH_2$) and symmetric (3277 cm^{-1}, ν_sNH_2) stretching vibration peaks of $-NH_2$ group only appeared in neat [Cho][Lys] because of the extra residue $-NH_2$ group of Lys^-. Yet, the asymmetric vibration peak of -COOH group couldn't be told from the ATR-FTIR spectrum of [Cho][Asp].

Table S1 The assignments of vibration modes of [Cho][Lys] dimer.

Assignments	ATR-FTIR spectrum (cm^{-1})	DFT calculations (cm^{-1})/Intensity
ν_{as}α-N2H$_2$	3351.02	3389.30 (5); 3383.02 (13)
ν_{as}R-N3H$_2$		3400.83 (19); 3361.28 (14)
ν_sα-N2H$_2$	3277.46	3318.90 (1); 3307.64 (16)
ν_sR-N3H$_2$		3267.72 (94); 3219.30 (117)
ν_sCho-OH	3024.47	3508.90 (387); 2833.95 (795)
$\nu_{as}CH_3$	2925.79	3014.42 (24); 2996.53 (32)
$\nu_{as}CH_2+\nu_sCH_3$	2851.00	2935.79 (49); 2933.60 (37); 2927.07 (34); 2917.99 (48); 2915.02 (39); 2914.78 (37); 2909.21 (33); 2903.92 (87)
$\nu_{as}COO^-$	1567.49	1608.85 (633); 1584.82 (401)
$\delta_{as}CH_3$	1479.57	1456.25 (39); 1447.94 (33); 1439.09 (33); 1437.64 (43)
ν_sCOO^-	1389.21	1380.35 (59); 1345.50 (68)
$\delta_{as}CH_2$-OH	1083.40	1122.57 (26); 1078.84 (91)
$\nu N-(CH_3)_3$	955.15	946.81 (30); 942.44 (31)
τNH_2	863.92	919.74 (178); 916.74 (88); 896.42 (60); 869.20 (69)

ν_{as}: asymmetrical stretching vibration; ν_s: symmetrical stretching vibration; δ_{as}: asymmetrical deformation vibration; τ: twisting vibration

Table S2 The assignments of vibration modes of [Cho][Asp] dimer.

Assignments	ATR-FTIR spectrum (cm^{-1})	DFT calculations (cm^{-1})/Intensity
ν_{as}α-N2H$_2$		3401.87 (14); 3390.69 (7)
ν_{s}α-N2H$_2$		3327.01 (6); 3313.77 (4)
ν_{s}Cho-OH	3027.92	3686.98 (68); 3190.00 (849)
$\nu_{as}CH_3$	2955.75	3071.35 (65); 3059.63 (21)
$\nu_{as}CH_2$+$\nu_{s}CH_3$	2850.79	2919.54 (28); 2907.97 (23); 2896.34 (40); 2870.10 (123)
ν_{as}R-COOH		1684.70 (399); 1647.80 (99)
$\nu_{as}COO^-$	1578.93	1599.76 (629); 1581.12 (973)
$\delta_{as}CH_3$	1476.64	1453.13 (31); 1447.49 (32); 1436.15 (48)
$\nu_{s}COO^-$	1374.96	1374.07 (135); 1371.65 (183)
ν_{s}R-COOH	1348.00	1331.23 (64); 1309.07 (646)
$\delta_{as}CH_2$-OH	1073.39	1123.46 (21); 1070.52 (67)
νN-$(CH_3)_3$	955.12	959.31 (29); 942.58 (36)
τNH$_2$	855.31	882.02 (129); 863.51 (107)

ν_{as}: asymmetrical stretching vibration; ν_{s}: symmetrical stretching vibration; δ_{as}: asymmetrical deformation vibration; τ: twisting vibration

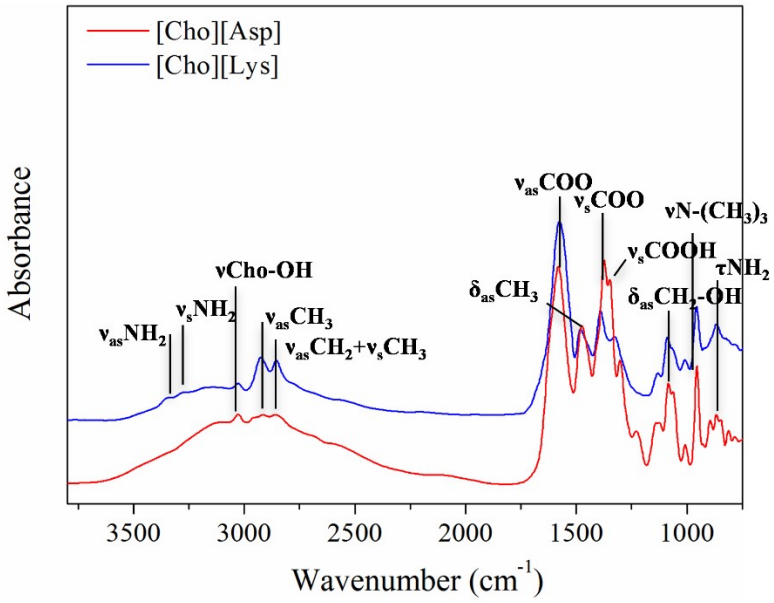

Fig.S2 The spectral assignments of [Cho][Lys] and [Cho][Asp] IL. These assignments were based on the above theoretical frequency calculations of [Cho][AA] dimer.

3. Atoms in molecules (AIM) analysis of [Cho][AA]-nH_2O (n=1, 2) complexes

The AIM analysis[1] was used to further identify the nature and strength of hydrogen bond (HB) interactions of tight [Cho][AA] ion pairs with one water molecule and water-separated [Cho][AA] ion pairs in Fig.7 by using Multiwfn 3.8 software.[2] And their bond critical point (BCP) properties of HB interacitons are reported in Table S3-S4.

Table S3 Properties of BCP (a.u.) for the interactions of tight [Cho][Lys] ion pairs with one water molecule (G1, G2, G3, G4), water-separated [Cho][Lys] ion pairs (G5, G6) in Fig.7, and the number (N_{HB}), length (L_{HB}, Å) and bond angle (deg) of HBs.

	N_{HB}	Range L_{HB}	Bond angle	Total ρ_{BCP}	Range ρ_{BCP}	Range $\nabla^2\rho$	Range G(r)	Range V(r)	Range H(r)
G1									
Cho^++H_2O									
O_{H2O}-H(CH_{Cho})	2	2.53~2.58	104.05~107.64	0.019	0.009~0.010	0.038~0.038	0.008	-0.007~-0.006	0.001~0.002
Lys^-+H_2O									
O_{COO}-H(O_{H2O}H)	1	1.76	165.02	0.036	0.036	0.134	0.034	-0.034	0.000
Cho^++Lys^-									
O_{COO}-H(O1H_{Cho})	1	1.77	165.78	0.035	0.035	0.130	0.032	-0.032	0.000
O_{COO}-H(CH_{Cho})	3	2.22~2.46	140.66~149.91	0.040	0.011~0.016	0.036~0.057	0.008~0.012	-0.012~-0.007	0.001~0.002
$N2_{Lys}$-H(CH_{Cho})	2	2.70~2.87	112.54~127.87	0.015	0.007~0.008	0.020~0.024	0.004~0.005	-0.005~-0.004	0.001
Intramolecular HBs									

$O1_{Cho}$-H(CH_{Cho})	1	2.36	107.56	0.015	0.015	0.055	0.012	-0.011	0.006
$N3_{Lys}$-H(CH_{Lys})	1	2.79	117.00	0.008	0.008	0.026	0.006	-0.005	0.001
G2									
Cho^{+}+H_2O									
$O1_{Cho}$-H(O_{H2O}H)	1	1.80	148.55	0.033	0.033	0.133	0.032	-0.031	0.001
O_{H2O}-H(CH_{Cho})	2	2.32~2.36	151.20~154.29	0.023	0.011~0.012	0.039~0.044	0.008~0.009	-0.008~-0.007	0.001~0.002
Cho^{+}+Lys^{-}									
$N3_{Lys}$-H(CH_{Cho})	1	2.70	125.93	0.008	0.008	0.023	0.005	-0.004	0.001
O_{COO}-H($O1H_{Cho}$)	1	1.59	168.05	0.058	0.058	0.153	0.050	-0.062	-0.012
O_{COO}-H(CH_{Cho})	3	2.13~2.31	141.54~147.12	0.051	0.013~0.020	0.045~0.068	0.010~0.015	-0.013~-0.008	0.002
Intramolecular HBs									
$O1_{Cho}$-H(CH_{Cho})	1	2.43	106.72	0.014	0.014	0.048	0.011	-0.010	0.001
G3									
Lys^{-}+H_2O									
$N2_{Lys}$-H(O_{H2O}H)	1	1.91	158.16	0.033	0.033	0.098	0.025	-0.026	-0.001
O_{H2O}-H(CH_{Lys})	2	2.45~2.66	128.11~157.58	0.016	0.007~0.009	0.021~0.038	0.005~0.008	-0.006~-0.004	0.001~0.002
Cho^{+}+Lys^{-}									

O_{COO}-H($O1H_{Cho}$)	1	1.66	168.66	0.050	0.050	0.146	0.043	-0.050	-0.007
O_{COO}-H(CH_{Cho})	3	2.12~2.21	139.76~143.65	0.054	0.017~0.020	0.060~0.071	0.013~0.016	-0.014~-0.012	0.002
Intramolecular HBs									
O_{COO}-H(CH)	1	2.49	126.98	0.012	0.012	0.037	0.008	-0.007	0.001
$O1_{Cho}$-H(CH_{Cho})	1	2.34	107.42	0.016	0.016	0.059	0.013	-0.011	0.002
O_{COO}-H($N3H_{Lys}$)	1	2.16	174.11	0.017	0.017	0.060	0.013	-0.012	0.002
G4									
$Cho^{+}+H_2O$									
O_{H2O}-H(CH_{Cho})	3	2.29~2.35	143.87~146.56	0.038	0.012~0.013	0.041~0.047	0.009~0.010	-0.009~-0.008	0.001~0.002
$Lys^{-}+H_2O$									
O_{H2O}-H($N3H_{Lys}$)	1	1.75	167.92	0.048	0.048	0.103	0.035	-0.043	-0.009
$Cho^{+}+Lys^{-}$									
$N3_{Lys}$-H(CH_{Cho})	1	2.81	115.04	0.006	0.006	0.0219	0.0047	-0.0039	0.001
O_{COO}-H($O1H_{Cho}$)	1	1.65	167.46	0.050	0.050	0.150	0.044	-0.050	-0.006
O_{COO}-H(CH_{Cho})	3	2.10~2.49	141.44~150.86	0.044	0.011~0.019	0.031~0.074	0.007~0.016	-0.013~-0.007	0.001~0.003
Intramolecular HBs									
O_{COO}-H($N3H_{Lys}$)	1	2.03	171.09	0.021	0.021	0.078	0.017	-0.015	0.002

O_{COO}-H($N2H_{Lys}$)	1	2.20	112.16	0.020	0.020	0.087	0.019	-0.016	0.003
G5									
Cho^{+}+H_2O									
O_{H2O}-H($O1H_{Lys}$)	1	1.71	163.36	0.043	0.043	0.146	0.039	-0.042	-0.003
O_{H2O}-H(CH_{Lys})	1	2.63	112.78	0.008	0.008	0.030	0.006	-0.005	0.001
Lys^{-}+H_2O									
O_{COO}-H($O_{H2O}H$)	1	1.57	178.66	0.061	0.061	0.159	0.053	-0.066	-0.013
Cho^{+}+Lys^{-}									
O_{COO}-H(CH_{Lys})	4	2.06~2.38	133.34~168.92	0.066	0.013~0.020	0.042~0.082	0.009~0.018	-0.015~-0.008	0.001~0.003
Intramolecular HBs									
$O1_{Lys}$-H(CH_{Lys})	2	2.32~2.38	121.01~124.01	0.028	0.013~0.015	0.047~0.051	0.010~0.011	-0.010	0.001~0.002
G6									
Cho^{+}+H_2O									
O_{H2O}-H($O1H_{Cho}$)	1	1.74	159.98	0.040	0.040	0.137	0.036	-0.038	-0.002
O_{H2O}-H(CH_{Cho})	3	2.36~2.46	147.85~171.32	0.030	0.010	0.031~0.040	0.007~0.008	-0.007~-0.006	0.001~0.002
Lys^{-}+H_2O									
O_{COO}-H($O_{H2O}H$)	2	1.61~1.76	167.08~173.88	0.047	0.038~0.056	0.130~0.153	0.034~0.048	-0.058~-0.035	-0.001

Cho^++Lys^-									
O_{COO}-H(CH_{Cho})	3	2.46~2.61	110.35~119.42	0.031	0.009~0.011	0.030~0.041	0.007~0.009	-0.008~-0.006	0.001
$N3_{Lys}$-H(CH_{Cho})	1	2.28	177.41	0.016	0.016	0.050	0.011	-0.009	0.002
Intramolecular HBs									
O_{COO}-H(CH_{Lys})	1	2.64	141.60	0.008	0.008	0.026	0.006	-0.005	0.001
$O1_{Cho}$-H(CH_{Cho})	1	2.49	106.93	0.012	0.012	0.044	0.010	-0.008	0.001

Table S4 Properties of BCP (a.u.) for the interactions of tight [Cho][Asp] ion pairs with one water molecule (H1, H2, H3, H4) and water-separated [Cho][Asp] ion pairs (H5, H6) in Fig.7, and the number (N_{HB}), length (L_{HB}, Å) and bond angle (deg) of HBs.

	N_{HB}	Range L_{HB}	Bond angle	Total ρ_{BCP}	Range ρ_{BCP}	Range $\nabla^2\rho$	Range G(r)	Range V(r)	Range H(r)
H1									
Cho^++H_2O									
O_{H2O}-H(CH_{Cho})	2	2.48~2.86	110.08~123.66	0.016	0.006~0.010	0.021~0.037	0.004~0.008	-0.007~-0.004	0.001
Asp^-+H_2O									
O_{COO}-H(O_{H2O}H)	1	1.81	164.72	0.030	0.030	0.123	0.029	-0.027	0.002
Cho^++Asp^-									
O_{COO}-H($O1H_{Cho}$)	1	1.82	151.04	0.033	0.033	0.124	0.031	-0.030	0.000

O_{COO}-H(CH_{Cho})	3	2.14~2.35	163.48~175.08	0.046	0.014~0.018	0.047~0.063	0.010~0.014	-0.009~-0.012	0.001~0.002
$N2_{Asp}$-H(CH_{Cho})	1	2.79	121.73	0.007	0.007	0.022	0.005	-0.004	0.001
Intramolecular HBs									
$O1_{Cho}$-H(CH_{Cho})	1	2.50	100.23	0.013	0.013	0.049	0.011	-0.009	0.001
$O5_{Asp}$-H($N2H_{Asp}$)	1	2.35	122.74	0.013	0.013	0.046	0.010	-0.009	0.001
H2									
Cho^++H_2O									
$O1_{Cho}$-H(O_{H2O}H)	1	1.78	158.38	0.036	0.0361	0.133	0.033	-0.033	-0.000
O_{H2O}-H(CH_{Cho})	2	2.28~2.31	130.78~143.01	0.026	0.013	0.048~0.048	0.010	-0.008	0.002
Cho^++Asp^-									
O_{COO}-H($O1H_{Cho}$)	1	1.55	170.21	0.067	0.067	0.149	0.055	-0.073	-0.018
O_{COO}-H(CH_{Cho})	3	2.05~2.20	146.16~175.21	0.056	0.018~0.021	0.058~0.078	0.013~0.017	-0.014~-0.011	0.002~0.003
$O5_{Asp}$-H(CH_{Cho})	1	2.70	112.43	0.006	0.006	0.024	0.005	-0.004	0.001
Intramolecular HBs									
$O1_{Cho}$-H(CH_{Cho})	1	2.49	104.89	0.017	0.017	0.046	0.010	-0.009	0.001
$O5_{Asp}$-H($N2H_{Asp}$)	1	2.46	118.45	0.011	0.011	0.039	0.009	-0.008	0.001
H3									

Asp^-+H_2O									
$N2_{Asp}$-H(O_{H2O}H)	1	1.85	172.35	0.038	0.038	0.098	0.027	-0.031	-0.003
Cho^++H_2O									
O_{H2O}-H(CH_{Cho})	1	2.46	108.87	0.011	0.011	0.042	0.009	-0.008	0.002
Cho^++Asp^-									
O_{COO}-H($O1H_{Cho}$)	1	1.73	165.65	0.036	0.036	0.139	0.036	-0.038	-0.002
O_{COO}-H(CH_{Cho})	3	2.05~2.28	146.06~161.31	0.051	0.014~0.022	0.048~0.080	0.011~0.018	-0.016~-0.009	0.002
Intramolecular HBs									
$O1_{Cho}$-H(CH_{Cho})	1	2.39	104.75	0.015	0.015	0.055	0.012	-0.011	0.002
$O5_{Asp}$-H($N2H_{Asp}$)	1	2.29	124.01	0.014	0.014	0.052	0.011	-0.010	0.002
H4									
Asp^-+H_2O									
O_{H2O}-H($O4H_{Asp}$)	1	1.82	155.50	0.031	0.031	0.119	0.029	-0.028	0.001
$O5_{Asp}$-H(O_{H2O}H)	1	1.96	135.74	0.025	0.025	0.096	0.022	-0.020	0.002
Cho^++Asp^-									
O_{COO}-H($O1H_{Cho}$)	1	1.69	167.33	0.043	0.043	0.147	0.040	-0.043	-0.003
O_{COO}-H(CH_{Cho})	4	2.16~2.41	125.37~145.93	0.065	0.012~0.019	0.044~0.064	0.010~0.014	-0.013~-0.008	0.001~0.002

Intramolecular HBs									
$O1_{Cho}$-H(CH_{Cho})	1	2.26	114.75	0.018	0.018	0.064	0.014	-0.012	0.002
$O5_{Asp}$-H($N2H_{Asp}$)	1	2.39	120.52	0.012	0.012	0.044	0.010	-0.009	0.001
H5									
Cho^{+}+H_2O									
O_{H2O}-H($O1H_{Cho}$)	1	1.71	162.85	0.042	0.042	0.148	0.039	-0.042	-0.003
O_{H2O}-H(CH_{Cho})	1	2.64	112.77	0.008	0.008	0.029	0.006	-0.005	0.001
Asp^{-}+H_2O									
O_{COO}-H($O_{H2O}H$)	1	1.58	177.56	0.059	0.059	0.159	0.052	-0.064	-0.012
Cho^{+}+Asp^{-}									
O_{COO}-H(CH_{Cho})	41	2.05~2.35	133.00~169.36	0.064	0.014~0.020	0.044~0.084	0.010~0.018	-0.015~-0.009	0.001~0.003
Intramolecular HBs									
$O1_{Cho}$-H(CH_{Cho})	2	2.33~2.38	121.10~123.97	0.027	0.013~0.014	0.048~0.050	0.010~0.011	-0.010~-0.009	0.001~0.002
$O5_{Asp}$-H($N2H_{Asp}$)	88	2.40	120.88	0.012	0.012	0.043	0.009	-0.008	0.001
H6									
Cho^{+}+H_2O									
O_{H2O}-H($O1H_{Cho}$)	1	1.79	157.05	0.037	0.037	0.126	0.033	-0.033	-0.001

O_{H2O}-H(CH_{Cho})	3	2.40~2.66	113.57~121.25	0.029	0.008~0.011	0.026~0.047	0.006~0.010	-0.008~-0.005	0.001~0.002
Asp^{-}+H_2O									
O_{COO}-H(O_{H2O}H)	2	1.69~1.82	164.98~172.19	0.076	0.032~0.044	0.120~0.142	0.029~0.039	-0.043~-0.028	-0.004~0.001
Cho^{+}+Asp^{-}									
O_{COO}-H(CH_{Cho})	4	2.15~2.55	136.10~162.97	0.049	0.009~0.017	0.029~0.062	0.007~0.013	-0.011~-0.006	0.001~0.002
$O5_{Asp}$-H(CH_{Cho})	2	2.61~2.64	103.56~109.47	0.017	0.008~0.009	0.028~0.036	0.006~0.008	-0.006~-0.005	0.001
Intramolecular HBs									
$O1_{Cho}$-H(CH_{Cho})	1	2.27	122.33	0.017	0.017	0.057	0.013	-0.011	0.002
$O5_{Asp}$-H($N2H_{Asp}$)	1	2.36	122.43	0.013	0.013	0.045	0.010	-0.009	0.001

4. The effect of mixture ratio on the vibration modes of -NH_2 group in [Cho][AA]-water mixtures

Fig.S3 shows the ATR-FTIR spectra (a) and second derivative spectra (b) of [Cho][AA]-water mixtures within the range of 3800~2750 cm^{-1}. For -NH_2 group, when water was added to [Cho][Lys], both asymmetric ($\nu_{as}NH_2$) and symmetric (ν_sNH_2) stretching vibrations of -NH_2 group moved to high wavenumbers, showing a blue shift phenomenon. Yet, these $\nu_{as}NH_2$ and ν_sNH_2 disappeared and were masked at high water amount (w:IL ≥ 7:3).

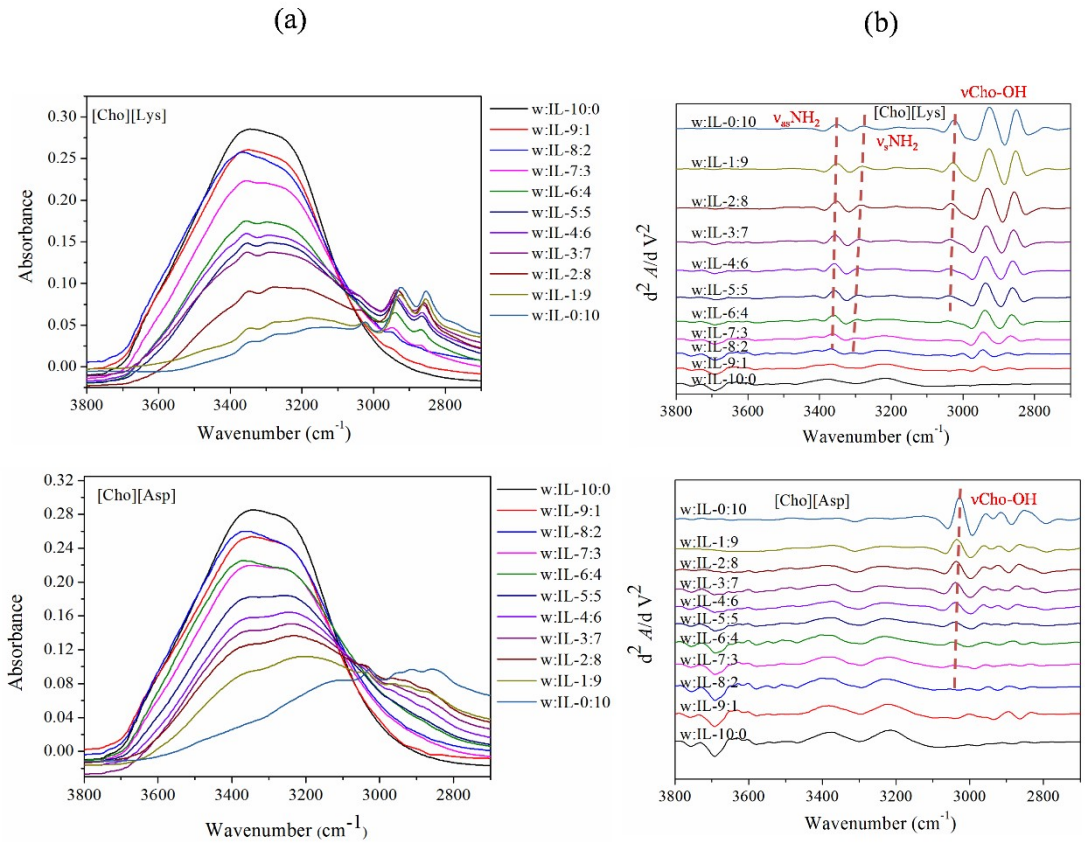

Fig.S3 The ATR-FTIR spectra (a) and second derivative spectra (b) of [Cho][AA]-water mixtures within the range of 3800-2750 cm^{-1}.

References

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2. T. Lu and F. Chen, *Journal of Computational Chemistry*, 2012, **33**, 580-592.