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THEORETICAL STUDY ON INTERACTIONS BETWEEN IONIC LIQUID AND CHITIN/CHITOSAN/ CELLULOSE

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ABSTRACT

In order to deepen understanding the interactions between ionic liquid and chitin/chitosan/ cellulose at the molecular level, we have performed a study on the electronic structures, topological properties, nonconvalent interactions between 1-ethyl-3-methyl imidazolium chloride and chitin/chitosan/cellulose by using density functional theory. The results indicate that interactions between chitin/chitosan/cellulose and 1-ethyl-3-methyl imidazolium chloride are stronger that the intra-interaction of chitin/chitosan/cellulose, implying that chitin/ chitosan/ cellulose can dissolve in 1-ethyl-3-methyl imidazolium chloride.

Key words: Ionic liquid, Chitin, Chitosan, Cellulose, Interactions.

1. INTRODUCTION

Chitin, chitosan and cellulose (Supplementary Fig. 1), as the biological macromolecular materials, are hardly soluble in many traditional solvents [1]. This behavior limits their wide application and chemical modification. Therefore, it will be of great importance to develop new solvent systems. Rogers et al. [2] firstly investigated the dissolution of cellulose with ionic liquids in 2002. Following this report, a variety of room temperature ionic liquids has been used to dissolve chitin, chitosan, and cellulose [3-12]. So the dissolution of chitin, chitosan and cellulose in the ionic liquid, as a kind of recycled solvent, becomes a hot topic in chemical research.

It is proposed that the high chemical and mechanical stability of cellulose and its hydrophobic nature is due to the huge degree of inter-unit hydrogen bonds. They not only act as interconnections between units but are also responsible for the hydrophilic nature of the biopolymer (Supplementary Fig. 2) [12]. While it was thought that both anions and cations of ionic liquids are involved in the dissolution process of cellulose, the dissolution mechanism of cellulose in ionic liquids has been proposed (Supplementary Fig. 3) [13]. Although there are some reports about the interaction between ionic liquid and chitosan/ cellulose [14-19], to the best of our knowledge, there is no theoretical report on the comparison of interactions between 1-ethyl-3-methyl-imidazolium chloride ([EMIM]Cl) ionic liquid and chitin/chitosan/cellulose clusters at the molecular level. We try to study the interactions between [EMIM]Cl and chitin/ chitosan/ cellulose clusters by means of density functional approach firstly. We hope that the present results could provide some useful information for the continuous exploitation and application of ionic liquids for dissolution of chitin, chitosan, and cellulose.

2. The specification of initial geometries and computational method

Because chitin, chitosan and cellulose are polymers, the cluster models are invoked to represent chitin, chitosan and cellulose, and the dangling atoms are terminated with hydroxyl groups. The cluster models of chitin/chitosan/ cellulose and the interacting models between 1-ethyl-3-methyl imidazolium chloride ([EMIM]Cl) and chitin/chitosan/cellulose were displayed in Fig. 1. The models are designated as chitin, chitosan, cellulose, [EMIM]Cl-chitin, [EMIM]Cl-chitosan, and [EMIM]Cl-cellulose.

The quantum chemical calculations were carried out by density functional theory (DFT). All the DFT optimizations were performed with DMol^3 method [20,21]. This method (GGA/PW91) is based on accurate and efficient local density functional calculations (LDF), which uses fast convergent three-dimensional numerical integrations to calculate the matrix elements occurring in the Ritz variation method. Typically a doubled numerical basis set (DNP) is used for calculations. The convergence criteria for these optimizations consisted of threshold values of 2×10^{-5} Ha, 0.004 Ha/Å and 0.005 Å for energy, gradient and displacement convergence, respectively, while a self consistent field (SCF) density convergence threshold value of 1×10^{-5} Ha was specified. For interaction energy, basis set superposition errors (BSSE) were considered using the counterpoise method [22]. To examine the nature of interactions, the topological properties and noncovalent interactions were illustrated in terms of AIM (atoms in molecules) [23] and NCI (noncovalent interaction) [24,25] analyses, respectively.

3. RESULTS AND DISCUSSION

3.1 The optimized geometries

The chitin, chitosan, cellulose, [EMIM]Cl-chitin, [EMIM]Cl-chitosan, and [EMIM]Cl-cellulose with the minimum energy were obtained by performing density functional optimizations and the geometries are illustrated in Fig. 2. In the configurations of chitin, the interacting distances involved of hydrogen and oxygen atoms are 1.823Å, 2.319 Å, 2.467 Å, 2.709 Å, shorter than the sum of Bondi's van der Waals radii of hydrogen (1.20 Å) and oxygen (1.52 Å) [26]. The H•••H distance of 2.174 Å is shorter than van der Waals radii of hydrogen (1.20 Å), indicating the interaction of hydrogen atoms. Chitosan is the *N*-deacetylated derivative of chitin, and N-deacetylation may improve the interactions for the chitosan in comparison to chitin. Both hydrogen bond and H•••H interaction exist in cellulose.

3.2 Interaction energies

The interaction energies of chitin, chitosan, cellulose, [EMIM]Cl-chitin, [EMIM]Cl-chitosan and [EMIM]Cl-cellulose are 14.7 kcal/mol, 19.8 kcal/mol, 16.7 kcal/mol, 34.4 kcal/mol, 30.0 kcal/mol, 56.6 kcal/mol, implying that the interactions between [EMIM]Cl and chitin/ chitosan/ cellulose are [EMIM]Cl-cellulose > [EMIM]Cl-chitin > [EMIM]Cl-chitosan, while the intra-interacting order of clusters is chitosan > cellulose > chitin. It can be concluded that the interactions between [EMIM]Cl and chitin/ chitosan/ cellulose are stronger than that of intra-chitin/ intra-chitosan/ intra-cellulose clusters, in consistent with the stronger intermolecular interactions between [EMIM]Cl and chitin/ chitosan/cellulose than that of intra-chitin/ intra-chitosan/ intra-cellulose clusters showing in the corresponding optimized structures, suggesting that chitin / chitosan/ cellulose can dissolve in [EMIM]Cl ionic liquid.

3.3 Topological properties of interactions

The interactions can be successfully investigated by means of topological properties of electron density distribution ρ(r). According to Bader's topological AIM theory [27], the chemical bonds can be illustrated in terms of the total electronic density ρ(r) and its corresponding Laplacian, $\nabla^2\rho(r)$. It has been proposed that the differences in the topological features of the electron density reflect the different interactions. There are many hydrogen bonds among chitin, chitosan, cellulose, [EMIM]Cl-chitin, [EMIM]Cl-chitosan and [EMIM]Cl-cellulose according to the criterion of hydrogen bonding (ρ=0.002~0.035 a.u., $\nabla^2\rho(r)$=0.024~0.139 a.u.) [27] (Supplementary Table 1). The large values of electronic density are consistent with the short distances of their hydrogen bonds, showing a close relationship between the topological properties of electron density and the distances of hydrogen-bonded systems [27]. Accompanying with hydrogen bonding interaction, the H•••H, O•••O, H•••N, H•••C, O•••N, O•••C, H•••Cl interactions also occur, so both anion and cation of ionic liquids are involved in the interaction between [EMIM]Cl and chitin/ chitosan/ cellulose. And the interactions between [EMIM]Cl and chitin/ chitosan/ cellulose are stronger than that of intra-chitin/ intra-chitosan/ intra-cellulose, respectively.

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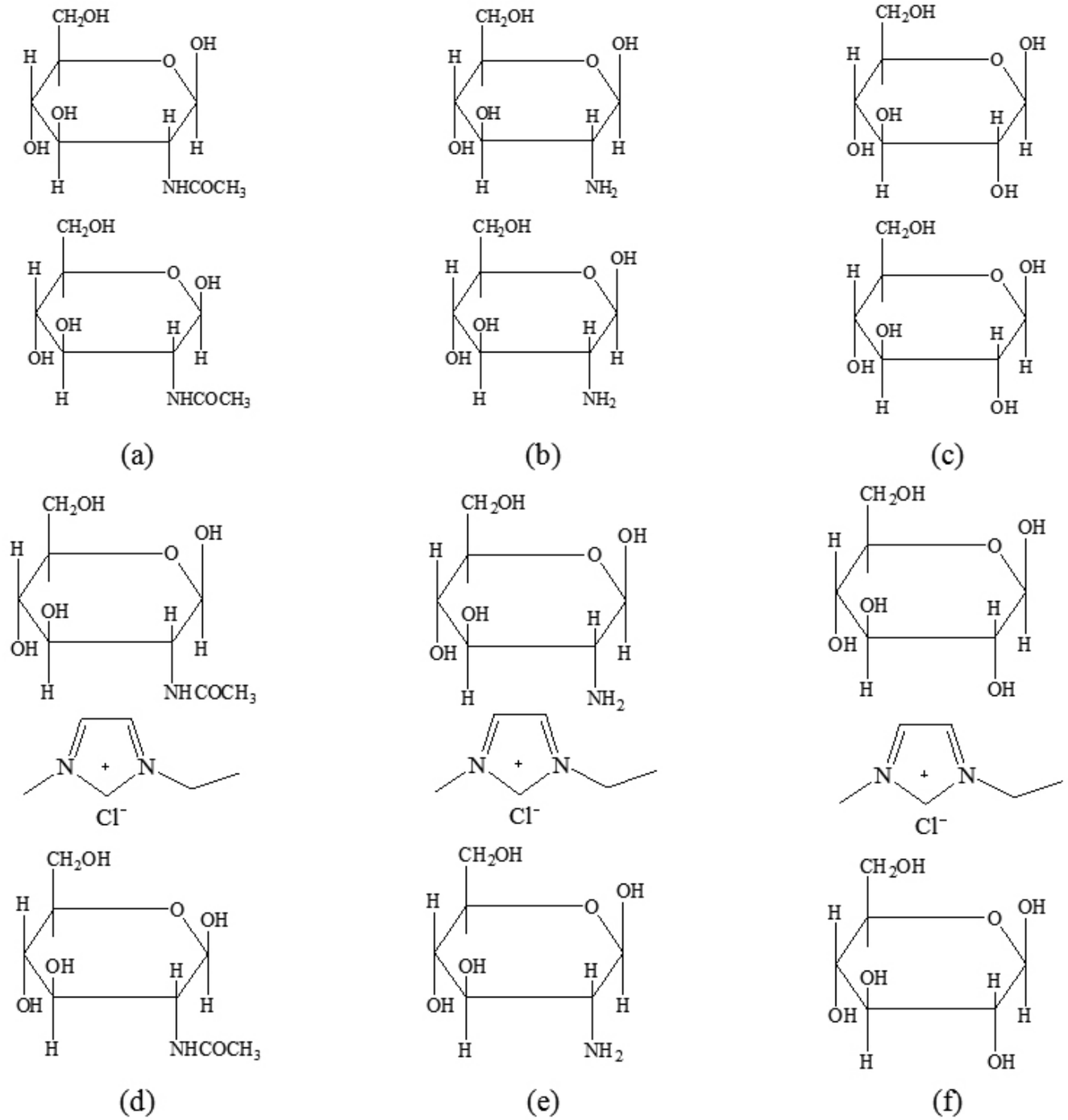

Fig. 1: The cluster models of (a) chitin, (b) chitosan, (c) cellulose, (d) [EMIM]Cl-chitin, (e) [EMIM]Cl-chitosan, and (f) [EMIM]Cl-cellulose.

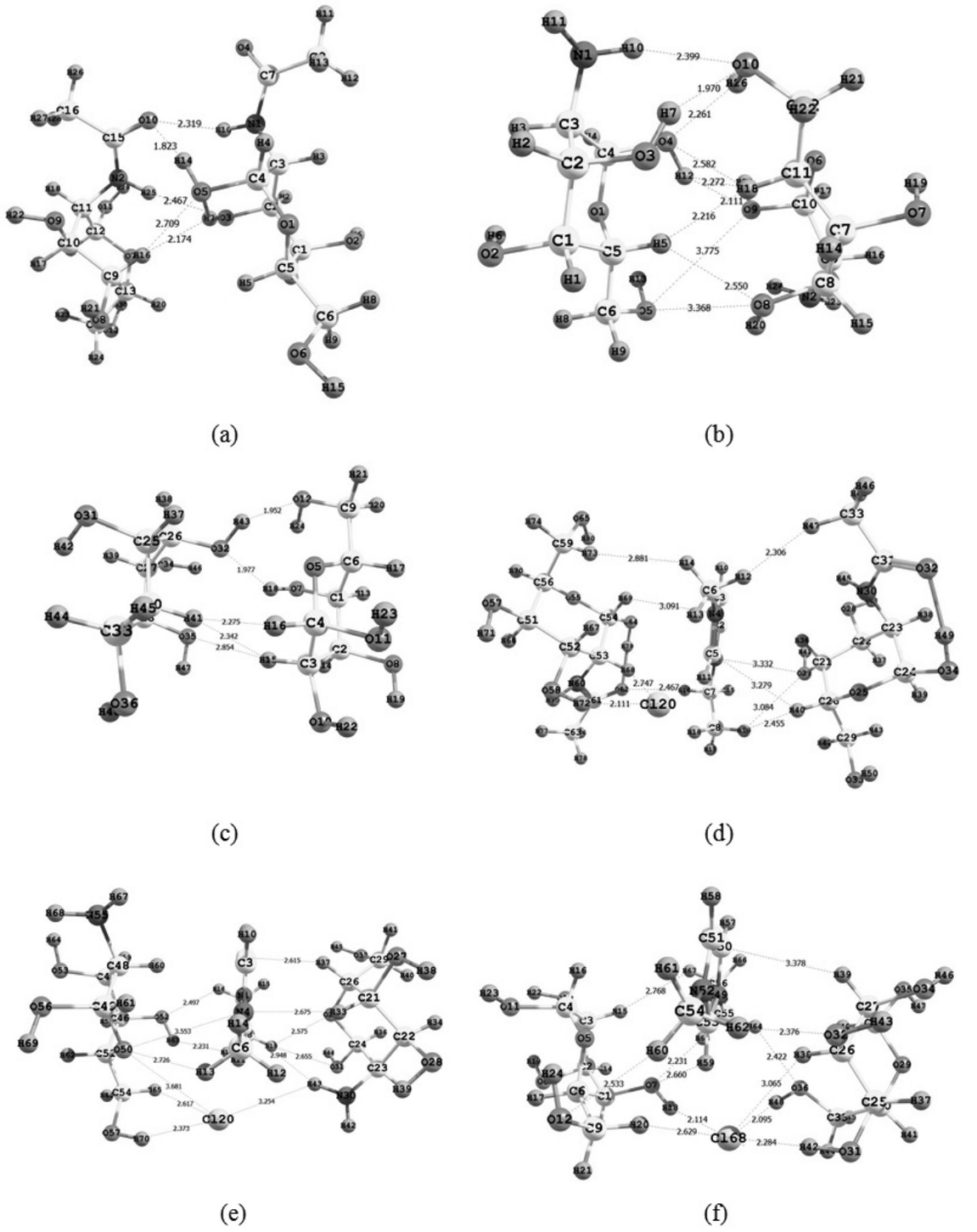

Fig. 2: The optimized structures of (a) chitin, (b) chitosan, (c) cellulose, (d) [EMIM]Cl-chitin, (e) [EMIM]Cl-chitosan, and (f) [EMIM]Cl-cellulose.

3.4 Visualization of noncovalent interactions

Reduced density gradient (RDG) and sign(λ_2)ρ raised by Yang et al. [28] are a pair of very important functions for revealing weak interactions. A way to identify interaction types is by analyzing the sign of λ_2. A negative λ_2 is a sign of attraction, while a positive value implies steric effect. Van der Waals interactions are described by low electron density (ρ), and thus sign(λ_2)·ρ ≤ 0. For this study, the diagrams of reduced density gradient (RDG) versus sign(λ_2) ρ (sign(λ_2)ρ-RDG(r)) of chitin, chitosan, cellulose, [EMIM]Cl-chitin, [EMIM] Cl-chitosan and [EMIM]Cl-cellulose are depicted in Fig. 3. It can be found that both chitin, chitosan, cellulose and [EMIM]Cl-chitin, [EMIM]Cl-chitosan, [EMIM]Cl-cellulose exhibit one spike in the low energy, low-density region (ρ ≈ 0.01 au), a typical signature of noncovalent attractions [28]. Comparing the sign(λ_2)ρ-RDG(r) diagrams of chitin and [EMIM]Cl-chitin, chitosan and [EMIM]Cl-chitosan, cellulose and [EMIM]Cl-cellulose, we can also see that the electron density of noncovalent interactions of [EMIM]Cl-chitin, [EMIM] Cl-chitosan and [EMIM]Cl-cellulose are larger than that of chitin, chitosan, and cellulose, respectively, indicating that the interactions between [EMIM] Cl and chitin/ chitosan/ cellulose are stronger than intra-interactions of chitin, chitosan, and cellulose.

The gradient isosurfaces can provide a rich visualization of weak interactions as broad regions of real space, rather than simple pairwise contacts between atoms. By plotting gradient isosurface in real space with respect to the geometry one can easily identify green region (attraction) and/or red region (steric effect) emerging as continuous surfaces. From the low gradient (s = 0.5 au) isosurface of chitin, chitosan, cellulose, [EMIM]Cl-chitin, [EMIM]Cl-chitosan and [EMIM]Cl-cellulose (Figure 4), we can easily find many green regions, red regions and green mixed with red regions between/among [EMIM] Cl and chitin, chitosan, cellulose, indicating the occurrence of noncovalent attraction (green regions) and steric repulsion (red regions). The attraction and weak steric repulsion (gray regions) of chitosan are strongest among chitin, chitosan and cellulose, in agreement with the results of interaction energies. While the attraction accompanied by weak steric effect between [EMIM]Cl and chitin/ chitosan/ cellulose are stronger than that of intra-interaction of chitin/ chitosan/ cellulose, in accordance with the results of sign(λ_2)ρ-RDG(r) and interaction energies.

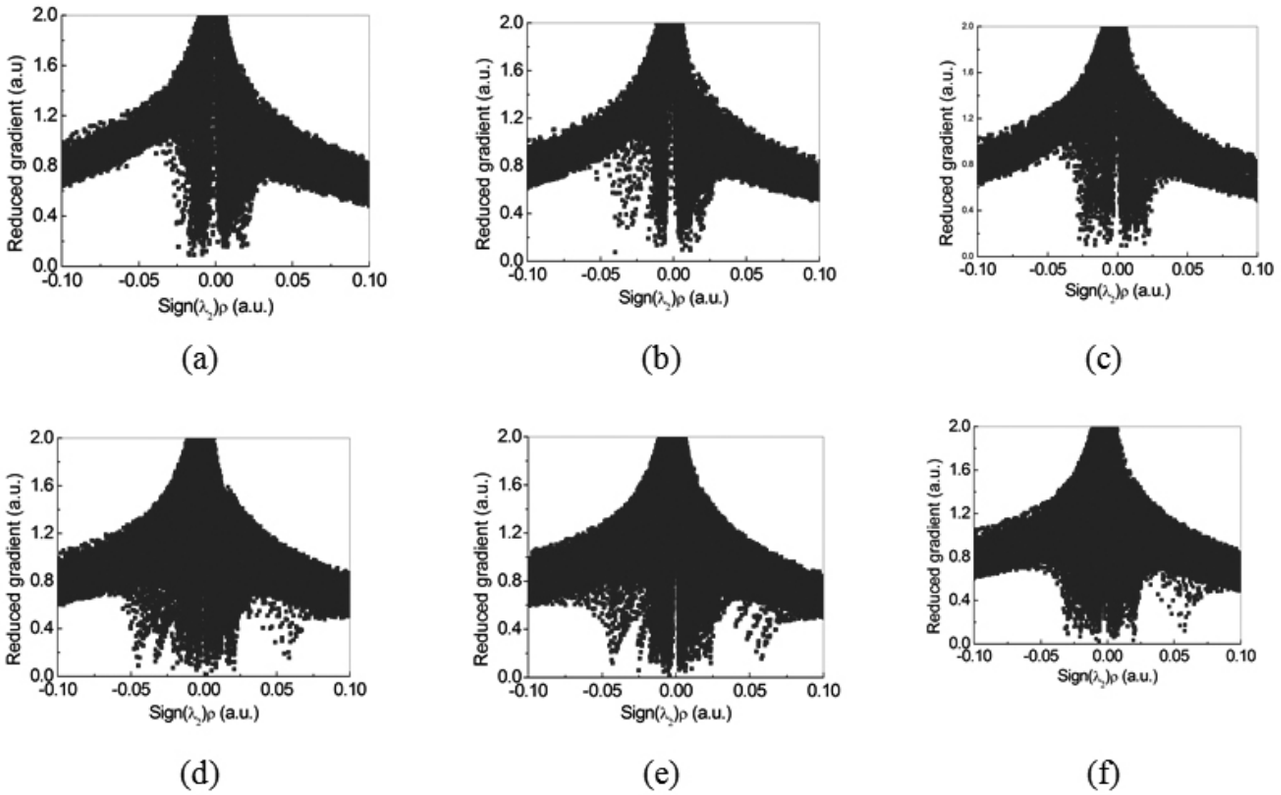

Fig. 3: Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue: (a) chitin, (b) chitosan, (c) cellulose, (d) [EMIM]Cl-chitin, (e) [EMIM]Cl-chitosan and (f) [EMIM]Cl-cellulose.

3.4 Electron density differences

Electron density difference is typically the difference between an assumed standard or model electron density and the actual observed or DFT computed electron density. For example, one can make a difference plot by subtracting atomic densities of two molecules from the density of two molecules formed complex. It can deduce information regarding interactions from theoretically determined electron density differences. The electron density differences in O, C1 and C4 plane of six-membered ring of chitin, chitosan, cellulose, [EMIM] Cl-chitin, [EMIM]Cl-chitosan and [EMIM]Cl-cellulose (Supplementary Fig. 4) show that variation of densities of [EMIM]Cl-chitin, [EMIM]Cl-chitosan and [EMIM]Cl-cellulose is remarkable, suggesting the stronger interactions between [EMIM]Cl and chitin/ chitosan/ cellulose.

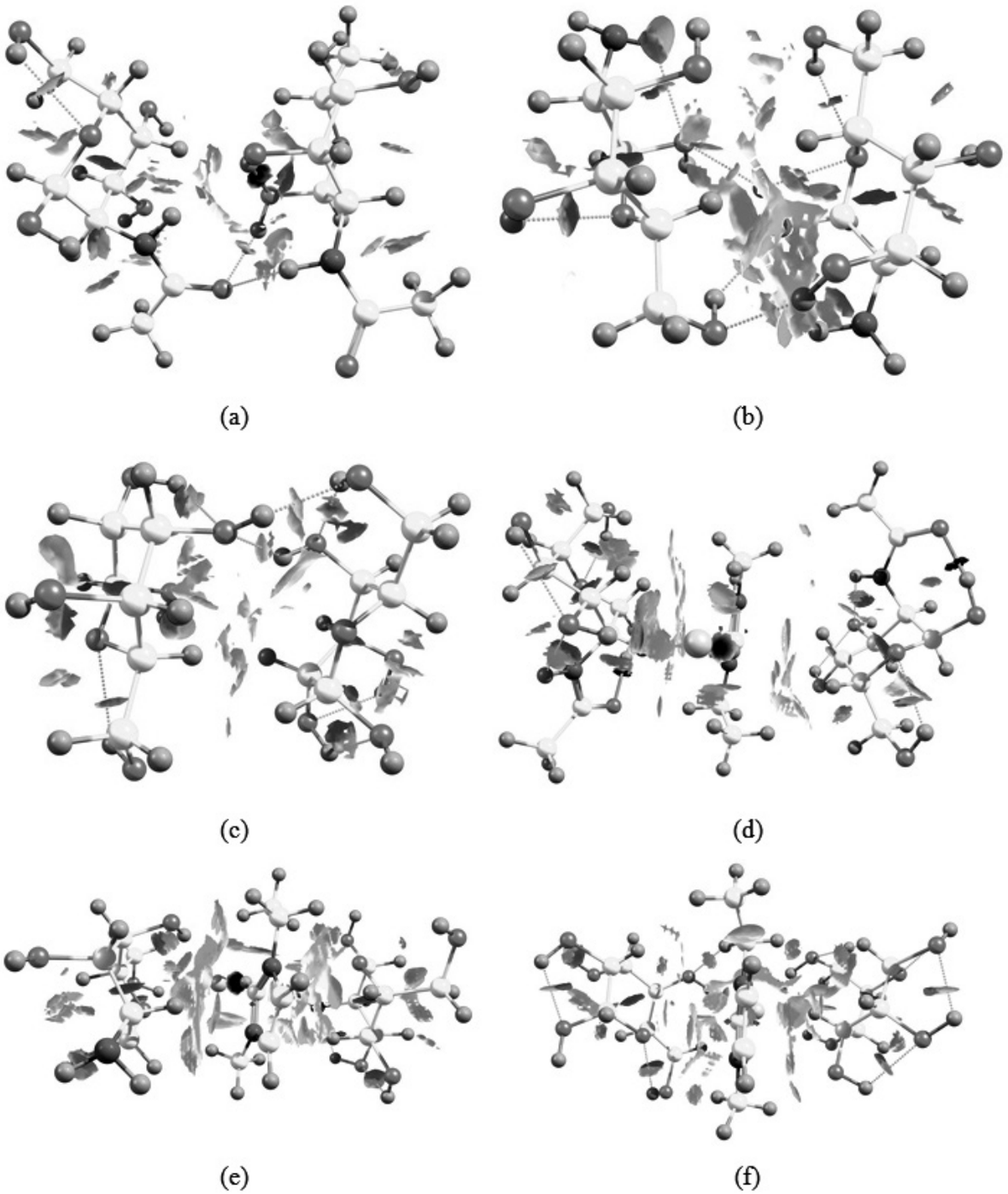

Fig. 4: Gradient isosurfaces for (a) chitin, (b) chitosan, (c) cellulose, (d) [EMIM]Cl-chitin, (e) [EMIM]Cl-chitosan and (f) [EMIM]Cl-cellulose. The surfaces are colored on a blue-green-red scale according to values of sign $(\lambda_2)\rho$, ranging from -0.04-0.02 au. Blue indicates strong attractive interactions, and red indicates strong nonbonded overlap.

4. CONCLUSIONS

In this report, density functional theory was employed to investigate the electronic properties and interactions between [EMIM]Cl and chitin/ chitosan/ cellulose. The topological properties, noncovalent interactions, and electron density difference were compared to present an interesting and useful interpretation of chitin/ chitosan/ cellulose dissolution in [EMIM]Cl ionic liquid due to stronger interactions between [EMIM]Cl and chitin/ chitosan/ cellulose.

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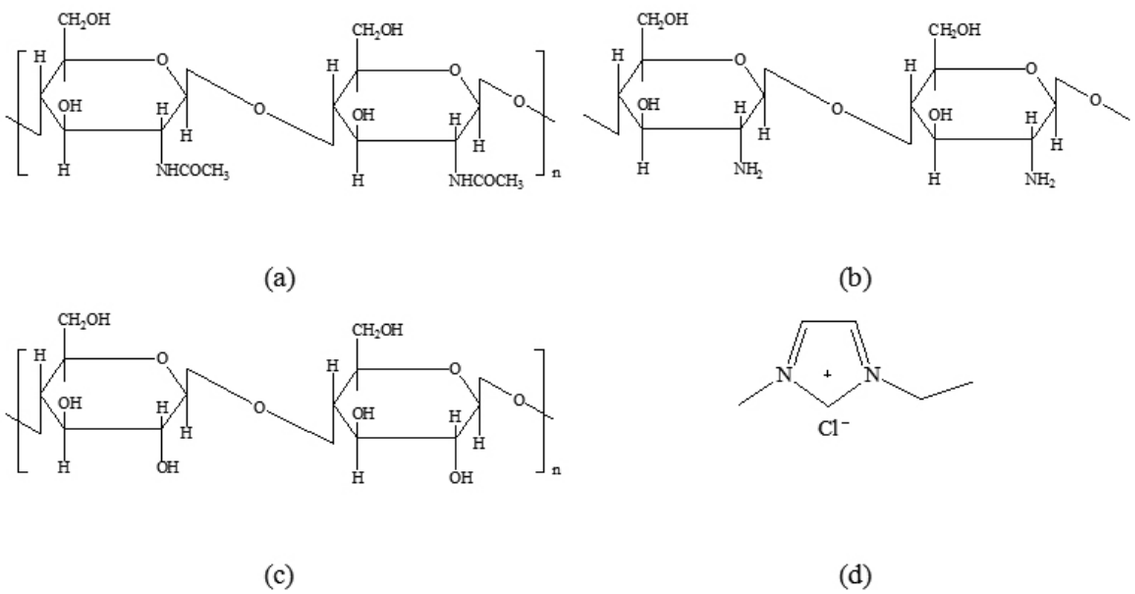
REFERENCES

1. M. Rinaudo, Prog. Polym. Sci., 2006, 31, 603-632.
2. R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, J. Am. Chem. Soc., 2002, 124, 4974-4975.
3. H. Wang, G. Gurau, R. D. Rogers, Chem. Soc. Rev., 2012, 41, 1519-1537.
4. H. Xie, S. Zhang, S. Li, Green Chem., 2006, 8, 630–633.
5. R. C. Remsing, R. P. Swatloski, R. D. Rogers, G. Moyna, Chem. Commun., 2006, 1271-1273.
6. D. A. Fort, R. C. Remsing, R. P. Swatloski, P. Moyna, G. Moyna, R. D. Rogers, Green Chem., 2007, 9, 63–69.
7. N. Sun, M. Rahman,Y. Qin, M. L. Maxim, H. Rodrıguez, R. D. Rogers, Green Chem., 2009, 11, 646–655.
8. B. Kosan, C. Michels, F. Meister, Cellulose, 2008, 15, 59–66.
9. S. Zhu, Y. Wu, Q. Chen, Z. Yu, C. Wang, S. Jin, Y. Ding, G. Wu, Green Chem., 2006, 8, 325–327.
10. J. Vitz, T. Erdmenger, C. Haensch, U. S. Schubert, Green Chem., 2009, 11, 417–424.
11. S. Barthela, T. Heinze, Green Chem., 2006, 8, 301-306.
12. A. Pinkert, K. N. Marsh, S. Pang, M. P. Staiger, Chem. Rev., 2009, 109, 6712–6728.
13. L. Feng, Z. Chen, J. Mol. Liq., 2008, 142, 1-5.
14. R. S. Payal, R. Bharath, G. Periyasamy, S. Balasubramanian, J. Phys. Chem. B, 2012, 116, 833–840.
15. Z. Ding, Z. Chi, W. Gu, S. Gu, J. Liu, H. Wang, Carbohyd. Polym., 2012, 89, 7-16.
16. Y. Zhao, X. Liu, J. Wang, S. Zhang, Carbohyd. Polym., 2013, 94, 723-730.
17. Q. Tian, S. Liu, X. Sun, H. Sun, Z. Xue, T. Mu, Carbohyd. Res., 2015, 408, 107-113.
18. Y. Yao, Y. Li, X. Liu, X. Zhang, J. Wang, X. Yao, S. Zhang, Chin. J. Chem. Eng., 2015, 23(11), 1894-1906.
19. B. Cao, J. Du, D. Du, H. Sun, X. Zhu, H. Fu, Carbohyd. Polym., 2016, 149, 348-356.
20. B. Delley, J. Chem. Phys., 1990, 92, 508-517.
21. B. Delley, J. Chem. Phys., 2000, 113, 7756-7764.
22. S. F. Boys, F. Bernardi, Mol. Phys., 1970, 19, 553-566.
23. F. Biegler-Konig, J. Schonbohm, J. Comput. Chem., 2002, 23, 1489-1494.
24. T. Lu, F. Chen, J. Mol. Graph. Model., 2012, 38, 314-323.
25. T. Lu, F. Chen, J. Comput. Chem., 2012, 33, 580-592.
26. A. Bondi, J. Phys. Chem., 1964, 68, 441-451.
27. P. Lipkowski, S. J. Grabowski, T. L. Robinson, J. Leszczynski, J. Phys. Chem. A, 2004, 108, 10865-10872.
28. E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen, W. Yang, J. Am. Chem. Soc., 2010, 132, 6498-6506

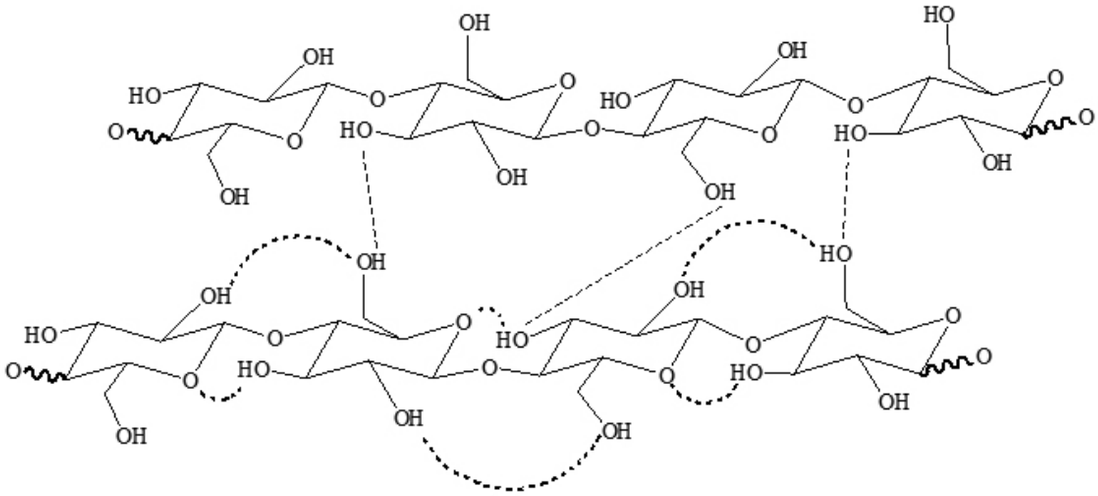
Suppl. Table 1 The topological properties of electron density (ρ), Laplacian of density ($\nabla^2\rho$), eigenvalues of the Hessian matrix (λ_1, λ_2, λ_3) of chitin, chitosan, cellulose, [EMIM]Cl-chitin, [EMIM]Cl-chitosan, and [EMIM]-cellulose (atomic units).

X•••Y	cp type	D/Å	ρ	$-\nabla^2\rho$	λ_1	λ_2	λ_3
chitin							
O10-H10	（3，-1）	2.319	0.01272	-0.04492	-0.01248	-0.01054	0.06797
O10-H14	（3，-1）	1.823	0.03175	-0.10944	-0.04750	-0.04484	0.20179
H25-O3	（3，-1）	2.467	0.00758	-0.02720	-0.00692	-0.00500	0.03914
H16-O5	（3，-1）	2.709	0.00631	-0.01948	-0.00545	-0.00232	0.02729
H16-H7	（3，-1）	2.174	0.00632	-0.02084	-0.00554	-0.00249	0.02889
chitosan							
H10-O10	（3，-1）	2.399	0.00991	-0.03316	-0.00886	-0.00676	0.04882
H7-O10	（3，-1）	1.970	0.02485	-0.08440	-0.03310	-0.03144	0.14898
O4-H26	（3，-1）	2.261	0.01398	-0.04908	-0.01495	-0.01201	0.07605
O4-H25	（3，-1）	2.582	0.00866	-0.02844	-0.00707	-0.00509	0.04062
H12-O9	（3，-1）	2.111	0.01722	-0.06164	-0.01995	-0.01885	0.10047
H5-H25	（3，-1）	2.216	0.00602	-0.01736	-0.00474	-0.00379	0.02593
O5-O9	（3，-1）	3.775	0.00178	-0.00748	-0.00094	-0.00083	0.00927
H5-O8	（3，-1）	2.550	0.00836	-0.02596	-0.00763	-0.00763	0.04082
O5-O8	（3，-1）	3.368	0.00414	-0.01704	-0.00333	-0.00186	0.02226
cellulose							
H43-O12	（3，-1）	1.952	0.02551	-0.08952	-0.03390	-0.03200	0.15546
O32-H18	（3，-1）	1.977	0.02179	-0.08628	-0.02770	-0.02553	0.13953
H41-H16	（3，-1）	2.275	0.00657	-0.02000	-0.00600	-0.00487	0.03091
H41-H15	（3，-1）	2.342	0.00524	-0.01540	-0.00454	-0.00316	0.02312
O35-H15	（3，-1）	2.854	0.00449	-0.01380	-0.00369	-0.00312	0.02066
[EMIM]Cl-chitin							
H73-H14	（3，-1）	2.881	0.00167	-0.00608	-0.00114	-0.00076	0.00802
H12-H47	（3，-1）	2.306	0.00488	-0.01352	-0.00449	-0.00444	0.02247
H69-N4	（3，-1）	3.091	0.00339	-0.01096	-0.00212	-0.00166	0.01476
H68-Cl20	（3，-1）	2.747	0.01071	-0.03128	-0.00799	-0.00683	0.04613
O62-H16	（3，-1）	2.467	0.00859	-0.02804	-0.00814	-0.00770	0.04391
Cl20-H72	（3，-1）	2.111	0.03081	-0.07252	-0.03771	-0.03752	0.14776
O27-N1	（3，-1）	3.332	0.00520	-0.01636	-0.00341	-0.00307	0.02285
C5-H40	（3，-1）	3.279	0.00240	-0.00808	-0.00126	-0.00037	0.00975
H19-O27	（3，-1）	3.084	0.00306	-0.01172	-0.00207	-0.00137	0.01516

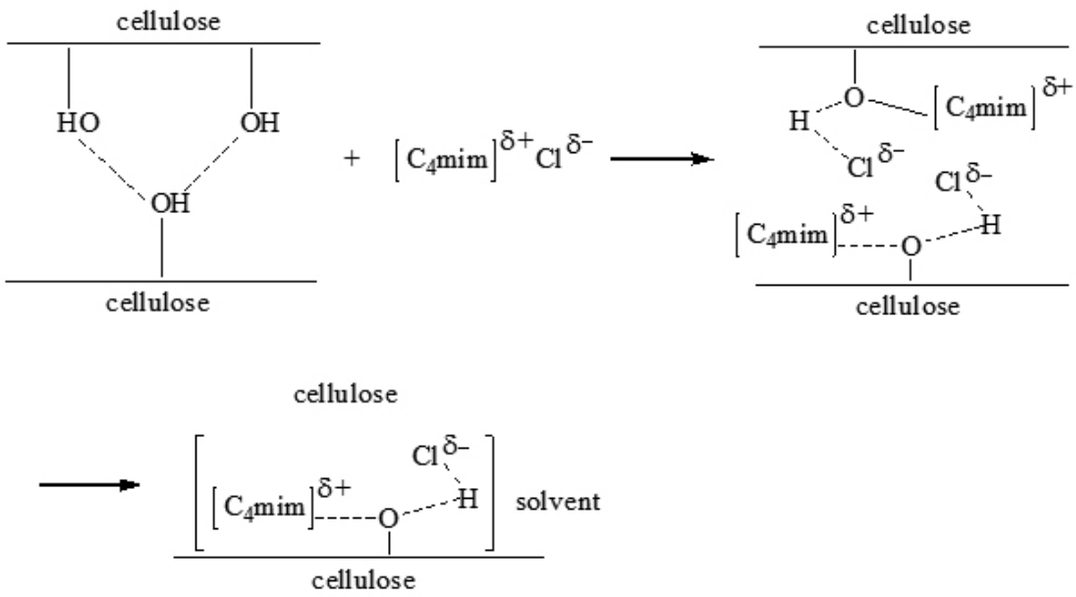
H19-H40	（3，-1）	2.455	0.00419	-0.01264	-0.00348	-0.00319	0.01934
[EMIM]Cl-chitosan							
O52-H16	（3，-1）	2.497	0.00955	-0.03440	-0.00847	-0.00716	0.05007
O50-N4	（3，-1）	3.553	0.00344	-0.01304	-0.00138	-0.00025	0.01470
H1-H63	（3，-1）	2.231	0.00610	-0.02248	-0.00501	-0.00387	0.03137
O50-H13	（3，-1）	2.726	0.00531	-0.01900	-0.00411	-0.00371	0.02683
O50-Cl20	（3，-1）	3.681	0.00432	-0.01372	-0.00183	-0.00128	0.01685
H65-Cl20	（3，-1）	2.617	0.01333	-0.04140	-0.01087	-0.00953	0.06181
H70-Cl20	（3，-1）	2.373	0.01747	-0.05184	-0.01735	-0.01720	0.08642
H37-C5	（3，-1）	2.615	0.00873	-0.02504	-0.00679	-0.00551	0.03734
H33-N4	（3，-1）	2.675	0.00732	-0.02128	-0.00596	-0.00440	0.03166
H19-O25	（3，-1）	2.575	0.00827	-0.02748	-0.00686	-0.00629	0.04064
H19-O31	（3，-1）	2.655	0.00678	-0.02028	-0.00545	-0.00461	0.03034
H43-C8	（3，-1）	2.948	0.00375	-0.01328	-0.00271	-0.00129	0.01731
Cl20-H43	（3，-1）	3.254	0.00366	-0.01040	-0.00215	-0.00147	0.01405
[EMIM]Cl-cellulose							
H15-H67	（3，-1）	2.768	0.00211	-0.00744	-0.00165	-0.00122	0.01035
O12-H60	（3，-1）	2.533	0.00844	-0.02584	-0.00772	-0.00639	0.03998
H61-O7	（3，-1）	2.231	0.01439	-0.05036	-0.01581	-0.01422	0.08040
H59-O7	（3，-1）	2.660	0.00792	-0.02884	-0.00654	-0.00063	0.03605
H18-Cl68	（3，-1）	2.114	0.03001	-0.07496	-0.03681	-0.03559	0.14739
H20-Cl68	（3，-1）	2.629	0.01194	-0.03564	-0.00947	-0.00941	0.05455
C50-H39	（3，-1）	3.378	0.00215	-0.00656	-0.00131	-0.00083	0.00871
H62-O32	（3，-1）	2.376	0.01117	-0.03872	-0.01154	-0.01022	0.06052
H64-O36	（3，-1）	2.422	0.00953	-0.03188	-0.00870	-0.00834	0.04895
H38-Cl68	（3，-1）	3.065	0.00623	-0.01748	-0.00305	-0.00226	0.02279
H48-Cl68	（3，-1）	2.095	0.03176	-0.07632	-0.03953	-0.03872	0.15458
H42-Cl68	（3，-1）	2.284	0.01995	-0.05836	-0.02147	-0.02100	0.10085



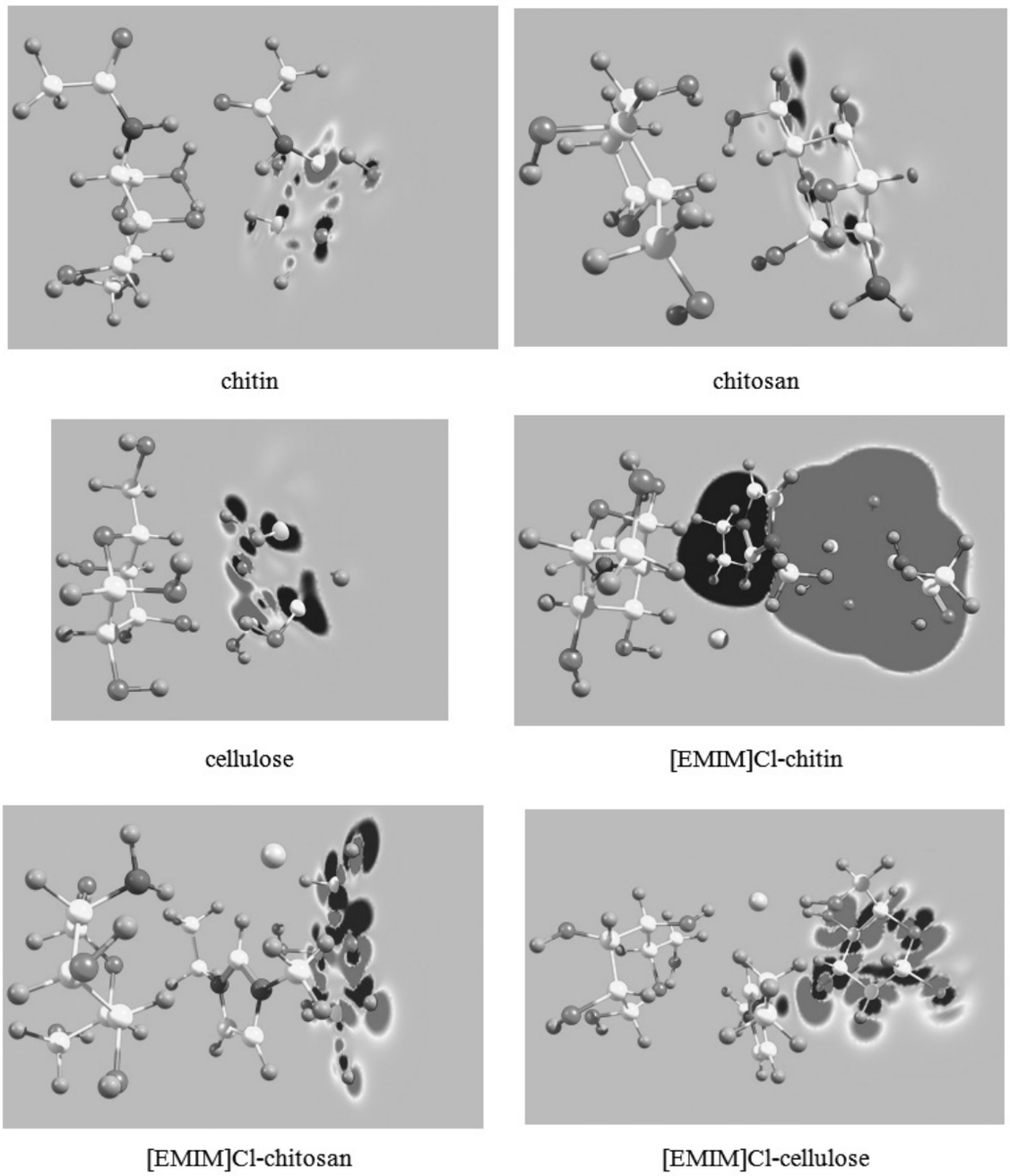
Suppl. Fig. 1 Chemical structures of (a) chitin, (b) chitosan (fully deacetylated), (c) cellulose and (d) 1-ethyl-3-methylimidazolium chloride.



Suppl. Fig. 2 Intra- and intermolecular hydrogen bonds in cellulose.



Suppl. Fig. 3 Proposed dissolution mechanism of cellulose in ionic liquid.



Suppl. Fig. 4 The electron density difference of (a) chitin, (b) chitosan, (c) cellulose, (d) [EMIM]Cl-chitin, (e) [EMIM]Cl-chitosan and (f) [EMIM]Cl-cellulose. Blue indicates decreasing of electron density, and red indicates increasing of electron density.