THEORETICAL STUDY ON INTERACTIONS BETWEEN CU-BASED IONIC LIQUID AND PROPANE/PROPYLENE

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ABSTRACT

Density functional theory has been employed to investigate the interactions between copper(I) bis(trifluoromethylsulfonyl)imide ($\text{Cu}[\text{Tf}_2\text{N}]$) and $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$. The calculations were based on the model of $\text{Cu}[\text{Tf}_2\text{N}]$, and performed at X3LYP/6-31++G** level. The calculated interaction energies indicated that the adsorption ability of $\text{Cu}[\text{Tf}_2\text{N}]$ for $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$ followed the order of $\text{C}_3\text{H}_8 < \text{C}_3\text{H}_6$. The noncovalent interactions in real space, based on the electron density and its derivatives, reveal the nature of interactions between $\text{Cu}[\text{Tf}_2\text{N}]$ and $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$. The natural bond orbital (NBO) analysis of the second-order perturbation energy has been performed to investigate the interaction mechanism of $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$ on ionic liquid $\text{Cu}[\text{Tf}_2\text{N}]$.

Key Words: Cu-Based Ionic Liquid, Interaction, $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$

1 INTRODUCTION

The recovery of light olefins from the off-gas of catalytic crackers is an important process in the petrochemical industry. Propylene is the raw material for the polypropylene production, a polymer of extensive applications. The separation of olefin/paraffin gas mixtures by low temperature distillation is one of the most important but also most energy-consuming separation processes. Development of economically viable propylene/propane separation processes is becoming increasingly important, but it is extremely challenging due to the physicochemical similarities between those two molecules. Among a number of alternatives separation processes, reactive absorption of olefins from olefin/paraffin mixtures using a silver salt solution as absorption liquid in a gas/liquid membrane contactor may be attractive in this respect [1-7]. Room temperature ionic liquids are proposed as potential substitutes for conventional solvents

as reaction media, such as a negligible volatility, which enables a relatively easy recovery, a wide range of polarities, non-flammable compounds, and high chemical and thermal stability. Besides, their lack of volatility gives ionic liquids the feature that they can perform gas separations without solvent losses or gas stream pollution.

The bis(trifluoromethanesulfonyl)imide (also known as bis(triflyl)imide, NTf_2^-) salts of the coinage metal ions Cu^+ and Ag^+ have been synthesized [8-10]. It was reported that $\text{Ag}[\text{Tf}_2\text{N}]$ ionic liquid can be used to separate propane/propylene or ethylene/ethane [1,3,11,12]. Due to the cheap metal of copper and its similar properties in contrast to silver, $\text{Cu}[\text{Tf}_2\text{N}]$ may be potential to be as sorbent for separation of propane/propylene, so the interactions between $\text{Cu}[\text{Tf}_2\text{N}]$ and propane/propylene by theoretical methods were compared. The structures of $\text{Cu}[\text{Tf}_2\text{N}]$, propane, and propylene are shown in Fig. 1.

Fig. 1 The structures of (a) $\text{Cu}[\text{Tf}_2\text{N}]$, (b) C_3H_8 and (c) C_3H_6

2 Computational details

The extended hybrid density functional X3LYP [13], which is widely used in ionic liquids [14,15], reveals excellent performance, hence we used this method which is good at describing the van der Waals and hydrogen bonding interactions [16]. The 6-31++G(d,p) basis set (5d, 7f spherical-harmonic type) has been employed in all the calculations since they can give a fine compromise between accuracy and computational cost. No symmetry constraint was imposed on the optimization of initial structures. To examine the nature of interactions, the electronic properties for stationary points were illustrated in terms of natural bond orbital (NBO) analysis [17]. The NBO analysis was obtained with 6-31++G** basis set to provide information of hydrogen bonding and halogen bonding. Multiwfn software [18,19] was employed to analyze the interaction properties.

For interaction energy, basis set superposition errors (BSSE) were considered using the counterpoise method [20] and the relative energy of certain structure is defined as the difference relative to the most stable structure, which was calculated as following:

$$E = E([\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8/\text{C}_3\text{H}_6) - (E([\text{Cu}[\text{Tf}_2\text{N}]] + E(\text{C}_3\text{H}_8/\text{C}_3\text{H}_6))$$

3 RESULTS AND DISCUSSION

3.1 Geometric, electronic properties and interaction energies

In this section, we discuss the most stable geometries of $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$ and $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$. Fig. 2 shows the two most stable geometries optimized at the X3LYP/6-31++G(d,p) level, frequency analyses of all stationary points have been performed with the same level calculations to guarantee the most stable geometries of the molecules. Some important structural parameters, including the distances and NBO charge between $\text{Cu}[\text{Tf}_2\text{N}]$ and $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$ are listed. The distances of $\text{Cu}\cdots\text{H11}$, $\text{Cu}\cdots\text{H12}$ and $\text{Cu}\cdots\text{C1}$ in $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$ are 1.833 Å, 1.836 Å and 2.157 Å, less than the sum of van der Waals radii of Cu (1.4 Å), H (1.20 Å), and C (1.70 Å) [21]. While the $\text{Cu}\cdots\text{C1}$ and $\text{Cu}\cdots\text{C2}$ distances in $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$ are 2.004 Å, 2.053 Å, respectively, which suggest the strong interactions between $\text{Cu}[\text{Tf}_2\text{N}]$ and C_3H_6 .

The interaction energies between $\text{Cu}[\text{Tf}_2\text{N}]$ and $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$ were 18.63 Kcal/mol and 40.16 Kcal/mol, respectively, demonstrating that the interaction between $\text{Cu}[\text{Tf}_2\text{N}]$ and C_3H_8 is weaker than that between $\text{Cu}[\text{Tf}_2\text{N}]$ and C_3H_6 .

Fig. 2 The optimized structures and NBO charge of (a) $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$ and (b) $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$

3.2 NBO analysis

The optimized structures were employed for NBO analysis. NBO analysis is based on a method for optimally transforming a given wave function into localized form, corresponding to the one-center (lone pairs) and two-center (bonds) elements of the chemist's Lewis structure picture. It provides a better description of the electron distribution in complexes. The NBO analysis were performed for $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$ and $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$. The NBO charges (Fig. 2) of N and Cu in $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$ and $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$ are -1.35701, 0.78874, and -1.34923, 0.89375, respectively, suggesting that the more negative charges of H11 and H12 migrate to Cu in $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$ and the more positive Cu in $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$ may be ascribed to its back-donation.

Table 1 gives the natural electron configurations of Cu, N, S2, S1, H11, H12 or C1, C2 of $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$ and $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$. The electron configurations of copper in $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$ and $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$ are $[\text{core}] 3d^{9.84}4s^{0.35}4d^{0.01}5p^{0.01}$ and $[\text{core}] 3d^{9.74}4s^{0.35}4d^{0.01}5p^{0.01}$, respectively, indicating

the more decreasing of 3d orbital electrons of $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$ in contrast to that of $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$. The C1 and C2 electron configurations in $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$ are $[\text{core}]2s^{1.09}2p^{3.48}4s^{0.01}4p^{0.01}$ and $[\text{core}]2s^{1.02}2p^{3.23}4s^{0.01}4p^{0.02}$, respectively, demonstrating the net electron migration from copper to C1 and C2.

The linear combination of natural atomic orbitals (NAOs) of $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$ and $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$ are tabulated in Table 2. It can be seen the fact that the occupancy for $\text{LP}(5)\text{Cu}$ (3d) and $\text{LP}^*(6)\text{Cu}$ (4s) in $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$ and $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$ are 1.97755, 0.25213 and 1.81391, 0.29997 is remarkably different, implying the more charge transfer of 3d orbital from $\text{Cu}[\text{Tf}_2\text{N}]$ to C_3H_6 and more charge back donation to $4s^*$ orbital of $\text{Cu}[\text{Tf}_2\text{N}]$ from C_3H_6 . The occupancy of $\sigma^*(\text{C1-H13})$, $\sigma^*(\text{C1-H12})$, and $\sigma^*(\text{C1-H11})$ indicates the charge transfer to anti-orbital of C_3H_8 , while the occupancy of $\sigma(\text{C1-C2})$, $\pi(\text{C1-C2})$, $\sigma^*(\text{C1-C2})$ and $\pi^*(\text{C1-C2})$ is 1.99157, 1.83797, 0.01166 and 0.23584, demonstrating the main charge transfer between $\text{Cu}[\text{Tf}_2\text{N}]$ and $\pi(\text{C1-C2})$, $\pi^*(\text{C1-C2})$ orbitals of C_3H_6 .

Table 1 The natural electron configurations of Cu, N, S2, S1, H11, H12 or C1, C2 of $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$ and $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$

$\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$		$\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$	
Cu	$[\text{core}] 3d^{9.84}4s^{0.35}4d^{0.01}5p^{0.01}$	Cu	$[\text{core}] 3d^{9.74}4s^{0.35}4d^{0.01}5p^{0.01}$
N	$[\text{core}]2s^{1.61}2p^{4.72}3s^{0.01}3p^{0.02}$	N	$[\text{core}]2s^{1.61}2p^{4.71}3s^{0.01}3p^{0.02}$
S2	$[\text{core}]3s^{1.08}3p^{2.47}3d^{0.17}4p^{0.01}5s^{0.01}5p^{0.02}$	S2	$[\text{core}]3s^{1.07}3p^{2.46}3d^{0.14}4p^{0.02}5s^{0.01}5p^{0.01}$
S1	$[\text{core}]3s^{1.08}3p^{2.47}3d^{0.17}4p^{0.02}5s^{0.01}5p^{0.01}$	S1	$[\text{core}]3s^{1.08}3p^{2.47}3d^{0.16}4p^{0.03}5s^{0.01}$
H11	$1s^{0.77}$	C1	$[\text{core}]2s^{1.09}2p^{3.48}4s^{0.01}4p^{0.01}$
H12	$1s^{0.77}$	C2	$[\text{core}]2s^{1.02}2p^{3.23}4s^{0.01}4p^{0.02}$

Table 2 The linear combination of natural atomic orbitals (NAOs) of $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$ and $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$

$\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$			$\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$		
NBO	occupancy	NAO	NBO	occupancy	NAO
LP(1)Cu	1.99900	3d	LP(1)Cu	1.99769	3d
LP(2)Cu	1.99746	3d	LP(2)Cu	1.99656	3d
LP(3)Cu	1.98856	3d	LP(3)Cu	1.99076	3d
LP(4)Cu	1.97873	3d	LP(4)Cu	1.98905	3d
LP(5)Cu	1.97755	3d	LP(5)Cu	1.81391	3d
LP*(6)Cu	0.25213	4s	LP*(6)Cu	0.29997	4s
$\sigma^*(\text{C1-H13})$	0.00948	$0.5595(\text{sp}^{3.05})_{\text{C1}} - 0.8004(\text{s})_{\text{H13}}$	$\sigma(\text{C1-C2})$	1.99157	$0.7034(\text{sp}^{1.95})_{\text{C1}} + 0.7108(\text{sp}^{1.93})_{\text{C2}}$
$\sigma^*(\text{C1-H12})$	0.02281	$0.6230(\text{sp}^{3.33})_{\text{C1}} - 0.7822(\text{s})_{\text{H12}}$	$\pi(\text{C1-C2})$	1.83797	$0.7340(\text{sp}^{2.42})_{\text{C1}} + 0.6792(\text{sp}^{3.53})_{\text{C2}}$
$\sigma^*(\text{C1-H11})$	0.02259	$0.6249(\text{sp}^{3.36})_{\text{C1}} - 0.7807(\text{s})_{\text{H11}}$	$\sigma^*(\text{C1-C2})$	0.01166	$0.7108(\text{sp}^{1.95})_{\text{C1}} - 0.7034(\text{sp}^{1.93})_{\text{C2}}$
			$\pi^*(\text{C1-C2})$	0.23584	$0.6792(\text{sp}^{2.42})_{\text{C1}} - 0.7340(\text{sp}^{3.53})_{\text{C2}}$

Table 3 Some donor-acceptor interactions in Cu[Tf₂N]-C₃H₈, Cu[Tf₂N]-C₃H₆ and their second order perturbation stabilization energies, *E*(2) (kcal/mol)

Donor	Acceptor	<i>E</i> (2) (kcal/mol)	Donor	Acceptor	<i>E</i> (2) (kcal/mol)
Cu[Tf ₂ N]-C ₃ H ₈					
LP(2)Cu	σ*(C1-H12)	0.19	LP(2)Cu	σ*(C1-H11)	0.16
LP(4)Cu	σ*(C1-H11)	3.39	LP(3)Cu	σ*(C1-H13)	0.61
LP(5)Cu	σ*(C1-H12)	3.04	LP(4)Cu	σ*(C1-H12)	0.74
LP*(6)Cu	σ*(C3-H33)	0.17	LP(5)Cu	σ*(C1-H11)	0.42
LP*(6)Cu	σ*(C2-C1)	0.46	LP*(6)Cu	σ*(C3-H32)	0.05
LP*(6)Cu	σ*(C1-H11)	0.65	LP*(6)Cu	σ*(C1-H13)	0.80
σ(C3-H31)	LP*(6)Cu	0.35	LP*(6)Cu	σ*(C1-H12)	0.59
σ(C2-C1)	LP*(6)Cu	0.18	σ(C3-H32)	LP*(6)Cu	0.41
σ(C2-H22)	LP*(6)Cu	0.16	σ(C2-H21)	LP*(6)Cu	0.17
σ(C1-H12)	LP*(6)Cu	19.61	σ(C1-H11)	LP*(6)Cu	20.19
Cu[Tf ₂ N]-C ₃ H ₆					
LP(1)Cu	σ*(C3-C2)	0.10	LP(3)Cu	σ*(H11-C1)	0.41
LP(2)Cu	σ*(H12-C1)	0.10	LP(3)Cu	σ*(H21-C2)	0.24
LP(3)Cu	σ*(C3-C2)	0.22	LP(5)Cu	σ*(H11-C1)	0.18
LP(3)Cu	σ*(H12-C1)	0.39	LP(5)Cu	σ*(H21-C2)	0.15
LP(5)Cu	σ*(H12-C1)	0.16	LP(5)Cu	π*(C1-C2)	28.98
LP*(6)Cu	σ*(C3-H32)	0.14	LP*(6)Cu	σ*(C3-C2)	0.14
LP(N)	π*(C1-C2)	1.33	LP(O21)	σ*(C3-H33)	0.72
LP(O11)	π*(C1-C2)	0.78	σ*(S2-O21)	σ*(C3-H33)	0.17
σ(C1-C2)	LP*(6)Cu	7.48	π(C1-C2)	LP*(6)Cu	64.82
π(C1-C2)	RY*(3)/Cu	2.37	σ(C1-H11)	LP*(6)Cu	4.60
σ(C1-H12)	LP*(6)Cu	3.99	σ(C2-C3)	LP*(6)Cu	2.03
σ(C2-H21)	LP*(6)Cu	3.58	π*(C1-C2)	LP*(6)Cu	3.11

Some donor-acceptor interactions in Cu[Tf₂N]-C₃H₈, Cu[Tf₂N]-C₃H₆ and their second order perturbation stabilization energies are given in Table 3. The main interactions in Cu[Tf₂N]-C₃H₈ are LP(4)Cu→σ*(C1-H11), LP(5)Cu→σ*(C1-H12), σ(C1-H12)→LP*(6)Cu, and σ(C1-H11)→LP*(6)Cu, exhibiting the strong interactions between σ(C1-H12), σ(C1-H11) and 4s* orbital. While the main interactions in Cu[Tf₂N]-C₃H₆ are LP(5)Cu→π*(C1-C2), σ(C1-C2)→LP*(6)Cu, π(C1-C2)→LP*(6)Cu, σ(C1-H11)→LP*(6)Cu, σ(C1-H12)→LP*(6)Cu, σ(C2-C3)→LP*(6)Cu, σ(C2-H21)→LP*(6)Cu, π*(C1-C2)→LP*(6)Cu, demonstrating the strong interactions due to charge transfer from π(C1-C2) to 4s* and back donation from d orbital to π*(C1-C2). The significant differences between Cu[Tf₂N] and C₃H₈/C₃H₆ are that π(C1-C2) and π*(C1-C2) are involved in the interactions.

3 Visualization of weak interactions with real space functions

Yang and co-workers recently presented a new method for studying non-covalent interactions in and between molecules [22]. The non-covalent interaction analysis is based on considering three components of the electron density distribution: the density itself (ρ), the reduced gradient of the density ($s = |\nabla\rho|/(2(3\pi^2)^{1/3}\rho^{4/3})$), and the Laplacian of the density ($\nabla^2\rho$). The Laplacian is further decomposed into three eigenvalues ($\lambda_1 \leq \lambda_2 \leq \lambda_3$). The second component, λ_2 , contains the interesting information; when $\lambda_2 < 0$, the interaction is bonding, while $\lambda_2 > 0$, the interaction is nonbonding [23]. According to the above three properties of the electron density, three main types of non-covalent interactions: attractive, moderately strong (e.g., hydrogen bonds), repulsive, moderately strong (e.g., steric interactions), and weak dispersion type interactions were identified. The $\text{Sign}(\lambda_2)\rho$ -RDG(r), and the color-filled graph of weak interaction regions($\text{Sign}(\lambda_2)\rho$ -RDG(r) isosurface) of Cu[Tf₂N]-C₃H₈, and Cu[Tf₂N]-C₃H₆ were depicted in Fig. 3 and Fig. 4.

The weak interactions always exist in the place of small $\rho(r)$ and 0 ~ medium RDG(r). The scatter diagrams of $\rho(r)$ -RDG(r) are helpful for notarizing the existence of weak interactions. The subsistent splattering area of small $\rho(r)$ and 0 ~ medium RDG(r) was addressed as “spike”, and it accounts

for the existence of weak interactions in the complex [22]. It can be found that plots of the electron density (ρ) and its reduced density gradient for Cu[Tf₂N]-C₃H₈ and Cu[Tf₂N]-C₃H₆ have “spikes”, suggesting the occurrence of weak interactions. In order to classify the types of weak interactions, the scatter diagrams of $\text{Sign}(\lambda_2)\rho$ -RDG(r) for Cu[Tf₂N]-C₃H₈ and Cu[Tf₂N]-C₃H₆ were depicted. Large, negative values of $\text{sign}(\lambda_2)$ are indicative of hydrogen bonding interactions, values near zero indicate van der Waals interactions, and large and positive $\text{sign}(\lambda_2)$ the steric effect. The hydrogen bonds, van der Waals interactions and steric effect occur, but the steric effect of Cu[Tf₂N]-C₃H₆ was weaker than that of Cu[Tf₂N]-C₃H₈. The gradient isosurfaces (Fig. 3) provide a rich visualization of weak interactions as broad regions of real space, rather than simple pairwise contacts between atoms. In the weak interaction pictures, the different interactions between Cu[Tf₂N] and C₃H₈/C₃H₆ are apparent. In Cu[Tf₂N]-C₃H₈, the attractive interaction, weak interaction and steric effect exist, while the strong interaction (covalent interactions) between Cu[Tf₂N] and C₃H₈ occur, giving rise to the strong interaction energy.

Dapprich, and Frenking [24] put forward a partitioning scheme for analyzing donor-acceptor interactions in a complex. The charge decomposition analysis constructs the wave function of the complex in terms of the linear combination of the donor and acceptor fragment orbitals (LCFO). Three terms, the charge donation d , the back donation b , and the charge depletion from the overlapping area (charge polarization) r were calculated for each LCFO orbital of the complex. The sum of the three contributions gives the total amount of donation, back donation and charge polarization in the complex. The number of electrons donated from Cu[Tf₂N] to C₃H₈/C₃H₆ (d), the number of electrons back donated from C₃H₈/C₃H₆ to Cu[Tf₂N] (b), and the number of electrons involved in repulsive polarization (r) are listed in Table 4. It can be seen that the weak electron donation Cu[Tf₂N]-C₃H₈ (0.0054 e) and strong back donation C₃H₈-Cu[Tf₂N] (0.1341 e) occur, while the net charge transfer from Cu[Tf₂N] to C₃H₆ is 0.761. The calculated charge polarization is quite different, it is -0.117 e for Cu[Tf₂N]-C₃H₈ and -0.082 e for Cu[Tf₂N]-C₃H₆, respectively.

Fig. 3 Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue. (a) Cu[Tf₂N]-C₃H₈ and (b) Cu[Tf₂N]-C₃H₆.

Fig. 4 Plots of gradient isosurfaces for (a) Cu[Tf₂N]-C₃H₈ and (b) Cu[Tf₂N]-C₃H₆.

Table 4 The number of electrons donated from Cu[Tf₂N] to C₃H₈/C₃H₆ (d), the number of electrons back donated from C₃H₈/C₃H₆ to Cu[Tf₂N] (b), and the number of electrons involved in repulsive polarization (r)

	d	b	d-b	r
	Cu[Tf ₂ N]→C ₃ H ₈ /C ₃ H ₆	Cu[Tf ₂ N]←C ₃ H ₈ /C ₃ H ₆		
Cu[Tf ₂ N]-C ₃ H ₈	0.005403	0.134097	-0.128694	-0.117491
Cu[Tf ₂ N]-C ₃ H ₆	-0.048576	-0.809535	0.760959	-0.082345

The density difference can be employed to locate ranges of charge depletion and charge concentration. A related scheme uses the calculation of the Laplacian $\nabla^2 \rho(r)$ of the density distribution $\rho(r)$, which determines the regions in space wherein electronic charge is locally concentrated and depleted. The electron density differences of Cu[Tf₂N]-C₃H₈ and Cu[Tf₂N]-C₃H₆ shown in Fig. 5 reflect the redistribution of electron. It can be found that the electronic charge between two hydrogen atoms is depleted and electronic charge of the two $\sigma^*(\text{C-H})$ is concentrated in Cu[Tf₂N]-C₃H₈. The depletion of electronic charge of π orbital in C₃H₆ and d orbital of Cu, the concentration of electronic

charge of π^* orbital in C₃H₆ demonstrate the charge transfer from π orbital in C₃H₆ to $4s^*$ orbital of Cu, and back donation from d orbital of Cu to π^* orbital in C₃H₆, in agreement with the NBO analysis.

Fig. 5 The electron density difference of (a) $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$, and (b) $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$

4 CONCLUSIONS

The molecular structures and nature of interactions between copper(I) bis(trifluoromethylsulfonyl)imide ($\text{Cu}[\text{Tf}_2\text{N}]$) and $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$ were investigated on the basis of ab initio method. The most stable structures of $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_8$ and $\text{Cu}[\text{Tf}_2\text{N}]\text{-C}_3\text{H}_6$ indicate the significant differences between $\text{Cu}[\text{Tf}_2\text{N}]$ and $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$. The nature of interactions between $\text{Cu}[\text{Tf}_2\text{N}]$ and $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$ were investigated by NBO analysis, charge decomposition analysis, and analyses of weak interactions with several real space functions, demonstrating the formation of chemical bonds between $\text{Cu}[\text{Tf}_2\text{N}]$ and C_3H_6 . The remarkably different interaction energies between $\text{Cu}[\text{Tf}_2\text{N}]$ and $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$ imply that $\text{Cu}[\text{Tf}_2\text{N}]$ ionic liquid may be used to separate $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$ mixture.

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