



Cite this: *Phys. Chem. Chem. Phys.*,  
2015, 17, 10925

# Interactions of CO<sub>2</sub> with various functional molecules

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The CO<sub>2</sub> capturing and sequestration are of importance in environmental science. Understanding of the CO<sub>2</sub>-interactions with various functional molecules including multi-N-containing superbases and heteroaromatic ring systems is essential for designing novel materials to effectively capture the CO<sub>2</sub> gas. These interactions are investigated using density functional theory (DFT) with dispersion correction and high level wave function theory (resolution-of-identity (RI) spin-component-scaling (scs) Möller–Plesset second-order perturbation theory (MP2) and coupled cluster with single, double and perturbative triple excitations (CCSD(T))). We found intriguing molecular systems of melamine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 7-azaindole and guanidine, which show much stronger CO<sub>2</sub> interactions than the well-known functional systems such as amines. In particular, melamine could be exploited to design novel materials to capture the CO<sub>2</sub> gas, since one CO<sub>2</sub> molecule can be coordinated by four melamine molecules, which gives a binding energy (BE) of ~85 kJ mol<sup>-1</sup>, much larger than in other cases.

Received 3rd February 2015,  
Accepted 17th March 2015

DOI: 10.1039/c5cp00673b

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## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is an important green-house gas, which is known to cause serious environmental damage to global weather and human life.<sup>1–3</sup> Power plant flue gases contain about 75% N<sub>2</sub>, 14% CO<sub>2</sub>, and 10% moisture. Natural gas reserves contain about 40% CO<sub>2</sub> and N<sub>2</sub> gases.<sup>4</sup> Since CO<sub>2</sub> gas can be converted into diverse valuable organic molecules, it is highly desirable to develop novel materials that capture CO<sub>2</sub> selectively.<sup>5,6</sup> Recently, new intriguing methods have been introduced for CO<sub>2</sub> capture, storage, and utilization.<sup>7,8</sup> Various materials are being developed, such as metal organic frameworks (MOFs),<sup>9–12</sup> zeolite-like sorbents,<sup>13,14</sup> covalent organic frameworks (COFs),<sup>15</sup> polymers with light organic functional groups,<sup>16–19</sup> boron nitride nanotubes,<sup>20</sup> and many kinds of amines including aminoalcohols,<sup>21–23</sup> aqueous ammonia,<sup>24</sup> and ionic liquids.<sup>25,26</sup> However, simple MOF and zeolite materials show low capacity for separating CO<sub>2</sub> from combustion-exhaust gas mixtures.<sup>6</sup> The amine-based wet processes of CO<sub>2</sub> capture show the degradation problem of amines. The CO<sub>2</sub>-covalent bonding interactions by amines, ammonia, and ionic liquids consume high energy in regeneration cycles. Furthermore, the aqueous ammonia processes show ammonia loss.<sup>27–30</sup> Various functionalized MOF/zeolite materials have been designed for selective CO<sub>2</sub> capture,<sup>31</sup> and their general functional group is an amine.<sup>32–34</sup> Recently a N-containing polymer sphere was reported to show high CO<sub>2</sub> adsorption capacity.<sup>35</sup> In this material the

porous carbon spheres contain intrinsic nitrogen-containing groups. The cooperative CO<sub>2</sub>-interactions enhance the CO<sub>2</sub> adsorption enthalpy with the CO<sub>2</sub>-interaction energy of a functional group.<sup>19,33</sup> To reduce the degradation problem of amines, aromatic molecules can be used to enhance the stability. Substituted aromatic or heteroaromatic systems can have enhanced CO<sub>2</sub>-BEs as compared with benzene.<sup>19,36</sup> On the other hand, CO<sub>2</sub> shows some solubility by physisorption in non-polar or weak polar solvents such as benzene, chloroform and dichloromethane.<sup>37,38</sup> Since CO<sub>2</sub> capture by physisorption shows low CO<sub>2</sub>-release energy, many CO<sub>2</sub> capture materials have been developed based on physisorption. It is thus vital to understand the physisorption strengths of CO<sub>2</sub> with many functional groups/molecules. However, limited theoretical investigations were performed.<sup>39–44</sup> Moreover, systematic investigation employing reliable high level *ab initio* methods has hardly been reported for the CO<sub>2</sub> interactions with diverse functional molecules. Therefore, we have systematically selected various functional molecules and calculated their BEs with CO<sub>2</sub>, using reliable high-level computational methods. We have found intriguing functional molecules showing large CO<sub>2</sub>-interaction energies, which can be used to design novel materials to capture CO<sub>2</sub>. Since ionic forms must have counter parts or special conditions to be used to capture CO<sub>2</sub>, ionic forms are excluded in this study.

## 2. Computational details

The CO<sub>2</sub> interactions with various functional molecules were calculated at the M06-2X<sup>45</sup> level with the aug-cc-pVDZ basis set (abbreviated as aVDZ) and the resolution-of-identity (RI)

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spin-component-scaling (scs) Møller–Plesset second-order perturbation theory (MP2) (RI-scs-MP2)<sup>46,47</sup> level with the aug-cc-pVTZ (aVTZ) basis set. The geometries were fully optimized without symmetry constraints at each calculation level. The M06-2X functional (hybrid-meta GGA with dispersion correction) has shown good performance in the investigation of the dispersion interaction as well as the electrostatic interaction (H-bonding, H- $\pi$  interaction,  $\pi$ - $\pi$  interaction, additional electrostatic and induction energies of neutral and charged dimeric systems).<sup>48</sup> Single point (SP) calculations using the RI-coupled cluster theory with single, double and perturbative triple excitations (RI-CCSD(T)) were performed by employing the aVTZ and aug-cc-pVQZ (aVQZ) basis sets at the RI-scs-MP2/aVTZ geometries. The CO<sub>2</sub>-BEs were calculated at the complete basis set (CBS) limit at the RI-CCSD(T) level with the aVTZ and aVQZ basis sets by employing the extrapolation approximation.<sup>49,50</sup> The complete basis set (CBS) energies were estimated with the extrapolation scheme utilizing the electron correlation error proportional to  $N^{-3}$  for the aug-cc-pVNZ basis set ( $N = 3$ : T,  $N = 4$ : Q). It is generally known that the zero-point-energy (ZPE)-uncorrected BE ( $-\Delta E_e$ ) is closer to the experimental CO<sub>2</sub>-adsorption enthalpy ( $\Delta H_{\text{ads}}$ ) than the ZPE-corrected BE ( $-\Delta E_0$ ).<sup>19,51</sup> Therefore, the values of  $-\Delta E_e$  are reported as the CO<sub>2</sub>-BEs.

Polar  $\sigma$ -bonding functional molecules give significant electrostatic interactions with CO<sub>2</sub>. Aromatic and heteroaromatic functional molecules give significant dispersion force contributions as well as electrostatic interaction contributions. We analyzed the compositions of BEs using symmetry-adapted perturbation theory (SAPT) at the DFT-PBE0 level with the aVDZ basis set, so-called DFT-SAPT.<sup>52</sup> The energy components are the electrostatic energy ( $E_{\text{es}}$ ), the effective induction energy including the induction-induced exchange energy ( $E_{\text{ind}}^* = E_{\text{ind}} + E_{\text{ind-exch}}$ ), the effective dispersion energy including the dispersion-induced exchange energy ( $E_{\text{disp}}^* = E_{\text{disp}} + E_{\text{disp-exch}}$ ), and the effective exchange repulsion energy with the induction-induced and dispersion-induced exchange energies excluded ( $E_{\text{exch}}^* = E_{\text{exch}} - (E_{\text{ind-exch}} + E_{\text{disp-exch}})$ ).<sup>53</sup> In this study, the asymptotically corrected PBE0 (PBE0AC) exchange–correlation (xc) functional with the adiabatic local density approximation (ALDA) xc kernel was used. In the PBE0AC-SAPT calculations, a purely local ALDA xc kernel was used for the hybrid xc functional.

The interaction energies were corrected with the basis set superposition error (BSSE) at the M06-2X and RI-CCSD(T) levels of theory. The RI-scs-MP2 method is known to produce slightly underestimated interaction energies,<sup>47</sup> thus, the BSSE corrections were not carried out at the RI-scs-MP2 level. Thermal energies were calculated by employing the M06-2X harmonic vibrational frequencies. The calculations were performed by using the Turbomole package<sup>54</sup> and the Molpro package.<sup>55</sup>

### 3. Results and discussion

#### 3.1. Understanding of CO<sub>2</sub> interactions with various normal functional molecules

The M06-2X CO<sub>2</sub>-binding structures and energies (in kJ mol<sup>-1</sup>) of all the functional molecules considered here are given in

Fig. 1 and Table 1. The first five structures show simple electrostatic interactions of each polar molecule with CO<sub>2</sub>. Among them, NH<sub>3</sub> having the largest BE ( $-\Delta E_e = 14.1$  kJ mol<sup>-1</sup>) with CO<sub>2</sub> implies that the sp<sup>3</sup> nitrogen atom is the best electron-pair donor to the electron deficient central C atom of CO<sub>2</sub>. The polar molecules containing the second-row elements have larger BEs with CO<sub>2</sub> than those containing third-row elements. The dipole moments of the polar molecules significantly affect their CO<sub>2</sub>-interactions. The increase of the atomic size or the polarizability in the same group elements has no significant effect on the electrostatic interaction component. Since the fluoric acid (HF) is a good proton donor rather than an electron donor, it shows the H-bond interaction with one electronegative O atom of CO<sub>2</sub> (Fig. 1).

Hydrogen cyanide (HCN) has an sp-hybrid N, which is a relatively poor electron donor and has a smaller BE with CO<sub>2</sub> than NH<sub>3</sub> does. On the other hand, for the trimethylamine (NMe<sub>3</sub>)-CO<sub>2</sub> binding, the methyl group is electron-donating to the electro-negative N and then enhances the electrostatic interaction strength of the sp<sup>3</sup> N as compared with the NH<sub>3</sub>-CO<sub>2</sub> binding ( $-\Delta E_e = 20.3$  kJ mol<sup>-1</sup> for NMe<sub>3</sub>-CO<sub>2</sub>; 14.1 kJ mol<sup>-1</sup> for NH<sub>3</sub>-CO<sub>2</sub>). As N changes from sp<sup>3</sup> to sp hybridization, the CO<sub>2</sub>-BE becomes smaller due to the contraction of the lone pair of electrons (20.3 kJ mol<sup>-1</sup> for NMe<sub>3</sub>-CO<sub>2</sub>, 17.4 kJ mol<sup>-1</sup> for NHCH<sub>2</sub>-CO<sub>2</sub>, 8.6 kJ mol<sup>-1</sup> for HCN-CO<sub>2</sub>). The OMe<sub>2</sub>-CO<sub>2</sub> interaction is stronger than the H<sub>2</sub>O-CO<sub>2</sub> interaction, and the OCH<sub>2</sub>-CO<sub>2</sub> interaction has a relatively small BE among the O-containing functional systems. In CO<sub>2</sub>-OMe<sub>2</sub>/CO<sub>2</sub>-NMe<sub>3</sub> systems, the simultaneous interactions of the electron deficient central C atom of CO<sub>2</sub> with the O/N atom of the functional molecules and the electron rich terminal O atoms of CO<sub>2</sub> with the methyl H atoms exhibit so-called cooperative intermolecular interactions, which increase the CO<sub>2</sub>-BEs. Therefore, the sp<sup>3</sup>-N containing functional groups (or amine-functionalization) have often been used.<sup>26,32–34</sup>

The fluoromethane (FCH<sub>3</sub>) has a considerable CO<sub>2</sub>-BE (10.1 kJ mol<sup>-1</sup>) but this is smaller than that of fluoric acid (HF). Nevertheless, some newly designed materials with F-containing functional groups have been introduced to enhance the CO<sub>2</sub>-adsorption enthalpy.<sup>18,56,57</sup> The carbonyl group (C=O) of formamide is more polar due to the resonance effect by the amino group (-NH<sub>2</sub>) than that of formic acid. Thus, formamide has a stronger CO<sub>2</sub>-BE ( $-\Delta E_e = 20.7$  kJ mol<sup>-1</sup>) than formic acid (20.3 kJ mol<sup>-1</sup>). This explains how MOF materials functionalized by carboxylic acid work well for CO<sub>2</sub> capture.<sup>58</sup> However, no amide-functionalized material has been investigated for CO<sub>2</sub> capture. Amide-based materials could show considerable performance. NMe<sub>3</sub> shows strong CO<sub>2</sub>-BE (20.3 kJ mol<sup>-1</sup>). The CO<sub>2</sub>-interaction energies of formic acid and formamide are compatible with that of NMe<sub>3</sub>. Some interesting research on environmentally friendly amino acids was reported by employing the amino acids as linkers in porous solid materials for CO<sub>2</sub> capture in the process of CO<sub>2</sub> physisorption.<sup>59</sup> The amino acids and aminoalcohols have multiple interaction sites. Neutral amino acids and aminoalcohols can have strong intramolecular H-bonding between their hydroxyl proton and their amine N atom, which can somewhat hinder the CO<sub>2</sub> physisorption. 1,2,3- and 1,2,4-triazole molecules also have



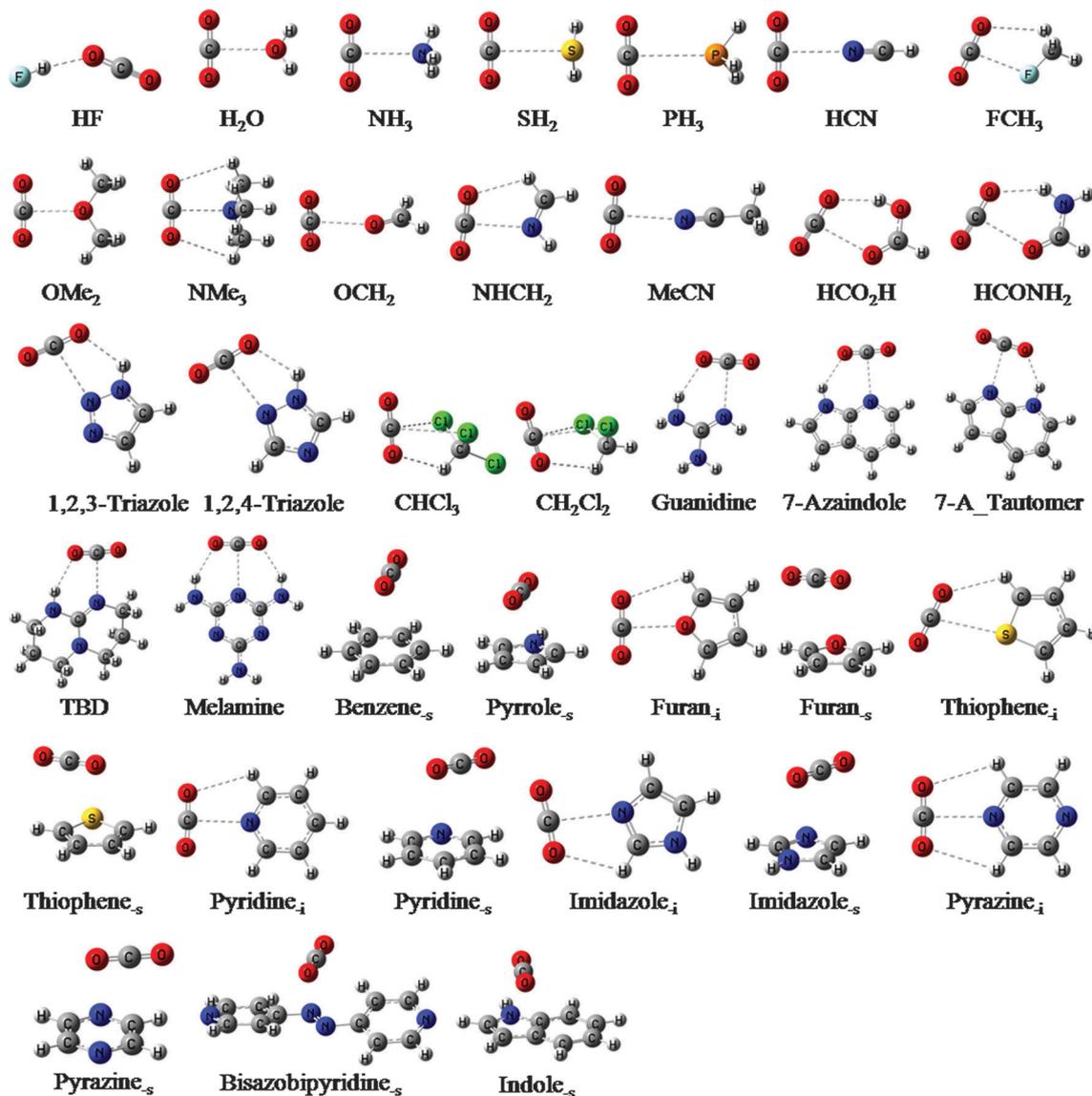


Fig. 1 M06-2X/aVDZ structures of various functional molecules involved in CO<sub>2</sub>-interaction.

large CO<sub>2</sub>-BEs (20.0 and 20.1 kJ mol<sup>-1</sup>). In the CO<sub>2</sub>-chloroform (CHCl<sub>3</sub>) and CO<sub>2</sub>-dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) interactions, two Cl atoms interact with the central C atom of CO<sub>2</sub>. The CO<sub>2</sub> gas is somewhat soluble in both chloroform and dichloromethane solvents.<sup>38</sup>

### 3.2. Special molecules showing strong CO<sub>2</sub>-interactions

Multi-N containing guanidine, 7-azaindole, 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD) and melamine are tautomerizable, showing strong amphoteric properties and having strong CO<sub>2</sub>-bindings (24.4, 24.4, 26.9 and 27.2 kJ mol<sup>-1</sup>, respectively). Guanidine and TBD are well known as superbases, and thus it is reasonable that they have large CO<sub>2</sub>-BEs. The tautomer (7-A\_Tautomer) of 7-azaindole shows a very strong CO<sub>2</sub>-BE (29.1 kJ mol<sup>-1</sup>). However, the tautomer is 13.4 kcal mol<sup>-1</sup> less stable than 7-azaindole at the M06-2X/aVDZ level. Thus, this tautomer cannot be used for practical materials, and so no discussion will be made here.

Analogues and derivatives (purine BS3, imidazopyridine, adenine and imidazopyridamine) of 7-azaindole have been reported to have large CO<sub>2</sub> BEs.<sup>44</sup> At the M06-2X/aVDZ level they show large CO<sub>2</sub>-BEs of 23.2, 24.3, 26.0 and 25.0 kJ mol<sup>-1</sup>, respectively. The intriguing point is that the molecules mentioned here show larger BEs than amine species. Their stronger binding with CO<sub>2</sub> could imply higher selectivity than amine species. Among the molecules studied here, melamine gives the largest CO<sub>2</sub> BE.

### 3.3. $\pi$ - $\pi$ stacking CO<sub>2</sub> interactions of aromatic functional molecules

As the intermolecular interactions become important in self-assembly,<sup>60,61</sup> the dispersion interactions of  $\pi$ -systems<sup>62-64</sup> have recently received much attention. The CO<sub>2</sub>-binding sometimes shows intriguing competition between electrostatic and dispersion interactions.<sup>39-44,65-71</sup> Aromatic systems have extra stability due to the resonance effect, which can reduce the



**Table 1** M06-2X/aVDZ CO<sub>2</sub>-interaction energies (kJ mol<sup>-1</sup>) with various functional molecules<sup>a</sup>

	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H_r$
HF	12.1	7.2	9.0
H <sub>2</sub> O	13.2	8.0	9.1
NH <sub>3</sub>	14.1	10.6	10.5
SH <sub>2</sub>	7.6	3.5	3.7
PH <sub>3</sub>	5.6	2.9	1.7
HCN	8.6	7.2	6.6
FCH <sub>3</sub>	10.1	7.4	6.5
OMe <sub>2</sub>	17.4	15.5	14.2
NMe <sub>3</sub>	20.3	19.6	18.2
OCH <sub>2</sub>	9.6	6.8	5.8
NHCH <sub>2</sub>	17.4	14.5	14.1
MeCN	10.5	8.6	6.9
HCO <sub>2</sub> H	20.3	16.8	16.4
HCONH <sub>2</sub>	20.7	17.4	17.1
1,2,3-Triazole	20.0	17.5	16.3
1,2,4-Triazole	20.1	17.1	16.0
CHCl <sub>3</sub>	11.6	9.5	7.7
CH <sub>2</sub> Cl <sub>2</sub>	12.9	10.7	9.3
Guanidine	24.4	21.3	20.3
7-Azaindole	24.4	21.4	20.1
7-A_Tautomer	29.1	—	—
TBD	26.9	24.5	23.0
Melamine	27.2	22.5	22.1
Benzene <sub>s</sub>	10.6	9.5	7.5
Pyrrrole <sub>s</sub>	15.7	12.6	11.4
Furan <sub>i</sub>	11.6	9.0	7.1
Furan <sub>s</sub>	10.1	7.8	6.1
Thiophene <sub>i</sub>	6.6	5.4	3.3
Thiophene <sub>s</sub>	11.3	10.9	8.7
Pyridine <sub>i</sub>	19.3	16.8	15.2
Pyridine <sub>s</sub>	11.0	8.5	6.7
Imidazole <sub>i</sub>	19.7	16.5	15.2
Imidazole <sub>s</sub>	15.1	12.3	10.9
Pyrazine <sub>i</sub>	17.0	14.4	12.9
Pyrazine <sub>s</sub>	9.0	6.6	4.8
Bisazobipyridine <sub>s</sub>	8.5	7.0	5.0
Indole <sub>s</sub>	16.7	13.1	11.5

<sup>a</sup>  $\Delta E_0$  is the zero-point-energy (ZPE) corrected interaction energy and  $\Delta H_r$  is the enthalpy change at room temperature (298 K). Each interaction energy was corrected by the basis set superposition error (BSSE). Subscripts “-s” and “-i” indicate “stacking” and “in-plane” conformations, respectively.

degradation problem of amine cases in the regeneration cycles. Some heteroaromatic systems can have two possible interaction structures with CO<sub>2</sub>. Subscripts “-i” and “-s” for the aromatic systems of Fig. 1 and Table 1 indicate “electrostatic in-plane” and “dispersive  $\pi$ - $\pi$  stacking” conformations, respectively. In most cases the in-plane conformations are more stable than the stacking conformations except for the case of thiophene. The CO<sub>2</sub>-binding of poly-thiophene was applied to CO<sub>2</sub> capture and CO<sub>2</sub> polymerization.<sup>72,73</sup> A poly-pyrrole shows good CO<sub>2</sub> adsorption capacity.<sup>74</sup> Pyrrole and indole do not have the in-plane conformations with CO<sub>2</sub>. For the N-containing heteroaromatic systems (imidazole, pyridine and pyrazine), the in-plane conformations ( $-\Delta E_e = 19.7, 19.3$  and  $17.0$  kJ mol<sup>-1</sup>) are much more stable than their stacking conformations with CO<sub>2</sub>. For the furan, the in-plane conformation ( $-\Delta E_e = 11.6$  kJ mol<sup>-1</sup>) is slightly more stable than the stacking conformation ( $10.1$  kJ mol<sup>-1</sup>) with CO<sub>2</sub>. The stacking conformation shows somewhat weak binding strength comparable to that of benzene ( $10.6$  kJ mol<sup>-1</sup>). The attractive dispersion interaction between CO<sub>2</sub> and a phenyl

ring was experimentally reported.<sup>75</sup> The stacking conformations of N-containing pyrazine and bisazobipyridine with CO<sub>2</sub> give weak CO<sub>2</sub>-BEs ( $9.0$  and  $8.5$  kJ mol<sup>-1</sup>). Although bisazobipyridine has small CO<sub>2</sub>-BE, it has been applied to the functionalized MOF material to capture CO<sub>2</sub>.<sup>76</sup> Heteroaromatic systems of pyrrole, thiophene, imidazole and indole show strong stacking interactions with CO<sub>2</sub>. Among them, indole has the largest CO<sub>2</sub>-BE ( $16.7$  kJ mol<sup>-1</sup>). Such heteroaromatic systems were reported as functional materials for CO<sub>2</sub> capture.<sup>19,72–74,77–80</sup> The stacking conformations of aromatic systems with CO<sub>2</sub> include the electrostatic interaction between the electronegative aromatic ring and electropositive central carbon atom of CO<sub>2</sub> and the bent H-bond interaction between one electropositive aromatic H atom and one electronegative O atom of CO<sub>2</sub>, as well as the dispersion interaction.

We performed SAPT calculations at the PBE0/aVDZ level for the in-plane and stacking complexes of CO<sub>2</sub> with benzene, pyrrole, thiophene, pyridine and indole. Their interaction energy decompositions are analyzed in Table 2. Their electrostatic interaction energy terms ( $E_{es}$ ) are over-compensated by

**Table 2** DFT–SAPT interaction energy decompositions (kJ mol<sup>-1</sup>) of the CO<sub>2</sub>-interactions with functional molecules for the stacking (-s) (in-plane (-i)) conformations ( $E_{tot}$  – total interaction energy;  $E_{es}$  – electrostatic interaction energy;  $E_{exch}^*$  – exchange energy term;  $E_{ind}^*$  – induction energy term;  $E_{disp}^*$  – dispersion interaction energy)

	Benzene <sub>s</sub>	Pyrrrole <sub>s</sub>	Thiophene <sub>s(-i)</sub>	Pyridine <sub>s(-i)</sub>	Indole <sub>s</sub>
$E_{tot}$	-7.98	-11.65	-8.30 (-5.68)	-6.31 (-15.74)	-12.47
$E_{es}$	-5.23	-10.77	-6.49 (-4.51)	-3.52 (-30.14)	-9.53
$E_{exch}^*$	7.12	12.40	9.12 (6.39)	5.64 (33.40)	11.53
$E_{ind}^*$	-0.61	-1.12	-0.74 (-0.50)	-0.46 (-3.65)	-0.99
$E_{disp}^*$	-8.97	-11.57	-9.80 (-6.82)	-7.77 (-13.90)	-12.95

**Table 3** RI-scs-MP2/aVTZ, RI-CCSD(T)/aVTZ and RI-CCSD(T)/CBS CO<sub>2</sub>-BEs ( $-\Delta E_e$  in kJ mol<sup>-1</sup>) on the RI-scs-MP2/aVTZ optimized geometries<sup>a</sup>

	scs-MP2	CCSD(T)/aVTZ	CCSD(T)/CBS
H <sub>2</sub> O	10.5	11.3	11.3
NH <sub>3</sub>	10.7	11.9	11.8
OMe <sub>2</sub>	15.5	15.9	15.5
NMe <sub>3</sub>	17.6	17.4	16.0
NHCH <sub>2</sub>	14.4	15.1	14.9
HCO <sub>2</sub> H	17.0	17.8	17.3
HCONH <sub>2</sub>	17.5	18.5	18.1
Guanidine	20.6	21.4	23.0
7-Azaindole	23.1	23.0	(24.3)
TBD	24.1	24.3	(25.9)
Melamine	24.0	24.1	(26.4)
Benzene <sub>s</sub>	11.8	9.4	(10.3)
Pyrrrole <sub>s</sub>	14.3	13.2	12.1
Furan <sub>i</sub>	11.5	11.7	10.8
Furan <sub>s</sub>	10.1	9.2	8.1
Thiophene <sub>i</sub>	7.3	6.8	5.2
Thiophene <sub>s</sub>	11.5	9.9	9.9
Pyridine <sub>i</sub>	17.3	17.6	16.9
Pyridine <sub>s</sub>	11.7	10.8	9.8
Imidazole <sub>i</sub>	17.5	16.4	17.3
Imidazole <sub>s</sub>	14.0	13.1	12.1
Indole <sub>s</sub>	17.5	14.6	(15.5)

<sup>a</sup> The values in parentheses are obtained with the CBS estimates obtained from the MP2 aVTZ and aVQZ energies and the CCSD(T) aVTZ energies.



the counter repulsive exchange interaction energy terms ( $E_{\text{exch}}^*$ ). In the case of benzene–CO<sub>2</sub> interaction, the dispersion interaction component is much larger than the electrostatic interaction component. For thiophene the stacking conformation has a large dispersion energy ( $-9.8 \text{ kJ mol}^{-1}$ ) in comparison with the in-plane conformation in the SAPT calculations. However, for pyridine, the electrostatic component is much larger in the in-plane conformation, and so the in-plane conformation is much more stable than the stacking conformation. The stacked thiophene–CO<sub>2</sub> structure has enhanced electrostatic and dispersion interaction energy components in comparison with benzene–CO<sub>2</sub>. Pyrrole and indole have enhanced electrostatic interaction energy components and enhanced repulsive exchange interaction energy components in comparison with benzene, while they have enhanced attractive dispersion interaction energy components. Indole–CO<sub>2</sub> interaction has the largest dispersion interaction component among them.

All the results of the BEs of ring compounds studied here are compatible with amine species, *e.g.* ammonia and NMe<sub>3</sub>. Moreover, unlike the amine-based wet processes, which exhibit covalent bond

breaking, followed by amine loss, the aromatic ring compounds are not expected to have such chemical reactions due to their non-covalent stacking interactions, and thus show no significant amine loss. Therefore, they can be applied to develop novel materials to capture the CO<sub>2</sub> gas.

### 3.4. High level calculations of strong CO<sub>2</sub>-interaction systems

Based on the M06-2X BEs of the functional molecules with a CO<sub>2</sub> molecule, we selected important complexes and calculated their optimal structures and interaction energies at the RI-scs-MP2/aVTZ level. The RI-CCSD(T)/CBS BEs were estimated by the RI-CCSD(T)/aVTZ and RI-CCSD(T)/aVQZ single point calculations at the RI-scs-MP2/aVTZ geometries. These CO<sub>2</sub>-BEs ( $-\Delta E_e$ ) are given in Table 3. Their RI-scs-MP2/aVTZ structures are shown in Fig. 2. Based on the RI-CCSD(T)/CBS BEs, NMe<sub>3</sub> has a large CO<sub>2</sub>-BE ( $16.0 \text{ kJ mol}^{-1}$ ). The CO<sub>2</sub>-BEs of formamide and formic acid are  $18.1$  and  $17.3 \text{ kJ mol}^{-1}$ , respectively, which are larger than that of NMe<sub>3</sub>. The tautomerizable multi-N-containing systems (guanidine, 7-azaindole, TBD and melamine) show much larger CO<sub>2</sub>-BEs ( $23.0$ ,  $24.3$ ,  $25.9$ , and  $26.4 \text{ kJ mol}^{-1}$ , respectively). Amine, carboxylic acid and amide

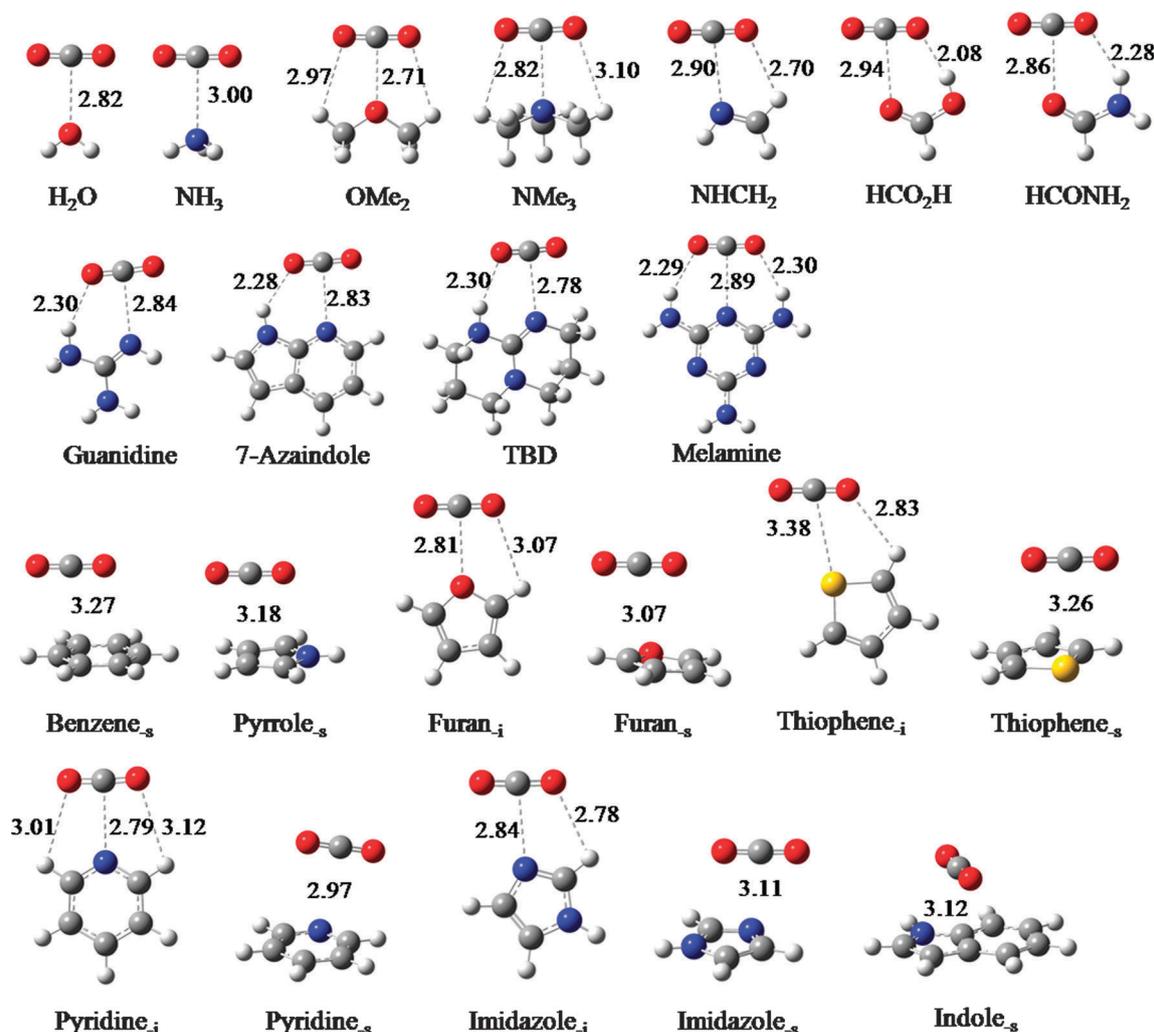


Fig. 2 RI-scs-MP2/aVTZ structures of selected functional molecules involved in the CO<sub>2</sub>-interaction.



have considerably large CO<sub>2</sub>-BEs. Pyridine and imidazole have larger CO<sub>2</sub>-BEs (16.9 and 17.3 kJ mol<sup>-1</sup>) than NMe<sub>3</sub> due to larger dipole moments (2.24/2.33 Debye for pyridine, 3.86/3.85 Debye for imidazole, and 0.62/0.79 Debye for NMe<sub>3</sub> at the M06-2X/RI-CCSD(T) level). This effect also appears in the 7-azaindole-CO<sub>2</sub> interaction. The CO<sub>2</sub>-BE of indole is 15.5 kJ mol<sup>-1</sup>. A polymer synthesized with indole shows a larger CO<sub>2</sub> adsorption enthalpy (49.0 kJ mol<sup>-1</sup>) at zero coverage, which is much more than three times the CO<sub>2</sub>-indole BE due to the cooperative interactions.<sup>19</sup> This indicates the binding of a CO<sub>2</sub> molecule mostly with three indole molecules and sometimes with four indole molecules. The BE of a CO<sub>2</sub> molecule with one indole molecule is 15.5 kJ mol<sup>-1</sup>, and so the CO<sub>2</sub>-BEs with three and four indole molecules can be roughly estimated to be 41.5 and 62 kJ mol<sup>-1</sup>, respectively, when the binding is assumed not to be seriously disturbed by the presence other indole molecules. This could be possible because the CO<sub>2</sub>-indole interaction is based on the stacking interaction, and the three or four fold interactions with one CO<sub>2</sub> molecule the same could be feasible when the stackings are made in the shape of three or four propeller blades of indole surrounding the linear CO<sub>2</sub> molecular axis (see, for example, Fig. 3). In reality, the side H-bond interaction of the CO<sub>2</sub>-indole system would be no more than that

of the CO<sub>2</sub>-water system in which the OC=O...H-OH interaction energy was 5.5 kJ mol<sup>-1</sup>.<sup>40</sup> Indole is an extended derivative of pyrrole, and carbazole is a larger extended derivative of indole. Among them, indole shows the strongest stacking interaction with CO<sub>2</sub>.<sup>19</sup> The bigger aromatic systems do not show larger CO<sub>2</sub>-BEs.

### 3.5. Applications of functional molecules to CO<sub>2</sub> capture

In CO<sub>2</sub> capture, not only does CO<sub>2</sub>-BE affect the selectivity but also the molecular weight of the absorbent affecting the weight capacity is an important factor. NMe<sub>3</sub>, formic acid, formamide, guanidine, 7-azaindole, TBD, and melamine show large CO<sub>2</sub>-BEs and their molecular weights are 59, 46, 45, 59, 118, 139, and 126 g mol<sup>-1</sup>, respectively. However, melamine has three CO<sub>2</sub>-binding sites and then the weight of melamine per CO<sub>2</sub> is 42 g mol<sup>-1</sup>, which shows an extremely impressive weight capacity. Formic acid and formamide have small molecular weights and large CO<sub>2</sub>-BEs. Formamide has a larger CO<sub>2</sub>-BE than formic acid. The CO<sub>2</sub> interacting systems of amides were experimentally studied in the vapor-liquid equilibrium state.<sup>81</sup> However, formamide is a liquid in the standard state. Since the amide-amide interaction is very strong ( $-\Delta E_e = 60.2$  kJ mol<sup>-1</sup> at the M06-2X level), CO<sub>2</sub> cannot be dissolved in the formamide solvent.

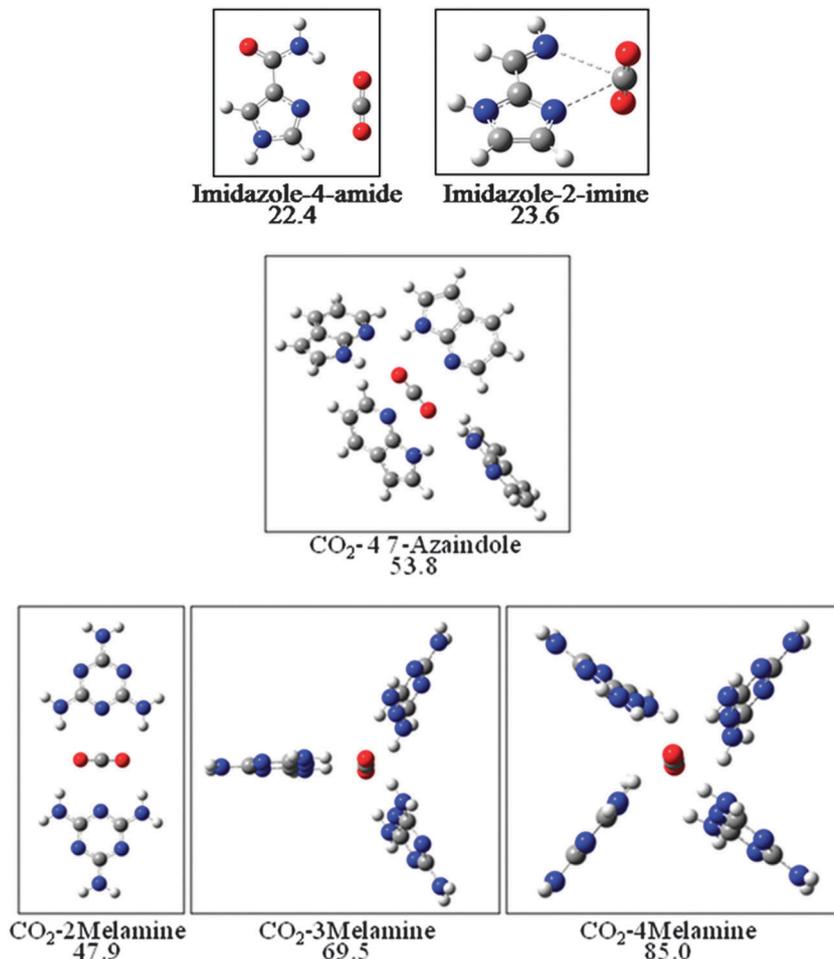


Fig. 3 Designed systems for CO<sub>2</sub> capture. The values are BEs ( $-\Delta E_e$ ) in kJ mol<sup>-1</sup> at the M06-2X/aVDZ level.



As exemplary host systems using imidazole, formamide and imine, we can design imidazole-4-amide and imidazole-2-imine, as shown in Fig. 3. The CO<sub>2</sub>-BEs of imidazole-4-amide and imidazole-2-imine ( $-\Delta E_e = 22.4$  and  $23.6$  kJ mol<sup>-1</sup>, respectively), are larger than those of imidazole, formamide and imine (19.7, 20.7, and 18.2 kJ mol<sup>-1</sup>) and that of imidazole-2-carboxylic acid (21.5 kJ mol<sup>-1</sup>). Thus, the imidazole-4-amide and imidazole-2-imine molecules show impressive CO<sub>2</sub> BEs. Indeed, an analogue of imidazole-4-amide was already synthesized and reported as a polymer.<sup>82</sup> Dacarbazine as a derivative of imidazole-4-amide is a well-known chemical. The imidazole-2-imine moiety is also found in many imidazole derivatives.

Indole was also successfully used in the polymer form to capture CO<sub>2</sub> gas.<sup>19</sup> In our study, guanidine, 7-azaindole, TBD and melamine show large CO<sub>2</sub>-BEs. Among them, 7-azaindole has a similar structure to indole. It is not easy to synthesize the 7-azaindole functional group into polymers due to the difficult oxidation reaction of 7-azaindole. However, if 7-azaindole is used as a functional unit of the materials for CO<sub>2</sub> capture, such materials could show high selectivity for CO<sub>2</sub> capture due to the large CO<sub>2</sub>-BE of 7-azaindole ( $-\Delta E_e = 24.4$  kJ mol<sup>-1</sup> at the M06-2X/aVDZ level). The CO<sub>2</sub>-BE of indole is 17.5 kJ mol<sup>-1</sup> at the M06-2X level. As mentioned in the previous section, CO<sub>2</sub> can interact with up to four 7-azaindole molecules (Fig. 3), as the experiment showed the CO<sub>2</sub> adsorption enthalpy of  $-49$  kJ mol<sup>-1</sup> at zero coverage of indole,<sup>19</sup> which indicates the interactions with 3 to 4 indole molecules. In this tetra-coordination, the CO<sub>2</sub>-BE is calculated to be 53.8 kJ mol<sup>-1</sup> ( $-\Delta E_e$ ) at the M06-2X/aVDZ level. The large adsorption enthalpy is critical to the high capacity and selectivity for CO<sub>2</sub> in the gas mixture.

A guanidine-functional polymer was reported to show good performance at high temperature.<sup>83</sup> Several applications of melamine were reported to show high capacity for CO<sub>2</sub> capture.<sup>84,85</sup> However, in most cases the central triazine ring was used as one or two stacking CO<sub>2</sub>-binding sites which have three N atoms,<sup>86</sup> which resulted in relatively weak CO<sub>2</sub>-BE. Melamine-terminal materials could show better performance due to the effective electrostatic CO<sub>2</sub>-binding as shown in Fig. 1 and 2. As shown in a model system (Fig. 3), CO<sub>2</sub>-two melamines, CO<sub>2</sub>-three melamines and CO<sub>2</sub>-four melamines show large CO<sub>2</sub>-BEs (47.9, 69.5 and 85.0 kJ mol<sup>-1</sup>, respectively) at the M06-2X/aVDZ level. Such large values arise from the maximized electrostatic interactions between CO<sub>2</sub> and melamine molecules associated with four-fold triple bindings comprised of two O<sup>δ-</sup>...H<sup>+</sup>N<sup>δ-</sup> electrostatic H-bonds and one C<sup>δ+</sup>...N<sup>δ-</sup> electrostatic bond. These model systems show much higher CO<sub>2</sub>-BEs. The multi-N-containing molecules (guanidine, 7-azaindole, TBD, and melamine) with large CO<sub>2</sub>-BEs could be used as multi-binding sites for a CO<sub>2</sub> molecule in devising absorbent materials with large CO<sub>2</sub> adsorption enthalpies.

## 4. Concluding remarks

Tautomerizable multi-N-containing strong bases (guanidine, 7-azaindole, TBD, and melamine) show considerably strong electrostatic interactions with CO<sub>2</sub> due to their strong amphoteric

properties. Among them, melamine shows the largest CO<sub>2</sub>-electrostatic BE. The stronger binding between these functional molecules with CO<sub>2</sub> could imply better selectivity than the amine species. Among the various aromatic systems considered, indole shows the largest dispersion interaction energy with CO<sub>2</sub>. The chemical units with large CO<sub>2</sub>-BEs could be applied to devising functional materials for efficient CO<sub>2</sub> capture. Furthermore, CO<sub>2</sub> by tetra coordination of melamines gives a very large CO<sub>2</sub>-BE (85.0 kJ mol<sup>-1</sup>). Thus, multi-N-containing molecules (guanidine, 7-azaindole, TBD, and melamine) with large CO<sub>2</sub>-BEs could be used as multi-binding sites for a CO<sub>2</sub> molecule. The present results could provide useful information for the development of promising functionalized materials for CO<sub>2</sub> capture/sequestration.

## Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0011222) and NRF (National Honor Scientist Program: 2010-0020414). It was also supported by the Research Fund of UNIST (project no. 1.140001.01). It was also supported by KISTI (KSC-2014-C3-020) and KISTI (KSC-2014-C3-030).

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