



The investigation of cavity-trapped electrons in the $\text{Na}_n@$ Tetracyanoethylene ($n=1-4$) systems

Navid Salehi ^a, Ladan Edjlali ^{a,*}, Esmail Vessally ^b, Ibon Alkorta ^c, Moosa Es'haghi ^a

^a Department of Chemistry, Tabriz Branch, Islamic Azad University, Tabriz, Iran

^b Department of Chemistry, Payame Noor University, Tehran, Iran

^c Instituto de Química Médica (CSIC), Juan de la Cierva, 3, Madrid 28006, Spain

ARTICLE INFO

Article history:

Received 9 April 2020

Received in revised form 10 May 2020

Accepted 10 May 2020

Available online 1 Oct 2020

Keywords:

Tetracyanoethylene
 Sodium salt
 Sodium electride
 confined electron

ABSTRACT

Electride materials are very interesting that have cavity-trapped electrons. In different systems, this materials can be used as source of electron donor. Hereby, we have explored the possible of electride materials based on tetracyanoethylene (TCNE) backbone, computationally. This is achieved through the addition of up to four Na-atoms to the TCNE backbone. Our results in this work, predict high thermodynamic stability for the $\text{Na}_n@$ TCNE ($n=1-4$) systems. Also, based on the evaluation of four criteria, non-nuclear attractor (NNA), electron localization function (ELF), electron density laplacian ($\nabla^2\rho(r)$), and non-linear optical (NLO), TCNE- Na_1 and TCNE- Na_2 and TCNE- Na_4 species are lithium salt. In contrast, the TCNE- Na_3 species can be introduced as sodium electride with cavity-trapped electrons. Therefore, Na:TCNE ratio is very significant factor to provide species with electride feature through the addition of Na atoms to TCNE backbone.

1. Introduction

Materials with electride property have achieved much attention in the recent years. The history of the electride materials begins by the introduction of alkali metal-ammonia solutions and solvated electrons in solution [1]. In addition, the first to postulate the existence of electrified, synthesize and characterize them was Dye et al [2-8]. The electrified (with cavity-trapped electrons) can be introduced as the smallest possible anions [9].

Note that the confined electrons in the electride do not belong to any specific atom. It is interesting to notice that the electrified have low work function. Therefore, they can be used as strong reducing agents in chemistry. Unique properties of electrified can provide suitable opportunity for researchers to study electron transfer process at room temperature. Moreover, the isolated electrons in the electrified cause its potential applications such as the improved cathode material for fluorescent

lights [10], emitting diodes for organic light [11], improved catalysts for the CO_2 activation [12], splitting of N_2 molecule [13-15], storage device of H_2 molecule with reversible features [16] and powerful and selective reducing agents [17-19].

In the electride materials, the density of the confined electrons is not big enough to identify through the X-ray. Therefore, experimental researchers used indirect evidence [20-22] to achieve its experimental characterization. Indeed, a few researchers have attempted to analyze the electronic structure of the electrified [23, 24]. This means that computational techniques can be more suitable tools to identify the electride materials. In this regards, researchers used different computational techniques to identify the electride material. For example, some researchers introduced materials as electride based on large non-linear optical properties (NLO) [25-27], non-nuclear attractors (NNAs) [28, 29] and electron localization

* Corresponding author. e-mail: L_edjlali@iaut.ac.ir

function (ELF) basins [30, 31]. Subsequently, some molecules presented these properties without the presence of confined electron in cavity of molecule. Therefore, none of these properties by itself can be used to identify electrified materials, unambiguously. Matito et al. [32]

presented that some molecules mentioned in literature as electrified material based on large NLOs or frontier orbitals are not really materials with electrified properties. They have suggested the simultaneous investigation of four criteria, the NNA and ELF basins, the Laplacian of the electron density ($\nabla^2\rho(r)$) and NLO as necessary conditions to assert the presence of confined electron in cavity and confirm the true nature of electrified material. Note that these four criteria can be used except when the NNAs are located in the close vicinity of an atom. More recently, Matito et al. [33] have established other computational protocol to identify, characterize, and design a new type of electrifieds which have the delocalized polyattractor character (metal cluster electrifieds).

In the present work, our main objective is to introduce materials with electrified property. To achieve this goal, we have focused on the tetracyanoethylene (TCNE) as backbone and carried out the systematic addition of the Na atoms (as strong electron donor) to TCNE backbone. By means of state of the art computational technique, we reveal details about the most stable geometry of $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems and incorporate them in either category of Sodium salts or Sodium electrifieds based on the investigation of the NNA and ELF basins, $\nabla^2\rho(r)$ and NLO criteria. The results of the present work can introduce materials with electrified properties.

2. Computational methods

In the present work, we have used the MP2 method conjugated to aug-cc-pVDZ [34] basis set to optimize possible geometries of the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems. Moreover, the calculation of all vibrational frequencies of the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems has been carried out to confirm lack of imaginary vibrational frequencies in the reported geometries. After the identification of the most stable geometries, we have calculated adsorption energy per Na atom (E_{ads}), vertical ionization (E_{VI}) and deformation energies (E_{d}) through equations (1)-(3), respectively.

$$E_{\text{ads}} = [E_1 - nE(\text{Li}) - E(\text{TCNE})]/n \quad (1)$$

$$E_{\text{VI}} = E_2 - E_1 \quad (2)$$

$$E_{\text{d}} = E_3 - E(\text{TCNE}) \quad (3)$$

In the equations (1)-(3), E_1 and E_2 show the energy of $\text{Na}_n\text{@TCNE}$ ($n=1-4$) and $[\text{Na}_n\text{@TCNE}$ ($n=1-4$)]⁺ systems, respectively. Moreover, E_3 stands for the energy of $\text{Na}_n\text{@TCNE}$ ($n=1-4$) system after elimination of the all Na atoms. We have used equations (4) and (5) to calculate the first hyper-polarizability (β_{total}) using the finite-field approach [35] and an electric field magnitude of 0.0010 a.u.

$$\beta_i = \frac{3}{5} (\beta_{iii} + \beta_{ijj} + \beta_{ikk}) \quad (4)$$

$$\beta_{\text{total}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}} \quad (5)$$

Finally, the optimization of geometry and the analysis of electron density in the present paper have been carried out by the Gaussian09 [36] and the multiwfn [37] programs, respectively.

3. Results and discussions

To design materials with electrified features, we have added systematically up to four Na atoms to TCNE backbone. In the $\text{Na}_1\text{@TCNE}$ system, one Na atom has been added to different positions of the TCNE backbone. After the optimization process without constraint, we have categorized all the obtained geometries for $\text{Na}_1\text{@TCNE}$ system based on total energy and selected the most stable geometry of $\text{Na}_1\text{@TCNE}$ system. In the next step, the second Na atom has been added to different positions of the most stable geometry of $\text{Na}_1\text{@TCNE}$ system to obtain possible structures of $\text{Na}_2\text{@TCNE}$ system through full optimization process.

The similar trend has been used to reveal the most stable geometry of $\text{Na}_3\text{@TCNE}$ and $\text{Na}_4\text{@TCNE}$ systems in the present work. It is necessary to say that the $\text{Na}_1\text{@TCNE}$, $\text{Na}_2\text{@TCNE}$ and $\text{Na}_3\text{@TCNE}$ systems are on the doublet, singlet and doublet potential energy surfaces (PESs), respectively. Because of comparable energies of $\text{Na}_4\text{@TCNE}$ system on the singlet and triplet PESs, we have reported the most stable geometry of $\text{Na}_4\text{@TCNE}$ system on both singlet (denoted as TCNE- $\text{Na}_4\text{-I}$) and triplet (denoted as TCNE- $\text{Na}_4\text{-II}$) PESs. Finally, solid lines have been used to present atomic connections in the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems based on atoms in molecules (AIM) [38] analysis.

3.1. Geometry and stability

Fig. 1 presents the most stable geometry of $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems. In the TCNE- Na_1 and the TCNE- Na_2 species, the Na atoms interact only with the Na atoms of the TCNE backbone. The Na - Na interaction has been found in the TCNE- Na_3 and the TCNE- $\text{Na}_4\text{-II}$ species. It is interesting to notice that Na - C interaction reveals

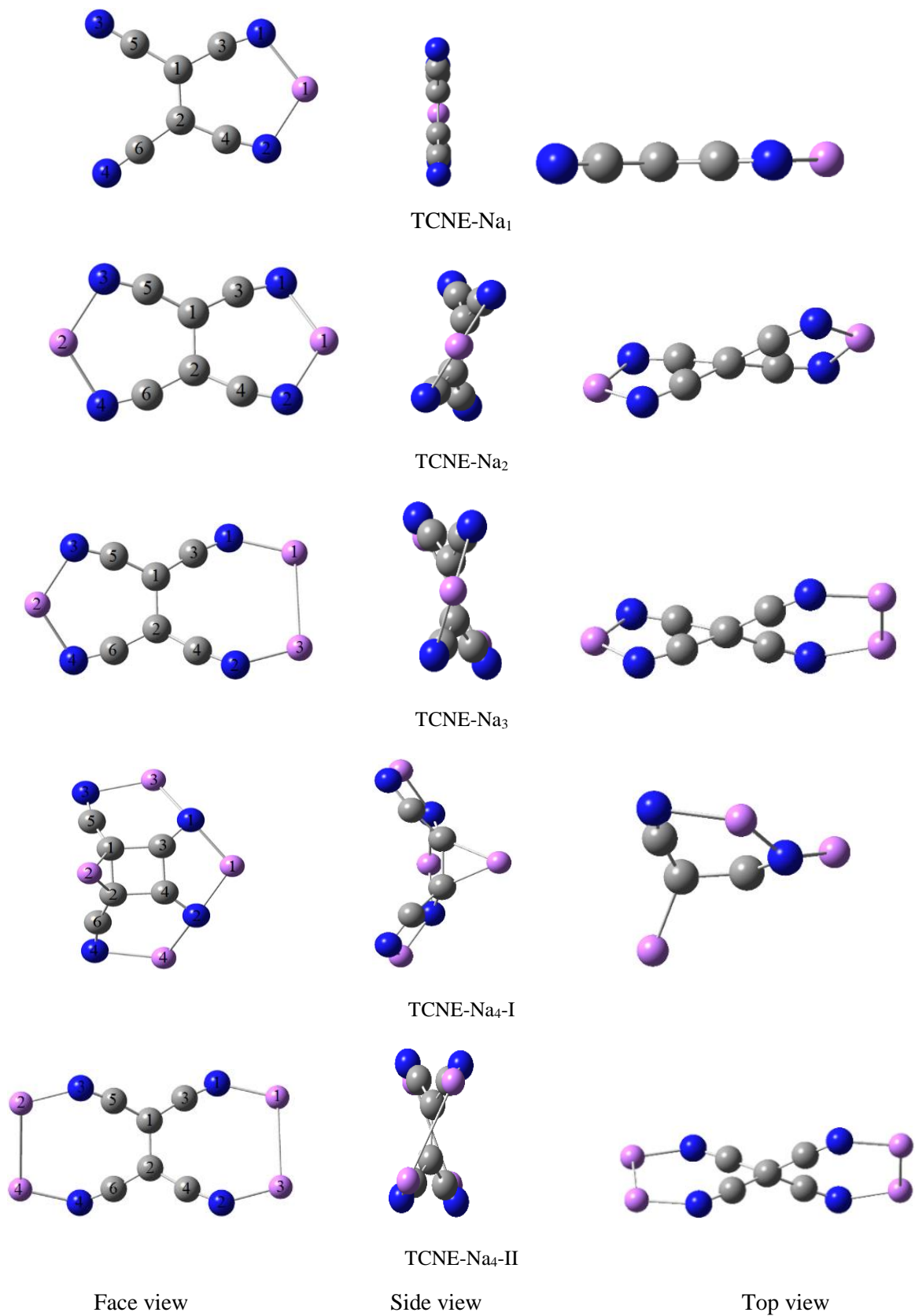


Fig. 1 The most stable geometry for Na_n@TCNE (n=1-4) systems.

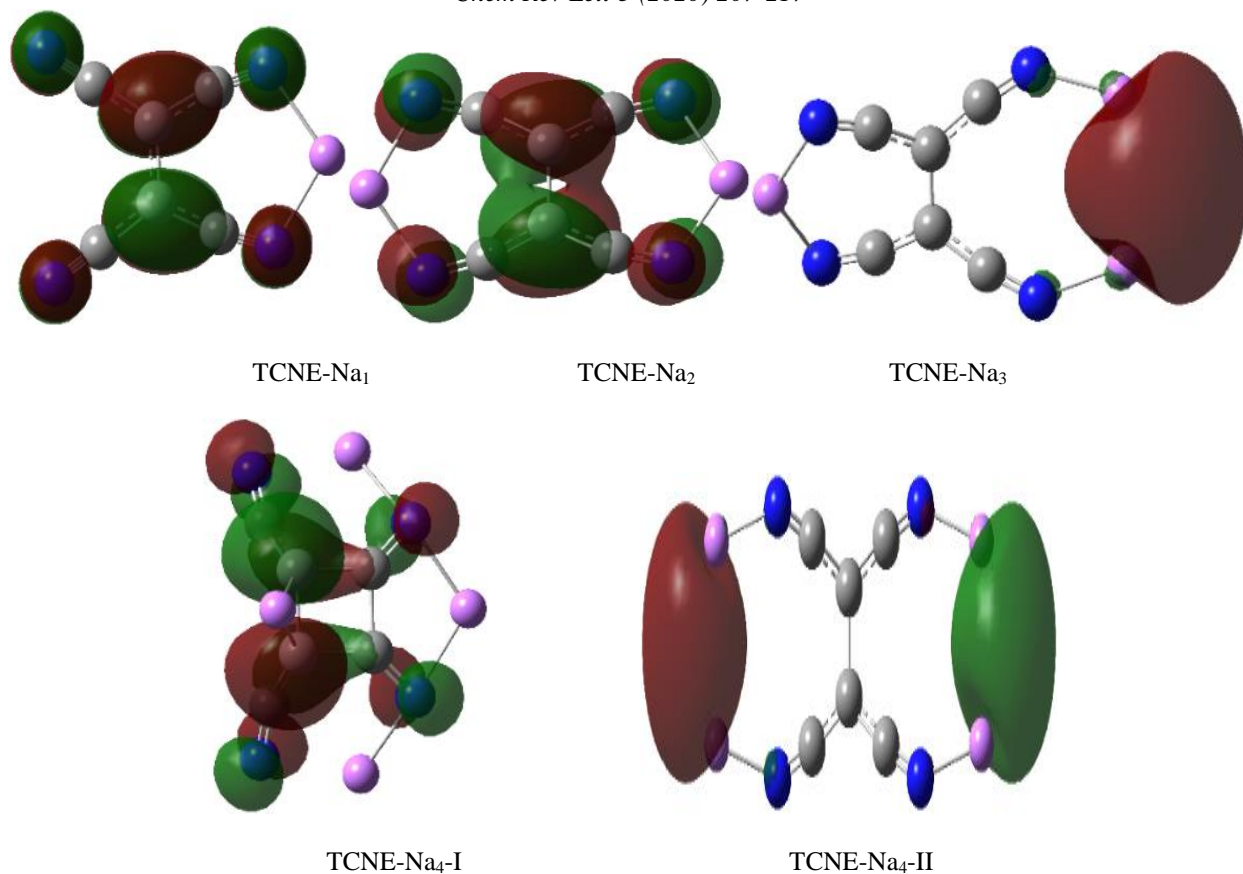


Fig. 2 HOMO distribution in the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems (isosurface=0.03 a.u.).

only in the TCNE- Na_4 -I species. To study thermodynamic stability, we have listed the adsorption energies (E_{ads}) per Na atom for the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems in Table 1. According to Table 1, the range of E_{ads} per Na atom is from -2.26 eV (in the TCNE- Na_2 species) to -1.08 eV (in the TCNE- Na_4 -I species). These big values indicate high thermodynamic stability of the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems. Note that E_{ads} per Na atom in the TCNE- Na_4 -I and the TCNE- Na_4 -II species is -1.08 eV and -1.39 eV, respectively. This means that there is no significant difference between thermodynamic stability of the TCNE- Na_4 -I and the TCNE- Na_4 -II species. In addition to E_{ads} , we have obtained the vertical ionization (E_{VI}) and deformation (E_{d}) energies for the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems to present other aspects of the electronic features. E_{VI} can be used to evaluate the suitability of these species as an electron donor in electron transfer reactions. From Table 1, the smallest value of E_{VI} belongs to the TCNE- Na_4 -I (4.88 eV) and the TCNE- Na_4 -II (5.04 eV) species. Therefore, these two species have the highest ability of electron donor among the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems and these values are comparable with E_{VI} of graphene (4.50 eV) [39] and graphite (4.80 eV) [39] which are used in the anode of Na based batteries. In the next step, we have calculated

deformation energy (E_{d}) of the TCNE backbone due to the addition of Na atoms. Our results show that the TCNE backbone in the TCNE- Na_4 -I species includes severe deformation (4.75 eV) due to addition of four Na atoms. In contrast, the range of E_{d} for other species is from 0.31 eV (in the TCNE- Na_1 species) to 1.83 eV (in the TCNE- Na_4 -II species).

We have listed the energy values of the highest occupied

molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and their corresponding gaps in Table 2 to investigate electrochemical stability of the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems. The range of 5.07 eV-7.72 eV has been found for HOMO-LUMO gap which indicates high electrochemical stability in the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems. Note that HOMO-LUMO gap of the TCNE- Na_3 (5.57 eV) species is comparable with that of the TCNE- Na_4 -II (5.53 eV) species. It is interesting to reveal the distribution of HOMO (Fig. 2) and LUMO (Fig. 3)

in the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems. In the TCNE- Na_1 , the TCNE- Na_2 and the TCNE- Na_4 -I species, the distribution of HOMO is on the TCNE backbone. In contrast, the HOMO of the TCNE- Na_3 and the TCNE-

$\text{Na}_4\text{-II}$ species distributes in the space between Na atoms. Different from HOMO distribution, a similar trend has been found for the distribution of the LUMOs. All LUMOs in the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems are on the Na atoms as shown in Fig. 3.

3.2. Spin density

In the next step, we have focused on spin density distribution of the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems (Fig. 4).

It is necessary to say that the TCNE-Na_1 , TCNE-Na_3 and $\text{TCNE-Na}_4\text{-II}$ species have odd electrons in their electronic structure. Our results present that odd electron of the TCNE-Na_1 species distributes only on the TCNE backbone. In contrast, more addition of Na atoms causes to transfer of odd electrons from the TCNE backbone to the space between Na atoms in the TCNE-Na_3 and the $\text{TCNE-Na}_4\text{-II}$ species.

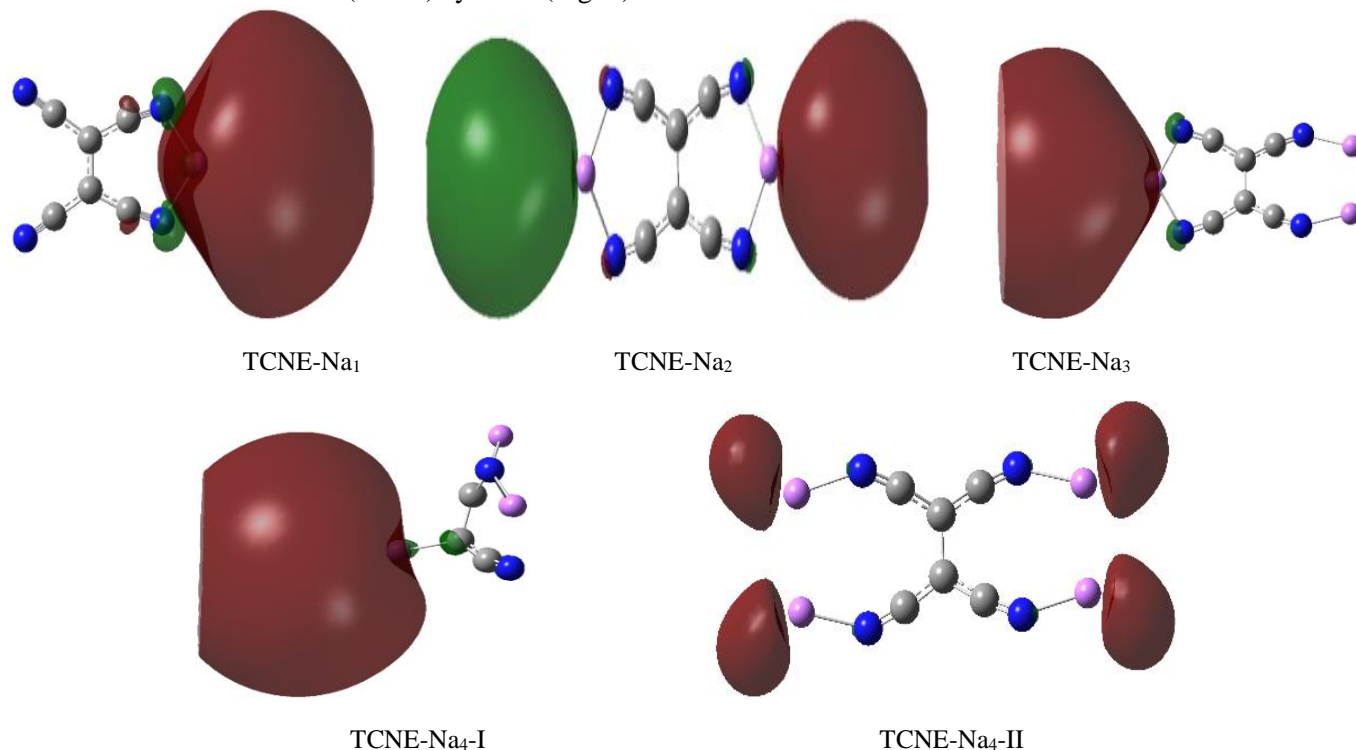


Fig. 3 LUMO distribution in the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems (isosurface=0.01 a.u.).

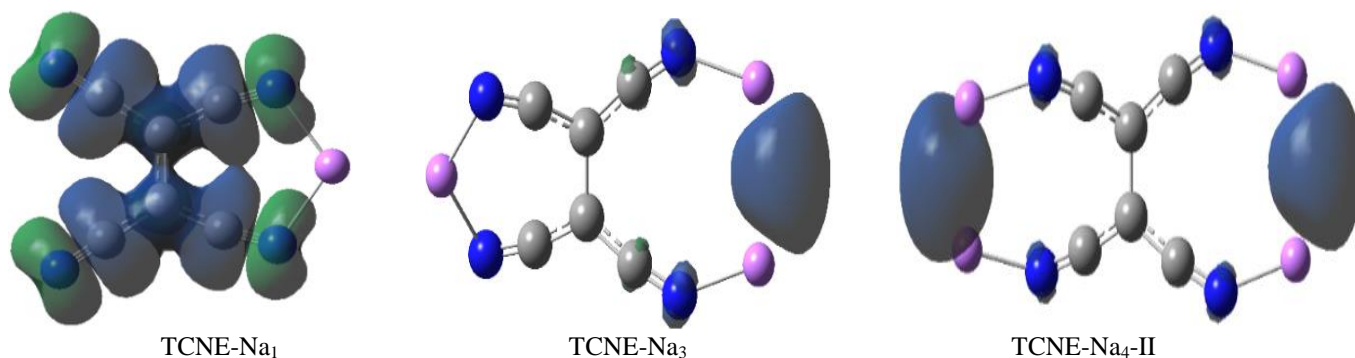


Fig. 4 Spin density distribution in the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems (isosurface=0.004 a.u.).

3.3. Charge transfer

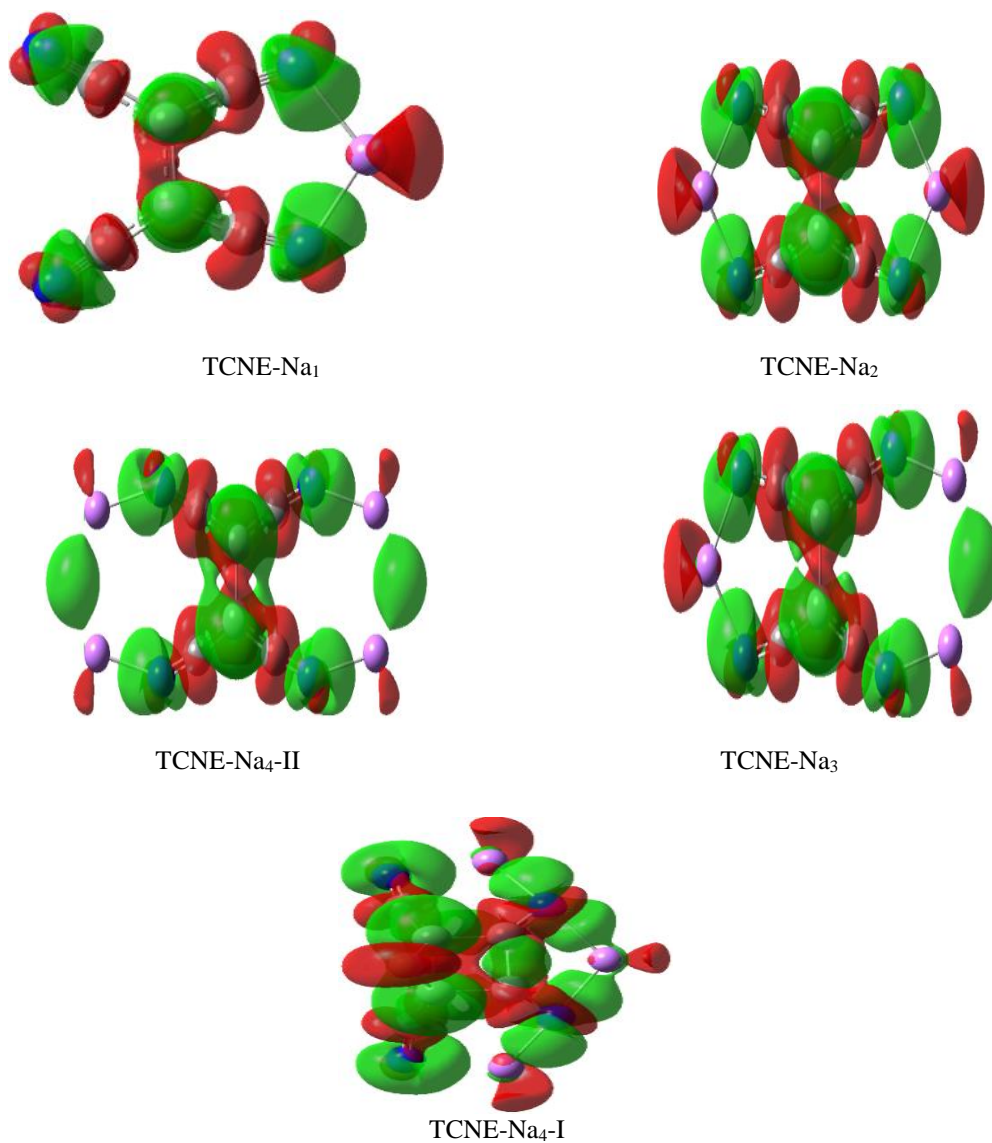
The electron density of both TCNE backbone and Na atoms change due to Na-TCNE interactions in the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems. To the best of our

knowledge, the source of electron density change is charge transfer process. Therefore, the difference map of electron density (Fig. 5) can be used as useful tool to visualize the details of the charge transfer process. We

Table 1. Adsorption energy (E_{ads}) per Li atom, vertical ionization energy (E_{VI}) and deformation energy (E_{d}) for the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems at the MP2/aug-cc-pVDZ computational level.

Species	E_{ads} per Na atom	E_{VI}	E_{d}
TCNE- Na_1	-1.57	5.94	0.31
TCNE- Na_2	-2.26	7.03	1.21
TCNQ- Na_3	-1.68	5.08	1.50
TCNE- Na_4 -I	-1.08	4.88	4.75
TCNQ- Na_4 -II	-1.39	5.04	1.83

All energies are in eV

Fig 5. Difference map of electron density for the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems (isosurface=0.003 a.u.).

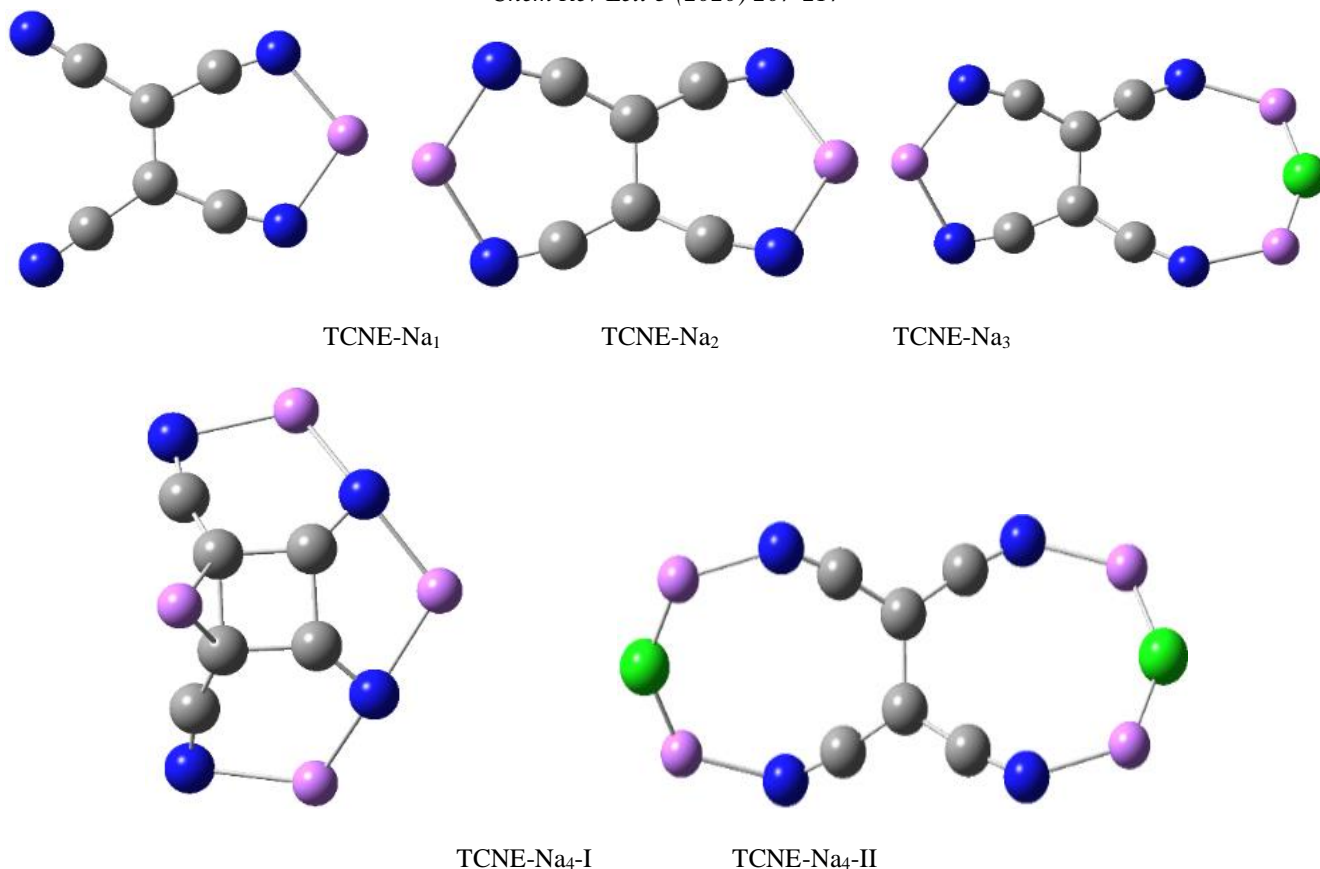


Fig. 6 Position of the center of NNA basins (green basins) in the Na_n@TCNE (n=1-4) systems.

have obtained the difference maps of electron density in Fig. 5 through the difference of electron density between the Na_n@TCNE (n=1-4) systems and its corresponding isolated subunits (the TCNE backbone and Na atoms) in the geometry of the complex. According to Fig. 5, the

green regions (electron increment) have localized mainly on nitrogen atoms and two central carbon atoms in the Na_n@TCNE (n=1-4) systems which confirm the role of electron acceptor for these atoms.

Table 2. HOMO and LUMO energies and the HOMO-LUMO gaps for the Na_n@TCNE (n=1-4) systems.

Species	Set α		Set β		HOMO-LUMO gap
	HOMO energy	LUMO energy	HOMO energy	LUMO energy	
TCNE-Na ₁	-8.24	-0.52	-8.85	-0.52	7.72
TCNE-Na ₂	-6.76	0.24	---	---	7.00
TCNE-Na ₃	-5.26	0.31	-6.92	0.31	5.57
TCNE-Na ₄ -I	-4.95	0.12	---	---	5.07
TCNE-Na ₄ -II	-5.20	0.33	-7.12	0.44	5.53

Italic values have been selected for the calculation of the energy gap between the HOMO and the LUMO. All reported energies are in eV.

In contrast, the localization of red regions on the Na atoms and four side carbon atoms shows electron depletion regions and the role of electron donor in these atoms. Therefore, charge transfer process is from the Na atoms and four side carbon atoms to nitrogen atoms and two central carbon atoms.

3.4. Category: sodium salt vs sodium electricle

The investigation of some electronic properties of the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems in the previous sections such as E_{VI} , distribution of HOMO and spin density indicates that the features of TCNE- Na_3 and the TCNE- Na_4 -II species are somewhat different from the TCNE- Na_1 , TCNE- Na_2 and TCNE- Na_4 -I species. These different features motivated us to categorize the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems using the following four criteria: NNA, ELF, $\nabla^2\rho(r)$ and NLO. At first, the existence of NNA basin has been investigated for all $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems. Note that NNA basin is not a frequent property of electron density and appears only in few species. According to Fig. 6, there are no NNA basin in the TCNE- Na_1 , the TCNE- Na_2 and the TCNE- Na_4 -I species. This means that we can incorporate the TCNE- Na_1 , the TCNE- Na_2 and the TCNE- Na_4 -I species in the category of lithium salts. In contrast, one and two NNA basins appear in the space between Na atoms in the TCNE- Na_3 and the TCNE- Na_4 -II species, respectively. It should be very interesting to determine the electron population in the obtained NNA basins. Based on the calculated results, 0.43 e exists in each of NNA basins of the TCNE- Li_3 and the TCNE- Li_4 -II species. More details regarding NNA basins are in Table 3. Subsequently, three additional criteria: ELF, $\nabla^2\rho(r)$ and NLO have been studied with more details to confirm the presence of isolated electron in the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems. The ELF [30, 31] has been known as a popular descriptor of electron rich regions among computational researchers.

The ELF has been widely used in different systems to confirm electron localization in a covalent bond, a lone pair, etc. Therefore, the detection of ELF basins is a useful tool for the confirmation of isolated electron associated to the electron density NNA basins. Fig. 7 presents the ELF isosurface with 0.80 value. From Fig. 7, the ELF displays a basins (with 0.90 e) in the space between Na atoms for the TCNE- Na_3 and TCNE- Na_4 -II species. This confirms the presence of an isolated electron in the NNA positions. In the next step, we have calculated $\nabla^2\rho(r)$ value in the NNA positions for the TCNE- Na_3 and TCNE- Na_4 -II species. The negative value of $\nabla^2\rho(r)$ (-0.010 a.u) reinforces possibility of electricle material in the TCNE- Na_3 and the TCNE- Na_4 -II species. As fourth criterion, we have investigated the NLO characteristics of the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems through the value calculation of the first hyperpolarizability (β_{total}) which has been shown in Fig. 8. Note that the NLO criterion may only be applicable to the molecular, rather than solid-state, electricle [40]. The β_{total} value of the TCNE- Na_4 -II species (3.02 a.u) is very small. This means that fourth criterion of electricle formation (NLO behavior) has been not fulfilled in the TCNE- Na_4 -II species. Therefore, the TCNE- Na_4 -II species should be incorporated in category of sodium salt. We have calculated the β_{total} value of 4298.5 a.u for the TCNE- Na_3 species which is the biggest value reported for the β_{total} in the present paper. Therefore, four criteria of NNA, ELF, $\nabla^2\rho(r)$ and NLO fulfill in the TCNE- Li_3 species and we can introduce the TCNE- Na_3 species as electricle material in the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems. It is necessary to say that Chen and Manzhos [41] have proposed the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems as promising candidate materials for organic battery electrodes which confirms significant application of $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems.

Table 3. The distance of the sodium atoms to the NNA $|\vec{r}_{(NNA-\text{Na})}|$, the values of the electron density ($\rho(\Omega)$) and the Laplacian of the electron density ($\nabla^2\rho(\Omega)$) at the Ω position, electron population of Ω ($N(\Omega)$), electron localization (LI) and percentage of electron localization (%LI) from the total electron population.

Species	Ω	$ \vec{r}_{(NNA-\text{Na})} $	$\rho(\Omega)$	$\nabla^2\rho(\Omega)$	$N(\Omega)$	LI	%LI
TCNE- Na_3	NNA1	3.42	0.010	-0.004	0.43	0.18	42
TCNE- Na_4 -II	NNA1	3.42	0.010	-0.004	0.43	0.18	42
	NNA2	3.42	0.010	-0.004	0.43	0.18	42

All values are in atomic units.

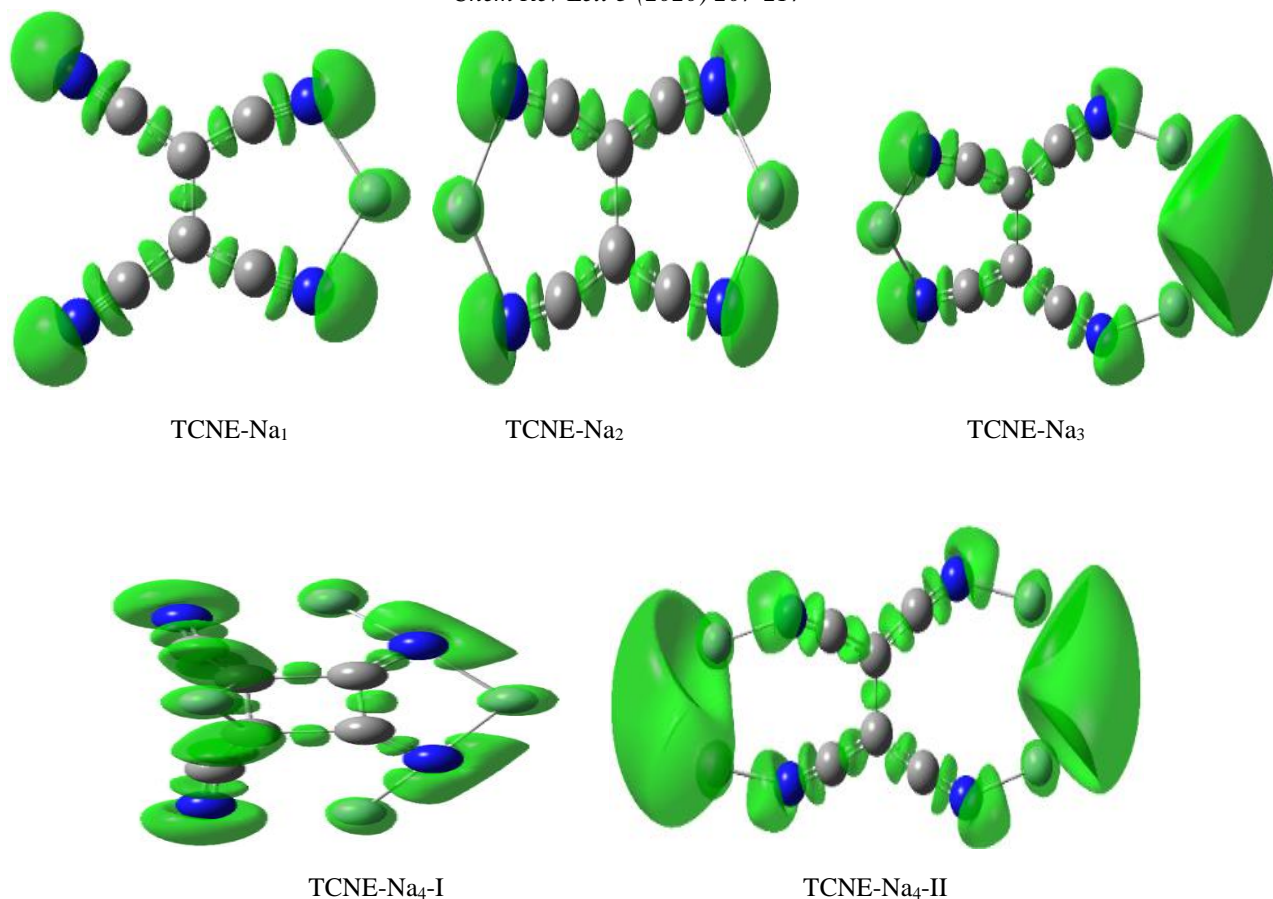


Fig 7. ELF isosurfaces in the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems (isosurface value =0.80)

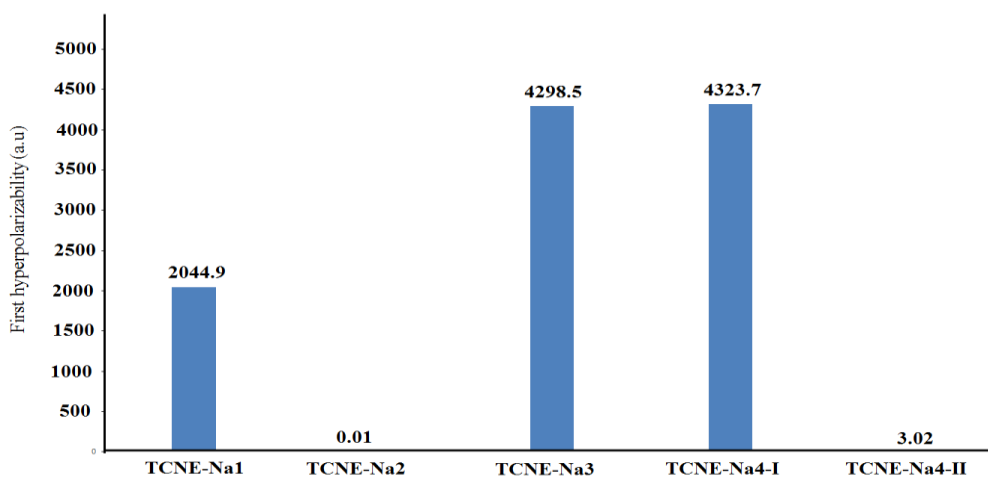


Fig. 8 Value of first hyperpolarizability for the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems.

4. Conclusions

In the present work, we have carried out a computational study based on MP2 method to report the electronic and structural properties of the $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems which includes systematic addition of four Na atoms to TCNE backbone. The obtained results can be summarized as follows:

a) The range of E_{ads} per Na atom is from -2.26 eV to -1.08 eV which presents high thermodynamic stability of $\text{Na}_n\text{@TCNE}$ ($n=1-4$) systems.

b) According to vertical ionization energy (E_{V1}), the smallest values of E_{V1} has been found for the TCNE- Na_3 (5.08 eV) species and the TCNE- $\text{Na}_4\text{-II}$ (5.04 eV) species

and the TCNE-Na₄-I (4.88 eV) species that shows their higher ability for using as source of electron donor.

c) The range of 7.72 eV - 5.07 eV has been found for HOMO-LUMO gap which confirms high electrochemical stability in the Na_n@TCNE (n=1-4) systems.

d) According to the difference map of electron density, Na and N atoms have the role of electron donor and electron acceptor, respectively. In contrast, C atoms can have both roles in the Na_n@TCNE (n=1-4) systems.

e) To classify the Na_n@TCNE (n=1-4) systems in two categories: sodium electride or sodium salt, we have studied four criteria: NNA, ELF, $\nabla^2\rho(r)$ and NLO. Our results show that TCNE-Na₁ and TCNE-Na₂ and TCNE-Na₄ species cannot fulfil simultaneously the four criteria of NNA, ELF, $\nabla^2\rho(r)$ and NLO. In contrast, all four criteria have been fulfilled for TCNE-Na₃ species. This means that the TCNE-Na₃ species can be considered as electride material with the isolated electrons in the space between the Na atoms. Therefore, Na:TCNE ratio is very important factor to provide species with electride property through the addition of Na atom to the TCNE backbone.

References

- [1] E. Zurek, P.P. Edwards, R. Hoffmann, A molecular perspective on lithium–ammonia solutions, *Angew. Chem. Int. Ed* 48 (2009) 8198–8232.
- [2] J.L. Dye, Electrons as Anions, *Science*, 301 (2003) 607–608.
- [3] J.L. Dye, Metal-Ammonia Solutions, *Colloque Weyl II*, Ithaca, New York, 1969; Butterworths, London, 1970, p. 1–17.
- [4] J.L. Dye, M.G. DeBacker, L.M. Dorfman, Pulse Radiolysis Studies. XVIII. Spectrum of the Solvated Electron in the Systems Ethylenediamine–Water and Ammonia–Water, *J. Chem. Phys.* 52 (1970) 6251–6258.
- [5] J.L. Dye, Electrides: Ionic Salts with Electrons as the Anions, *Science*, 247 (1990) 663–668.
- [6] T.A. Kaplan, J.F. Harrison, J.L. Dye, R. Rencsok, Relation of Li(NH₃)₄ to Electrides, *Phys. Rev. Lett.* 75 (1995) 978–978.
- [7] J.L. Dye, Electrides: From 1D Heisenberg Chains to 2D Pseudo-Metals, *Inorg. Chem.* 36 (1997) 3816–3826.
- [8] J.L. Dye, Electrides and alkalides-comparison with metal solutions *J. Phys. IV* 1 (1991) 259–282.
- [9] H. Hosono, Two classes of superconductors discovered in our material research: iron-based high temperature superconductor and electride superconductor, *Physica C* 469 (2009) 314–325.
- [10] S. Watanabe, T. Watanabe, K. Ito, N. Miyakawa, S. Ito, H. Hosono, S. Mikoshiba, Secondary electron emission and glow discharge properties of 12CaO-7Al₂O₃ electride for fluorescent lamp applications, *Sci. Technol. Adv. Mat.* 12 (2011) 034410-034417.
- [11] H. Yanagi, K.-B. Kim, I. Koizumi, M. Kikuchi, H. Hiramatsu, M. Miyakawa, T. Kamiya, M. Hirano, H. Hosono, Low Threshold Voltage and Carrier Injection Properties of Inverted Organic Light-Emitting Diodes with [Ca₂₄Al₂₈O₆₄]⁴⁺(4e⁻) Cathode and Cu_{2-x}Se Anode, *J. Phys. Chem. C* 113 (2009) 18379–18384.
- [12] Y. Toda, H. Hirayama, N. Kuganathan, A. Torrisi, P. V. Sushko, H. Hosono, Activation and splitting of carbon dioxide on the surface of an inorganic electride material, *Nat. Commun.* 4 (2013) 2378–2385.
- [13] M. Kitano, Y. Inoue, Y. Yamazaki, F. Hayashi, S. Kanbara, S. Matsuishi, T. Yokoyama, S.-W. Kim, M. Hara, and H. Hosono, Ammonia synthesis using a stable electride as an electron donor and reversible hydrogen store. *Nat. Chem* 4 (2012) 934–940.
- [14] M. Kitano, S. Kanbara, Y. Inoue, N. Kuganathan, P. V. Sushko, T. Yokoyama, M. Hara, H. Hosono, Electride support boosts nitrogen dissociation over ruthenium catalyst and shifts the bottleneck in ammonia synthesis, *Nat. Commun.* 6 (2015) 6731–6739.
- [15] Y. Lu, J. Li, T. Tada, Y. Toda, S. Ueda, T. Yokoyama, M. Kitano, H. Hosono, Water Durable Electride Y₅Si₃: Electronic Structure and Catalytic Activity for Ammonia Synthesis. *J. Am. Chem. Soc.* 138 (2016) 3970–3973.
- [16] M. Kitano, Y. Inoue, Y. Yamazaki, F. Hayashi, S. Kanbara, S. Matsuishi, T. Yokoyama, S.-W. Kim, M. Hara, H. Hosono, Ammonia synthesis using a stable electride as an electron donor and reversible hydrogen store, *Nat. Chem.* 4 (2012) 934–940.
- [17] H. Buchhammagari, Y. Toda, M. Hirano, H. Hosono, D. Takeuchi, K. Osakada, Room Temperature-Stable Electride as a Synthetic Organic Reagent: Application to Pinacol Coupling Reaction in Aqueous Media *Org. Lett.* 9 (2007) 4287–4289.
- [18] S. Choi, Y. J. Kim, S.M. Kim, J.W. Yang, S.W. Kim, E.J. Cho, Hydrotrifluoromethylation and iodotrifluoromethylation of alkenes and alkynes using an inorganic electride as a radical generator, *Nat. Commun.* 5 (2014) 1038–1046.
- [19] Y.J. Kim, S.M. Kim, H. Hosono, J.W. Yang, S.W. Kim, The scalable pinacol coupling reaction utilizing the inorganic electride [Ca₂N]⁺e⁻ as an electron donor, *Chem. Comm.* 50 (2014) 4791–4794.
- [20] J.L. Dye, Anionic electrons in electrides, *Nature.* 365 (1993) 10–11.
- [21] D.J. Singh, H. Krakauer, C. Haas, W.E. Pickett, Theoretical determination that electrons act as anions in the electride Cs⁺(15-crown-5)₂e⁻, *Nature.* 365 (1993) 39–42.
- [22] J.L. Dye, Electrides: from 1D Heisenberg chains to 2D pseudo-metals, *Inorg. Chem.* 36 (1997) 3816–3826.
- [23] M.-S. Miao, R. Hoffmann, High Pressure Electrides: A Predictive Chemical and Physical Theory, *Acc. Chem. Res.* 47 (2014) 1311–1317.
- [24] S.G. Dale, A. Otero-de-la Roza, E.R. Johnson, Density-functional description of electrides, *Phys. Chem. Chem. Phys.* 16 (2014) 14584–14593.
- [25] M. Garcia-Borra`s, M. Sola`, J.M. Luis, B. Kirtman, Electronic and vibrational nonlinear optical properties of five representative electrides, *J. Chem. Theory Comput.* 8 (2012) 2688–2697.
- [26] W. Chen, Z.-R. Li, D. Wu, Y. Li, C.-C. Sun, F.L. Gu, The Structure and the Large Nonlinear Optical Properties of Li@Calix[4]pyrrole, *J. Am. Chem. Soc.* 127 (2005) 10977–10981.
- [27] Y.-F. Wang, Z.-R. Li, D. Wu, C.-C. Sun, F.-L. Gu, Excess electron is trapped in a large single molecular cage C60F60, *J. Comput. Chem.* 31 (2010) 195–203.
- [28] K. Lee, S.W. Kim, Y. Toda, S. Matsuishi, H. Hosono, Dicalcium nitride as a two-dimensional electride with an anionic electron layer, *Nature.* 494 (2013) 336–340.
- [29] S.G. Dale, A. Otero-de-la Roza, E.R. Johnson, Density-functional description of electrides *Phys. Chem. Chem. Phys.* 16 (2014) 14584–14593.
- [30] A.D. Becke, K.E. Edgecombe, A simple measure of electron localization in atomic and molecular systems *J. Chem. Phys.* 92 (1990) 5397–5403.

- [31] M. Marque's, G.J. Ackland, L.F. Lundegaard, G. Stinton, R.J. Nelmes, M.I. McMahon, Potassium under Pressure: A Pseudobinary Ionic Compound, J. Contreras-García, Phys. Rev. Lett. 103 (2009) 115501-1155014.
- [32] V. Postils, M. Garcia-Borras, M. Sola, J.M. Luis, E. Matito, On the existence and characterization of molecular electrides, Chem. Commun. 51 (2015) 4865-4868.
- [33] O.E. Bakouri, V. Postils, M. Garcia-Borras, M. Duran, J.M. Luis, S. Calvello, A. Soncini, E. Matito, F. Feixas, M. Sola, Metal Cluster Electrides: a new Type of Molecular Electrides with Delocalised Polyattractor Character, Chem. Eur. J. 24 (2018) 9853-9859.
- [34] R.A. Kendall, T.H. Dunning, R.J. Harrison, Electron affinities of the first-row atoms revisited Systematic basis sets and wave functions. J. Chem. Phys 96 (1992) 6796-6806.
- [35] P.P. Edwards, P.A. Anderson, J.M. Thomas, Dissolved Alkali Metals in Zeolites, Acc. Chem. Res. 29 (1996) 23-29.
- [36] M.J. Frisch, et al. Gaussian 09, Revision A.01, Gaussian, Inc., Wallingford CT, 2009.
- [37] T. Lu, F. Chen, Multiwfn: a multifunctional wavefunction analyzer, J. Comput. Chem. 33 (2012) 580-590.
- [38] R.F.W. Bader In: Halpen J, Green MLH (Eds) The international series of monographs of chemistry, Clarendon Press, Oxford (1990).
- [39] I.K. Petrushenko, DFT Study on adiabatic and vertical ionization potentials of graphene sheets, Advances in Materials Science and Engineering, 2015 (2015) 1-7. DOI:10.1155/2015/262513.
- [40] S.G. Dale, E.R. Johnson, Theoretical descriptors of electrides, J. Phys. Chem. A, 122 (2018) 9371-9391.
- [41] Y. Chen, S. Manzhos, A computational study of lithium interaction with tetracyanoethylene (TCNE) and tetracyanquinodimethane (TCNQ) molecules, Phys. Chem. Chem. Phys. 18 (2016) 1470-1477.

How to Cite This Article

Navid Salehi; Esmail Vessally; Ibadan Edjlali; Ibon Alkorta; Moosa Eshaghi. "Nan@Tetracyanoethylene (n=1-4) systems: Sodium salt vs Sodium electride". Chemical Review and Letters, **3**, 2020, 207-217. doi: 10.22034/crl.2020.230543.1056