Theoretical Investigation on Structures and Nonlinear Optical Properties of the Alkalis and Low Coordination Acenes Salt

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Summary: The alkalis and low coordination acenes salts α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) were designed to investigate the effect of the increasing atomic number of alkali metals and the number n of conjugated benzenoid rings on the nonlinear optical responses. Alkalis Li, Na and K were selected herein, and both DFT (M05-2X, M06-2X and PBE0) and MP2 methods and 6-311+G(D) basis set are employed to optimize geometrical structures and to calculate the polarizability ($α_0$) and first hyperpolarizability ($β_{vec}$) of the α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3). Results show that the $α_0$ values of α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) increase with increasing number of n conjugated benzenoid rings and the atomic number of alkali metals and $β_{vec}$ values of α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) are opposite. The $β_{vec}$ values of α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) are inceasing remarkably (397.6 au. for α-Li@ benzene < 1196.5 au. for α-Na@benzene < 1608.6 au. for α-K@benzene and tending to decease with increasing number of n by M06-2X method. Our present research may be favorable to the development of excellent nonlinear optical (NLO) materials.

Keywords: α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3); Nonlinear optical properties; First hyperpolarizability; Theoretical Investigation; Polarizability; Interaction energy.

Introduction

Materials with nonlinear optical (NLO) characteristic [1] have been developed rapidly owing to their widespread applications research and development and optical communications improvement. Different types of unexceptionable NLO materials have been widely reported [2] and theoretical investigation plays a significant role in finding approaches to improve nonlinear optical response.[3] Under the influence of these effective ways the strength of donors and receptors were enhanced, π-electron systems were twisted, push-pull effects were increased, bond lengths were alternated (BLA), metals were doped into organic compounds, and the length of π conjugations were widened.[4] Some organic compounds which have extended π-delocalized systems have been paid close attention because of their low cost, feasibility of fabrication and so on. of improvement extremely recently.[5-8] In 2000, the lithiation effects of the conjugated benzenoid rings on the second hyperpolarizability were investigated first by Papadopoulos *et al*.[6] The results show that lithiation of the conjugated benzenoid rings with small planar π conjugation leads to a tremendous enhancement of the second hyperpolarizability. Further, the lithiation effects on the first hyperpolarizability of tubiform [5] cyclacenes with tubular π conjugation were investigated by Li's group [7] in 2009. Obviously, the first hyperpolarizability

was significantly increased about 1200 times from [5]cyclacenes to Li_5-[5]cyclacenes ascribed to the lithiation effect. Thus, the lithiation effect can remarkably increase the nonlinear optical response of π-conjugated systems. In 2011 the relationship between the first hyperpolarizability and the of the conjugated benzenoid rings number of Li@n-Acenes Salt (n =1, 2, 3, and 4) was studied by Cui-Cui Zhang.[9] The results revealed that the tot values for α-Li@n-acenes are slowly decreasing with increasing number n of conjugated benzenoid rings.

Since there are interesting effects of Li to the conjugated benzenoid rings we had like to know what will Na and K ions do in the similar systems, and what regulations can be found for such potential nonlinear optical materials. Inspired by the information above, the α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) were designed to research the nonlinear optical responses to acquire different alkali metals doped NLO molecules. The α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) were formed by a Li(or Na and K) atom substituting α-H. We are interested in the changing polarizability and first hyperpolarizability on changing the element of alkali metals and increasing the number n of conjugated benzenoid rings. Some useful regulations have been found in the paper herein.

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Computational Details

The geometrical structures of the α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3) were optimized by using the B3LYP/6-311+g(d) level.[10] The level is sufficient to optimize the structures of the α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3), and the geometric parameters are listed in Table-1. Li@benzene was taken as an example to test the basis set, and the results were reliable. We use ab initio MP2 and DFT (M06-2X, M05-2X and PBE0) together with FF to analyze their nonlinear optical characteristics. However, the MP2[11] method is a dependable method compared with B3LYP, but it is resources and time consuming. It was lucky that the results of the DFT methods M05-2X, M06-2X and PBE0 together with FF are similar to those of the MP2 results. M05-2X is a new kind of density functional which is proposed by Zhao and Truhlar and can be used well to describe medium-range correlations and is satisfactory for some organic compounds research.[12] Zhao and Truhlar have recently developed the M06 family of local hybrid (M06, M06-2X)that how promising performance for studying main group elements themochemistry, kinetics ,noncovalent interactions, excited states, and

transition elements.[13] Meanwhile, PBE0 is the 1996 gradient-corrected correlation functional of Perdew, Burke and Ernzerh.[14] Most calculations using the MP2, M05-2X and PBE0 were carried out with the Gaussian 09 program package,[15] whereas the NBO (natural bond orbit) analysis was performed by the Gaussian 03 program package.[16] The dipole moment (μ_0) and polarizability (α_0) are expressed as follows.

$$\mu_0 = \left(\mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2\right)^{\frac{1}{2}} \quad (1)$$

$$\alpha_0 = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \quad (2)$$

We use ab initio (i.e. MP2) DFT (M05-2X, M06-2X and PBE0 together with FF (Finite Field Method)) to analyze their nonlinear optical characteristics. FF means the finite field method, in which E is the energy of the molecule system and μ_i is the total dipole moment, and they can be represented by the following two Taylor expansions [17,18]:

Table-1: Symmetry (PG), Energy (HF), Geometrical parameters (bond length and bond angle) and NBO charge distribution of α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3)

System	PG	HF(eV)	Bond length(Å)	Bond angle θ(deg)	NBO(C)	NBO(M) Q(X)/e
1a-Li	C_{2v}	-6507.6	1.958[1],1.958[2],1.958[3]	122.9[1],122.9[2],122.9[3]	-0.649	0.897
1a-Na	C_{2v}	-10719.1	2.297[1]	122.4[1]	-0.574	0.886
1a-K	C_{2v}	-22626.8	2.715[1]	122.9[1]	-0.562	0.921
2a-Li	C_s	-10688.7	1.975[1]	121.0[1]	-0.597	0.894
2a-Na	C_s	-14900.1	2.309[1]	122.6[1]	-0.524	0.888
2a-K	C_s	-26807.9	2.719[1]	119.0[1]	-0.511	0.922
3a-Li	C_s	-14869.5	1.974[1]	120.6[1]	-0.590	0.897
3a-Na	C_s	-19084.1	2.314[1]	121.7[1]	-0.518	0.890
3a-K	C_s	-30992.8	2.663[1]	116.4[1]	-0.906	0.924

Note: C⁻ refers to the carbon atom combined with M (alkali metal atmos: Li, Na and K), on which the value means NBO charge distribution.1.B3LYP /6-311+g(d) method ;2.MP2/6-311+g(d) method ; 3.MP2 method with which the basis set of C and H atoms are 6-311+g(d) and the basis set of Li is 6-311+g(3df)

$$E(F) = E^0 - \sum_i \mu_i^0 F_i - 1/2 \sum_{ij} \alpha_{ij} F_i F_j - 1/3 \sum_{ijk} \beta_{ijk} F_i F_j F_K - 1/4 \sum_{ijkl} \gamma_{ijkl} F_i F_j F_k F_l + \Lambda \quad (3)$$

$$\mu_i(F) = \mu_i^0 + \sum_j \alpha_{ij} F_j + \sum_{jk} \beta_{ijk} F_j F_k + \sum_{jkl} \gamma_{ijkl} F_i F_j F_k F_l + \Lambda \quad (4)$$

where E^0 is the energy of the molecule in the absence of an electric field, μ_i is its permanent dipole moment, α_{ij} is the dipole polarizability, and β_{ijk} and γ_{ijkl} are the first and second hyperpolar-izablities, respectively. As implied by this, the polarizabilities can be computed by employing derivatives of the energy or dipole moment with respect to the incident electric

field. Tocomputethe polarizability and hyperpolarizability, one option is to take the derivates either analytically or numerically. In the present work, we have investigated the difference between analytical derivative methods and FF Method in order to get better results of systems selected.

The static first hyperpolarizability β_{vec} was calculated by M06-2X Method combined with FF(finite field method), which is more efficient and less expensive than other methods compared with, where β_{vec} represent the hyperpolarizability along the molecular dipole moment defined as follows:

$$\beta_{vec} = \sum_{i=x,y,z} \frac{\mu_i \beta_i}{|\mu|} \qquad (5)$$

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{j \neq i}\left(\beta_{ijj} + \beta_{jij} + \beta_{jji}\right) \qquad (6)$$

Results and Discussion

Geometrical Parameters

The optimized structures of α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3) are named as 1a-Li, 2a-Li and 3a-Li in *α*-Li@*n*-acences system, and 2a-Li, 2a-Na and 2a-K belong to α-Na@*n*-acences and α-K@*n*-acences systems, (as shown in

Fig. 1) The parameters of structures of the α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3) are listed in Table-1. From Table-1, noticeably, the C-Li bond lengths of α-Li@*n*-acenes are from 1.958 Å to 1.975 Å, and the changes of C-Li bond lengths are more slightly than those of α-Na@*n*-acences and α-K@*n*-acences (C-Na: from 2.297 Å to 2.309 Å, C-K: from 2.715 Å to 2.719 Å) in which the number n of conjugated benzenoid rings is from 1 to 3, and bond lengths of C-M (M=Li, Na and K) become larger when the number n is increased according to the same alkali metal atom. We can see that bond lengths of C-M (M=Li, Na and K) become larger and larger from Li to K when n is equal in different system, which is consistent with atom radiuses of Li, Na and K. Interestingly, the C-Li bond lengths of α-Li@*n*-acenes salts all increase with increasing number n, and the adding of the conjugated effect obviously increases the C-Li bond lengths than others.
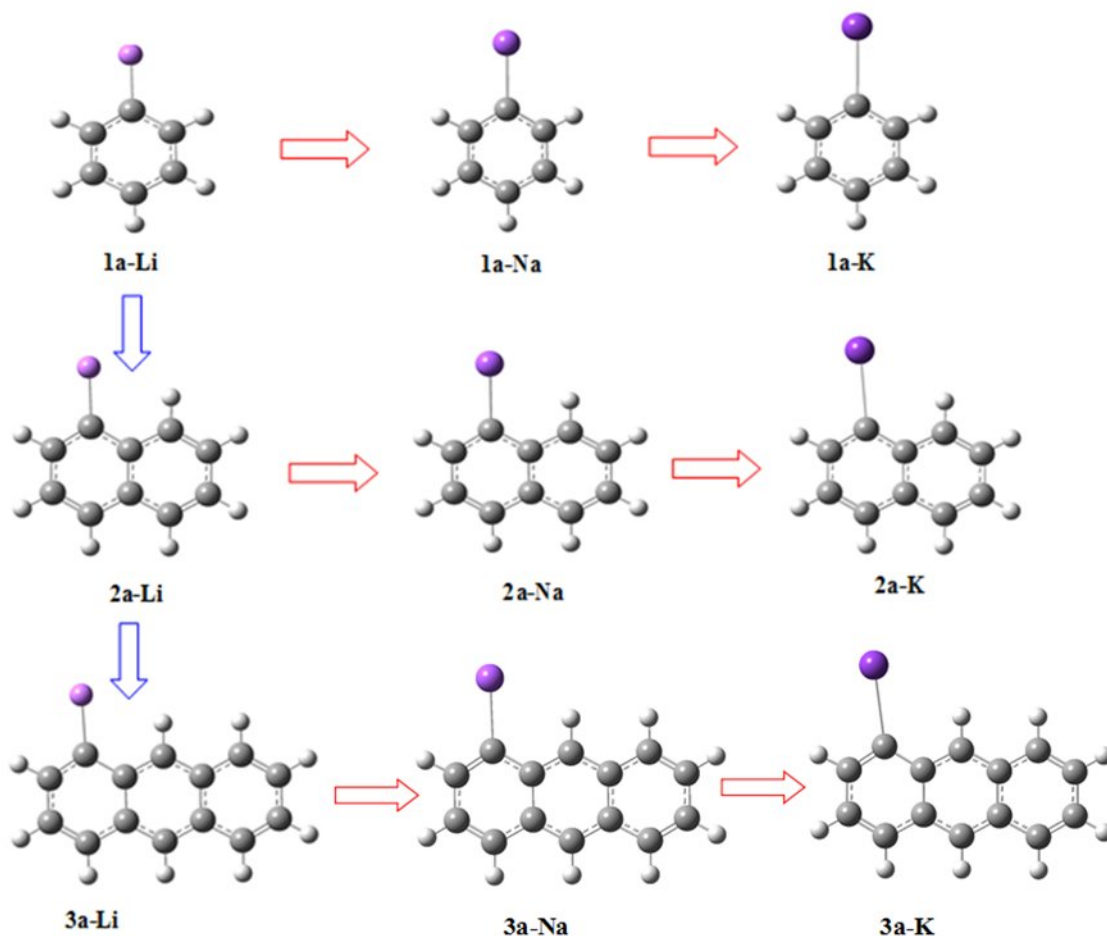

Fig. 1:   Optimized structures of α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3).

From Fig. 2, the bond angles which are formed by the Li(K)-C-C atoms are expressed as θ. On the contrary we can see from the C-Li bond lengths that the θ values decrease with increasing number n, while the values of bond angle which are formed by the Na-C-C atoms increases with increasing number n. Also, the θ values, 122.9 degree formed by the Li (K)-C-C atoms which is somewhat larger than that formed by the Na-C-C atoms 122.4 degree when the number n is equal to 1, but the opposite result appears when n is equal to 2.
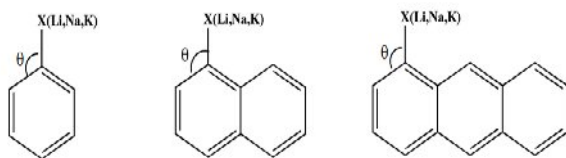

Fig. 2:   Diagram of Bond angle of α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3).

The natural bond orbit (NBO) charges of C⁻ combined with alkali metal atom, Li⁺, Na⁺, K⁺ are acquired by the B3LYP method. NBO charge of α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3) alkalis ions are larger on Li⁺ to K⁺ than that on Na⁺, and the values of NBO charge exceeds +0.886 on all alkalis ions, which indicates that α-M@n-acenes (M=Li, Na and K) are new type alkalis salts, especially on K⁺ ion where the NBO charge value is over +0.920. The variation ranges of the C-Na bond properties and the NBO charge are very small, while which of C-K (Li) are varying in relatively obvious ranges.

Optical Characteristic

Linear Optical Characteristic Dipole Moment(μ_0)

The μ_0 values of α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3) were computed with B3LYP method, which are in detail listed in Table-2. From Table-2 in α-Li@*n*-acences system μ_0 values are 0.86, 1.05 and 1.11 a.u., respectively. The same changing tend can be found in α-Na@*n*-acenes salts which μ_0 values are and 0.86, 0.93 and 1.24 a.u., and in α-K@*n*-acenes salts with μ_0 values 1.05, 1.58 and 1.81 a.u., respectively. The μ_0 values increase with increasing number n in α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3) system, and interestingly the same regulation can be found in them when the number n is equal according to the different alkali metal atoms from Li to K. Properties of α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3) are

together affected by adding the conjugated benzenoid rings and different alkali metal atoms with different losing electron feasibility and atomic radius, which also obviously increases μ_0 values when losing electron feasibility and atomic radius of alkali metals increase μ_0 values are increase correspondingly.

Linear Optical Characteristic Polarizability (α_0)

The polarizability (α_0) of α-Li@*n*-acenes was calculated by using MP2, PBE0, M06-2X and M05-2X methods and the results were listed in Table-2. α_0 values of α-Li@*n*-acenes are uniformly uptrended. The α_0 values acquired by the three methods above are enhancive with the increasing number n. The M05-2X α_0 values are highest and the PBE0 α_0 values are lowest while the MP2 α_0 values are middle among these α_0 values, and the α_0 values by M06-2X method are close to those by MP2 method. After all the three methods were compared for α_0 values, we found that M06-2X and PBE0 α_0 values are in good consistent regularity with MP2 does. Yet, the α_0 values acquired by M06-2X methods are very consistent with that obtained by the MP2 and the method M06-2X are better computing time and resources saving than MP2 does, therefore we choose the two methods to perform all calculations for α_0. Furthermore, taking M06-2X as an example to compare the α_0 values of α-Li@*n*-acenes, α_0 values (81.8 a.u. to 188.2 a.u.) increase when the number n increases, and in α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3) system α_0 values (81.8 a.u. to 97.4 a.u.) increase when the number n is equal to 1 similar regularity when the number n is equal to 2 with α_0 values from 119.2 a.u. to 134.1 a.u. in α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3) when atoms are from Li to K. We can see from Table-2 that α_0 values increase when n increases as far as the same alkalis ion is concerned.

Nonlinear Optical Characteristic First Hyperpolarizability (β_{vec}) in Static State

First hyperpolarizability (β_{vec}) values in static state of α-Li@*n*-acenes acquired from different methods are listed in detail in Table-2. Interestingly, Table-2 reveals that the β_{vec} values of α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3) are not changed dramaticlly with increasing number n, and the β_{vec} values are the largest ones when n is equal to 2, while β_{vec} values increase obviously when the number n is equal and when atoms are from Li to K. From Table-2, the β_{vec} values acquired by the PBE0 method are the largest ones compared with the other

two methods. The PBE0 method sometimes overestimates the β_{vec} values, and the method of M06-2X exhibits similar β_{vec} values and it reproduces the MP2 results for the α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3). As a comparison, M05-2X method is also performed to get a kind of β_{vec} values, but the results from which are not regular as PBE0 and not close to those from MP2. Therefore, the MP2, M06-2X methods are in good compromise situation for their quality and efficiency in calculations of polarizability and hyperpolarizability, but M06-2X method is better computing time and resources saving than MP2 does, therefore we choose the M06-2X and PBE0 methods to perform all calculations for β_{vec} because the results from PBE0 method reveals the same regularity and changing tend with M06-2X method. We can see from Table-2 that the β_{vec} values of α-Li@n-acenes reduce slowly from 397.6 a.u. for α-Li@benzene to 407.8 a.u. when the number n is changed from 1 to 2 at the same time, and which is decreases to 331.2 a.u. when n is equal to 3, which is consistent with geometrical parameters such as bond length and bond angle, and it might be the warping induced by large anthrecene molecule with the M06-2X method. On the contrary, from Table-2 the β_{vec} values of α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) are significantly enhanced when atoms are from Li to K at different methods from 397.6 a.u. to 1608.6 a.u., and the β_{vec} values are more and more larger contrasted to α-Li@n-acenes because the feasibility of losing electron increases from Li to K. The orders of the β_{vec} values in the α-Na@n-acenes and those of the β_{vec} values of α-K@n-acenes are concordant. As is shown in the above discussion, the β_{vec} values of α-Li@n-acenes salt have been overestimated by the PBE0 method. The M06-2X method acquired the extremely close β_{vec} values compared with the MP2 result, whereas the β_{vec} values acquired by the M06-2X method are smaller than those of the other methods. Comparing these β_{vec} values from different methods shows amazing

variation trends as is shown in Table-2. Thus, the β_{vec} values of α-Li@n-acenes (by the reliable M06-2X method) are reducing and the β_{vec} values of α-Na(K)@n-acenes are increasing with the increasing number n. The data from Table-2 reveals that the α_0 values and β_{vec} values show remarkable specialties of the α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3). Thus, all the α_0 values and β_{vec} values are likely about to the structure of α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3). On the basis of the two-level formula, [19] the first hyperpolarizability is mainly affected by the transition energy, and it can interpret the relationship between components and composing structures with nonlinear optical property.[9] To further understand the first hyperpolarizability, the transition energies of α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) were computed by the TD-PBE0 method and the results of which are listed in Table-3.

$$\beta_0 \propto \frac{\Delta\mu_{eg} \bullet f_{eg}}{\Delta E_{eg}^3} \qquad (7)$$

where $\Delta\mu_{eg} = \Delta\mu_e - \Delta\mu_g$, which means the difference value of dipole moments between the basic state and the excited state, ΔE_{eg} refers to the transition energy, and f_{eg} refers to the oscillator strength. From Formula (4) we can see β_{vec} values are in proportion to the oscillator strength f_{eg} and in inverse proportion to the cube of ΔE_{eg}. Theoretical research indicates that PBE0 method can obtain much reliable prediction of the transition energy.[20]

Table-2: Dipole moment (μ_0), polarizability (α_0)and Static First Hyperpolarizability (β_{vec}) at Different Levels of α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3)

System	μ_0(a.u.)	α_0(a.u.)				β_{vec}(a.u.)				
1a-Li	0.86	79.6[a]	83.3[b]	81.8[c]	82.4[d]	379.0[a]	450.4[b]	397.6[c1]	381.4[c2]	399.5[d]
1a-Na	0.93	95.6[a]	102.0[b]	94.0[c]		1291.9[a]	1633.5[b]	1196.5[c]		
1a-K	1.24	97.3[a]	109.8[b]	97.4[c]		2103.1[a]	3637.9[b]	1608.6[c]		
2a-Li	1.05	129.3[a]	131.6[b]	119.2[c]		287.6[a]	332.8[b]	407.8[c]		
2a-Na	1.13	141.8[a]	149.2[b]	141.0[c]		1093.5[a]	1508.6[b]	1001.7[c]888		
2a-K	1.58	145.4[a]	155.8[b]	134.1		1699.1[a]	2765.4[b]	1606.4[c]		
3a-Li	1.11	187.0[a]	193.0[b]	188.2[c]		329.8[a]	389.1[b]	331.2[c]		
3a-Na	1.22	198.6[a]	198.5[b]	197.8[c]		1151.5[a]	1148.6[b]	1035.9[c]		
3a-K	1.81	200.7[a]	215.3[b]	188.5[c]cc[c]cc		1241.7[a]	2638.0[b]	1445.9[c]		

a. M05-2X method; b. PBE0 method; c1.M06-2X; c2.Analytical derivative method; d. MP2 method

Table-3: Transition energy ΔE_{eg} and oscillator strength f_{eg} and correspongding dominant molecular orbital(MO) tran sitions of α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3)

System	ΔE_{eg}	f_{eg}	main assignments (coefficient)
1a-Li	6.88	0.3311	HOMO-2→LUMO+8(44%) HOMO-3→LUMO+7(30%)
1a-Na	6.80	0.4940	HOMO-2→LUMO+9(36%) HOMO-1→LUMO+7(20%)
1a-K	6.74	0.5222	HOMO→LUMO+14(19%) HOMO-2→LUMO+9(43%) HOMO-1→LUMO+8(19%)
2a-Li	5.87	0.5096	HOMO→LUMO+11(23%) HOMO-2→LUMO+1(13%)
2a-Na	5.75	0.6309	HOMO-2→LUMO+1(24%) HOMO→LUMO+6(17%)
2a-K	5.71	0.4156	HOMO→LUMO+16(23%) HOMO→LUMO+15(22%)
3a-Li	5.10	0.9210	HOMO-2→LUMO+14(17%) HOMO→LUMO+9(27%) HOMO-2→LUMO+1 (17%)
3a-Na	5.12	1.23	HOMO-2→LUMO+1(24%) HOMO→LUMO+4(22%)
3a-K	5.02	1.383	HOMO-2→LUMO+1(31%) HOMO→LUMO+6(24%)

The ΔE_{eg} values show an decreasing trend for α-Li@n-acenes (6.88 eV >5.87 eV >5.10 eV) with the increasing number n and a decreasing trend of ΔE_{eg} values for α-M@n-acenes (M = Li, Na and K) salts (n = 1) (6.88>6.80>6.74 eV) when the number n is equal with the metal atoms are changed from Li to K from Table-3. Thus, the ΔE_{eg} values of α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) are decreasing with the increasing number n, which is inconsistent with the increasing alkali metal atomic number from Li to K. From corresponding β_{vec} values of α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) we can see the results are coincident with Formula (4), which can interpret well why in α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) system β_{vec} values decrease with the increasing number n and in α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) system β_{vec} values increase with the increasing alkali metal atomic number from Li to K. Therefore, systems selected herein, α-H on benzenoid rings substituted by alkali metals with more feasibility of losing electron atoms which can gain more stronger nonlinear optical response in α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) system.

Electronic Transition

It is well-known that the frontier molecular orbits (FMOs) and HOMO-LUMO gaps (Eg) are heavily related to the optical and electronic properties. An electronic excitation results electron density redistribution that affects the molecular geometry.[21] To gain insight into the influence of the optical and electronic properties, the distributions of the FMOs in α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) are investigated, and their sketches are plotted in Fig. 3. The FMOs transition energies from EHOMO to ELUMO, ΔE_{eg}, and HOMOs and LUMOs contributions of individual fragments (in %) to the FMOs of α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) using the TD-PBE0/6-311+G(D) method are given in Table-3. The major assignment of the lowest electronic transitions for α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) are basically HOMO (0,-2) →LUMO and HOMO →LUMO (+1 to +16), while the corresponding lowest electronic transitions for α-Li @n-acenes salts are mainly HOMOs (-2, 0) →LUMOs (+8 to +11). The lowest electronic transitions for α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) correspond to a σ-π* excited singlet state as visualized in Fig. 3. In α-Li @1-acene salt, in HOMO-2，electronic cloud concentrates on benzenoid ring, while in LUMO+8 electronic cloud concentrates on benzenoid ring and α-Li, which indicates charge has been transferred from benzenoid ring to α-Li. For α-Li@2-acenes salt the HOMO is mainly composed of contributions of benzenoid rings at HOMO fragments, with major contributions to the whole molecule in LUMO+11, but the electronic cloud is more on conjugated benzenoid rings than that on α-Li. As to α-Li@3-acenes salt, in HOMO, electronic cloud distributes on conjugated benzenoid rings equally, while LUMO+11, electronic cloud distributes on the whole molecule unequally, and it is minor on the benzenoid ring combined with α-Li. In compare of the three systems, we can see that the largest transiting distance is in α-Li @1-acene salt, which might be the right reason for its maximum first hyperpolarizability β_{vec} value. In α-Na(K)@n-acenes salt systems , when n is equal to 1 in HOMO-2 orbit, the electronic cloud concentrates on benzenoid rings, while in LUMO+8 orbit the electronic cloud decentralizes on α-Li and

benzenoid rings which reveals that there is charge transfer from benzenoid rings to α-Li. In α-Na@1-acenes salt system in HOMO-2 orbit, the electronic cloud totally concentrates on benzenoid ring in average from the right side to the left side by a line via α-Na atom, while in LUMO-9 orbit the electronic cloud averages on the whole benzenoid ring shared by every carbon atom. The same electron transition phenomenon appears in α-K@1-acenes salt, and the maximum electronic cloud concentrates on C-K bond, therefore the obvious charge transition occurs there.

   Comparison of the three systems, we can see the transferring distance in α-K@1-acenes salt is longer than the other two, which maybe the fundamental reason for its larger first hyperpolarizability β_{vec} values. In α-Na(K)@*n*-acenes salt systems , when n is equal to 2 in α-Li@2-acene salt the electronic density totally concentrates on conjugated benzenoid rings in HOMO orbit, while the electronic density decentralizes on the whole system in LUMO+11 orbit which is somewhat more on the conjugated benzenoid rings than that of other parts of the complex, which indicates that charge has been transferred from conjugated benzenoid rings to α-Li. As to α-Na@2-acenes salt system in HOMO-2 orbit the electronic density totally concentrates on conjugated benzenoid rings in three parts equally and vertically, while in LUMO+1 orbit the electronic cloud decentralizes on the conjugated benzenoid

rings in average, which reveals that there is no obvious charge transition. From the electron transiting Fig we can see that in HOMO orbit the electron density concentrates on α-K and its combining conjugated benzenoid ring in α-K@2-acenes salt, while in LUMO+16 orbit, the electronic cloud are almost concentrated on α-K, but there is very little of which on the conjugated benzenoid rings. Comparison of the three systems, we can see the transferring distance in α-K@2-acenes salt is longer than the other two, which maybe the fundamental reason for its larger first hyperpolarizability β_{vec} values. In α-Na@3-acenes salt system in HOMO-2 orbit the electronic density totally concentrates on conjugated benzenoid rings in three parts equally and vertically, while in LUMO+1 orbit the electronic cloud decentralizes on the conjugated benzenoid rings in average, which reveals that there is no obvious charge transition. It is interesting that the distribution of electronic cloud in α-K@3-acenes salt system is similar to that of α-Na@3-acenes salt system, and the percentage of orbits is nearly the same, too. From Fig. 3 we can see that with the increasing atomic number of alkali metal atom, the radius of which increases and the feasibility of losing electron increases also, therefore, the electronic cloud is easy to be polarized, which maybe the right reason for its increasing first hyperpolarizability β_{vec} values.
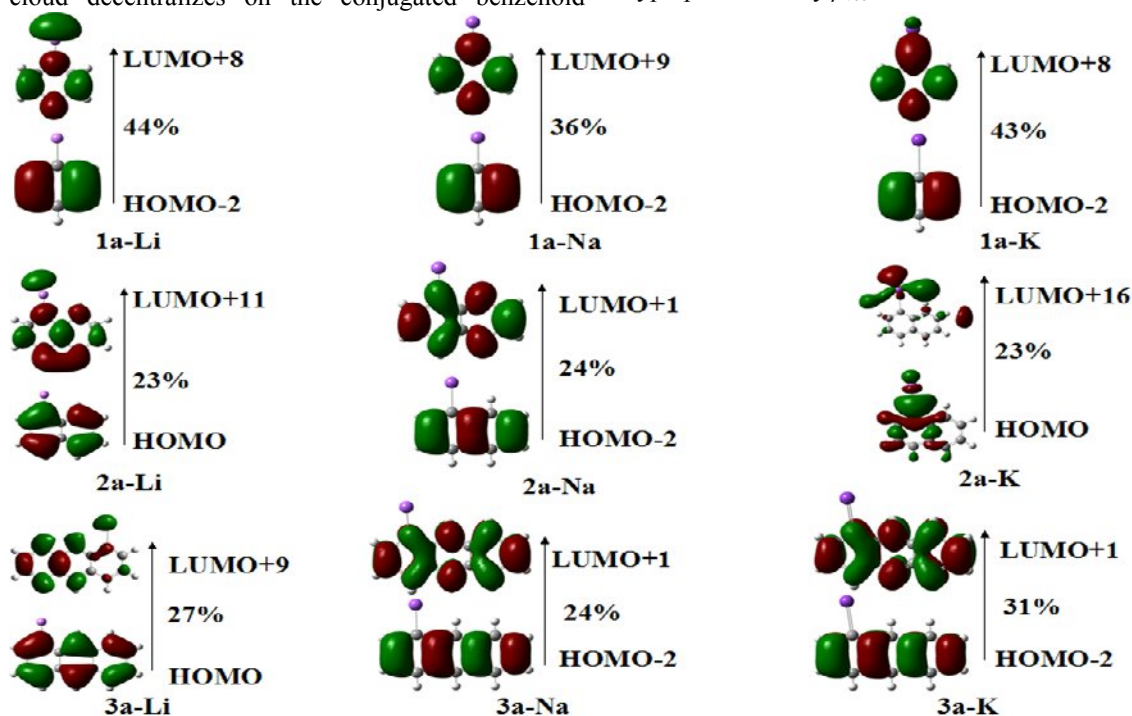

Fig. 3:   The frontier molecular orbitals of α-M@*n*-acenes (M = Li, Na and K) salts (*n* = 1, 2 and 3) involved in the dominant electron transitions.

Conclusion

Three computational methods CAM-B3LYP, M05-2X, M06-2X and PBE0 have been used to calculate the nonlinear optical property of α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) alkali metal salts, among which we get the relationship between their structures and the first hyperpolarizability β_{vec} values as follows: With the increasing of the number n, the β_{vec} values of α-Li@n-acence reveal the tend of decreasing. But when the n is equal, with the increasing of the atomic number of alkali metal atoms which substitutes the α-H and the increasing feasibility of losing electron, the values of the first hyperpolarizability β_{vec} are increasing dramatically in α-Na(K)@n-acenes alkali metal salts, therefore the change regulation of the values of the first hyperpolarizability β_{vec} are opposite in α-Li@n-acence and in α-Na(K)@n-acenes alkali metal salts. The values of the first hyperpolarizability β_{vec} and their corresponding transition energy ΔE_{eg} in α-Li@n-acence salts are not coincident with the simple two-level energy formula, while in α-Na(K)@n-acenes alkali metal salts the values of the first hyperpolarizability β_{vec} are in good relationship of inverse proportion to the cube of ΔE_{eg}, which indicates that α-Na(K)@n-acenes alkali metal salts have higher nonlinear response than those of α-Li@n-acence alkali metal salts. From the figure of electron transition we can see, if a system has longer distance of electron transition, it maybe has larger first hyperpolarizability β_{vec} value among α-M@n-acenes (M = Li, Na and K) salts (n = 1, 2 and 3) alkali metal salts herein.

Acknowledgments

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