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Deciphering the Role of Alkali Metals (Li, Na, K) Doping for Triggering Nonlinear Optical (NLO) Properties of T-Graphene Quantum Dots: Toward the Development of Giant NLO Response Materials

Saadia Sarwar, Junaid Yaqoob, Muhammad Usman Khan,* Riaz Hussain, Sobia Zulfiqar, Abida Anwar, Mohammed A. Assiri, Muhammad Imran, Mohamed M. Ibrahim, Gaber A. M. Mersal, and Ashraf Y. Elnaggar



ABSTRACT: Nanoscale nonlinear optical (NLO) materials have received huge attention of the scientists in current decades because of their enormous applications in optics, electronics, and telecommunication. Different studies have been conducted to tune the nonlinear optical response of the nanomaterials. However, the role of alkali metal (Li, Na, K) doping on triggering the nonlinear optical response of nanomaterials by converting their centrosymmetric configuration into noncentrosymmetric configuration is rarely studied. Therefore, to find a novel of way of making NLO materials, we have employed density functional theory (DFT) calculations, which helped us to explore the effect of alkali metal (Li, Na, K) doping on the nonlinear optical response of tetragonal graphene quantum dots (TGQDs). Ten new complexes of alkali metal doped TGQDs are designed theoretically. The binding energy calculations revealed the stability of alkali metal doped TGQDs. The NLO responses of newly designed complexes are evaluated by their polarizability, first hyperpolarizability (β_o), and frequency dependent hyperpolarizabilities. The Li@r8a exhibited the highest first hyper-



polarizability (β_{o}) value of 5.19 × 10⁵ au. All these complexes exhibited complete transparency in the UV region. The exceptionally high values of β_{o} of M@TGQDs are accredited to the generation of diffuse excess electrons, as indicated by NBO analysis and PDOS. NCI analysis is accomplished to examine the nature of bonding interactions among alkali metal atoms and TGQDs. Our results suggest alkali metal doped TGQD complexes as potential candidates for nanoscale NLO materials with sufficient stability and enhanced NLO response. This study will open new doors for making giant NLO response materials for modern hi-tech applications.

1. INTRODUCTION

The fabrication of innovative materials with exceptionally high nonlinear optical (NLO) response has been an area of concentration for researchers over the previous decades. The widespread use of NLO materials in a variety of optical and optoelectronic devices has peaked researchers' curiosity.^{1–5} Some of their applications include optical data processing, data storage, signal processing, and communication and also for producing second as well as higher order harmonic generations (HHG).^{6–11} The main focus of researchers is to discover the crucial factors that can cause a tremendous increase in first and higher order hyperpolarizability values.^{12–16} Previous studies have proved that along with first-order hyperpolarizabilities, second- and the third-order hyperpolarizabilities are also equally important properties of the NLO materials.^{17–19}

Several systems having high NLO response are reported in the literature.^{20–22} These systems include organic molecules with conjugated donor– π –acceptor system^{13–15} noncentrosymmetric crystals with NLO properties, π -conjugated chiral oligomers, etc.²³ Furthermore, several π -conjugated molecules including polyenes, polyphenylenes, their diphenyl derivatives, and heterocyclic π -conjugated molecules are also studied to examine the effect of π -conjugation on the nonlinear optical response.^{24,25}

An important class among NLO materials is carbon-based nanoscale materials. These carbon-based materials have highly delocalized π -electrons, which are responsible for their NLO response.^{26–30} Nonlinear optical materials with exceptionally high values of hyperpolarizabilities have been developed by doping and structural modifications of graphene, which is a two-dimensional (2D), sp² hybridized allotrope of carbon.³⁰ A graphene-based donor–nanoribbon–acceptor (D–NR–A)

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 $(NH_2-graphene nanoribbon-NO_2)$ is studied for the NLO response.³¹ The NLO response of graphene quantum dots (GQDs) has also been investigated, and it has been found that changing the shape, size, and edge modifications with different atomic species causes a change in the NLO response.^{28,29}

In addition to hexagonal graphene, Enyashin et al. also reported two-dimensional (2D), nonhexagonal allotropes of carbon.³² Liu et al. investigated sp² hybridized graphene with tetragonal geometry, namely, tetragonal graphene (T-graphene).³³ The thermodynamic stability of planner T-graphene is found to be greater than that of graphyne and graphdiyne. Current studies prove T-graphene as potential candidates to be used in many fields, including gas sensors,³⁴ hydrogen storage devices,³⁵ spin electronic (spintronic) devices,³⁶ optronic devices,³⁷ etc.

Li investigated the alkali metal adsorbed graphdiyne (AM₃@ GDY) and tetrahedral Li₃NM adsorbed graphdiyne [Li₃NM@ GDY (M = Li, Na, K)] structures with β_{tot} values of ~1.61 × 10⁵ and ~2.88 × 10⁵ au, respectively.^{38,39} Single alkali metal adsorbed graphene, graphyne, and graphdiyne systems for enhancing NLO response properties were studied by Li et al. by employing first-principles calculations. Their β results were found in the span of 8.57 × 10⁴ to 3.93 × 10⁵ au.⁴⁰ Srivastava studied the single alkali atom decorated hexalithiobenzene, and adsorption of a single alkali atom on a lithiated graphene quantum dot (LiG) surface was found with an exceptional NLO response up to 5.4 × 10⁵ and 11.5 × 10⁵ au, respectively.^{41,42}

Recently, Deb et al. investigated the NLO response of various thermodynamically stable configurations of TGQDs. They have calculated first and second hyperpolarizabilities of TGQDs in the absence of an applied field and also after application of field. Their work proved that TGQDs possess a good NLO response especially in the presence of an external field. They reported a 777.30 au β_0 value and a 1249.18 au $\beta(-\omega;\omega,0)$ value for QD-10.⁴³ Various strategies have been reported in the literature to improve the NLO response. Introduction of diffuse excess electrons is one of the best strategies used for this purpose.44 Diffuse excess electrons reduce the HOMO-LUMO energy gaps significantly and improve the NLO response. Doping of metals is an efficient way to induce excess electrons in materials. Doping of alkali metals is frequently reported in the literature. Alkali metals have very low ionization energy values; therefore, their valence electrons can easily diffuse out to generate an excess electron system.

Studies revealed that the alkali metal, especially Li, doped π conjugated systems show very high hyperpolarizabilities.³⁰ Chen et al. investigated the effect of Na and K metals doping on calix[4]pyrrole and found a remarkable increase in firstorder hyperpolarizabilities. They calculated the β_o value of 7500 au for Na@calix[4]pyrrole, whereas for potassium doped calix[4]pyrrole, the β_o value increased to 17304 au.⁴⁵ Nazir et al. reported a 4.84 × 10⁴ au β_o value for Na @Cora 1N.⁴⁶

However, to our best knowledge, the NLO response of alkali metal decorated TGQDs (M@TGQDs) have not been testified until now, which motivates us to explore the outcomes of alkali metal doping on the NLO properties of TGQDs. We are interested in investigating the tuning of NLO properties of TGQDs by alkali metal (Li, Na, K) doping. This study will open new pathways to design novel alkali metal doped TGQD-based nanoscale NLO materials for optical and optoelectronic uses.

2. COMPUTATIONAL METHODS

The geometries of complexes have been optimized without any geometrical constrain through density functional theory (DFT). For this purpose, B3LYP ("hybrid Becke's" threeparameter exchange functional and the Lee, Yang, and Parr correlation functional) density functional has been utilized. All calculations have been performed by using teh 6-311+G(d,p) basis set. Frequency calculations have been done at the same density functional and basis set, to find the minima.⁴³

The stability of these alkali metal doped T-graphene quantum dots (TGQDs) is checked by calculating their binding energy, with the help of eq 1.

$$E_{\rm b} = E_{\rm complex} - (E_{\rm (substrate)} + E_{\rm (M)}$$
(1)

where $E_{\rm b}$ refers to the binding energy of complex, $E_{\rm complex}$ represents the energy of metal doped TGQD complexes, $E_{\rm (substrate)}$ is the energy of TGQD, and is $E_{\rm (M)}$ is the energy of doped metal atom (alkali metals, Li, Na, K).

Vertical ionization potential (VIP), ionization potential (IP), and electron affinity (EA) have been calculated by employing the following equations:

$$VIP = E_{(cation)} - E_{(neutral)}$$
(2)

Ionization potential = $IP = -E_{HOMO} (eV)$ (3)

$$Electronaffinity = EA = -E_{LUMO} (eV)$$
(4)

where $E_{(neutral)}$ refers to the energy of optimized alkali metal doped TGQD complexes. $E_{(cation)}$ refers to the energy of cationic states of alkali metal doped TGQD complexes, using the geometry of neutral alkali metal doped TGQD complexes. Then $E_{(neutral)}$ was subtracted from $E_{(cation)}$ of doped complexes obtained at the same equilibrium geometry as that of the neutral complexes.

Global reactivity descriptors such as chemical potential (μ) , chemical hardness (η) , and chemical softness (s) have been determined by using the following equations:

Chemical potential =
$$\mu = -\frac{(IP + EA)}{2}$$
 (5)

Hardness =
$$\eta = \frac{(IP - EA)}{2}$$
 (6)

Softness =
$$s = \frac{1}{2\eta} = \frac{1}{(IP - EA)}$$
 (7)

Dipole moment μ_0 , linear polarizability α_0 , and first hyperpolarizability β_0 values are calculated by the using following equations.⁴³

Dipole moment

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$
(8)

Polarizability

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{9}$$

First hyperpolarizability

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$
(10)

where





Side view

Figure 1. Optimized structure of undoped TGQD.

$$\beta_x = \beta_{xxx} + B_{xyy} + B_{xzz}$$
$$\beta_y = \beta_{yyy} + \beta_{yxx} + \beta_{yzz}$$
$$\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}$$

UV–visible spectral analysis has been carried out using TD-DFT, to examine the crucial electronic transitions in alkali metal doped TGQD complexes. The time dependent density functional theory (TD-DFT) has been performed at the CAM-B3LYP level of theory with the 6-311+G(d,p) basis set. Multiwfn software⁴⁸ is employed to generate the total density of states (TDOS) and the partial density of states (PDOS). Visual molecular dynamic (VMD) software⁴⁷ combined with Multiwfn software⁴⁸ is used to generate the three-dimensional noncovalent interactions (2D NCI) isosurfaces and twodimensional reduced density gradient (2D RDG) plots. Gaussian 16 computational package has been employed for all calculations.⁴⁹ Optimized structures are visualized by using the GaussView 6.0 software.⁵⁰

3. RESULTS AND DISCUSSION

TGQD $(C_{28}H_{12})$ was optimized without symmetry constraint conditions at the B3LYP/6-311+G(d,p) level of theory. The labeled optimized geometry of TGQD is displayed in Figure 1.

TGQD consists of four eight-membered rings (r8a, r8b, r8c, and r8d) and five four-membered rings (one central ring labeled as rc and four peripheral rings labeled as rp) of C-Cbonds. The calculated geometric parameters of TGQD revealed that all four b1 bonds are of equal length, i.e., 1.46 Å. Similarly, all four b2 bonds have exactly same bond length of 1.33 Å. The b3 bonds of rings r8a and r8b have a length of 1.47 Å. However, the b3' bonds of r8c and r8d have a bond length of 1.48 Å. Similarly, the b4 bonds of r8a and r8b are 1.44 Å in length, whereas the b4' bonds of r8c and r8d are 1.36 Å. Likewise, the b5 bonds of r8a and r8b are 1.37 Å, and the b5' bonds of r8c and r8d are 1.46 Å. The b6 bonds of all four peripheral four-membered rings (rp) have the bond length of 1.39 Å, whereas all b7 bonds are single having the bond length of 1.48 Å. TGQDs have the D_{4h} point group and possess a planar structure with the existence of σ h in it, one C₄ principal axis of rotation, and one C2 axis of rotation. It also contains four C_2 axes of rotation, which are perpendicular to the

principal C_4 axis. The bond length data of TGQD are given in Table S1 (Supporting Information).

All probable structures of alkali metal doped TGQD were considered for DFT calculations, but all these possibilities finally converged to just ten stable complexes. Four stable geometries were obtained for each Li doped TGQD, whereas three were obtained for each of Na and K doped TGQD, respectively. These optimized geometries of newly designed alkali metal doped TGQD complexes are presented in Figure 2.

3.1. Geometric Parameters. The distances between the doped alkali metal and carbon atoms of TGOD in vicinity have been calculated. It appeared that the alkali metal in all ten isomers is present almost on the top of the center of the rings. However, the calculated value of bond lengths between the doped alkali metal and all carbon atoms of the rings revealed that alkali metals are not doped exactly above the center of the ring except for M@rc isomers of Li, Na, and K doped TGQD. In the case of M@rc (where M is Li, Na, and K), the alkali metals are doped exactly above the center of the ring (rc), and all four M–C bonds are of equal length. Therefore, for isomers M@r8d as well as M@r8a (M = Li, Na, K) and Li@rp, the interaction distances between the alkali metal and the nearest carbon atoms have been calculated. The nearest atoms in the case of M@r8d are C21 and C22 and for Li@rp are C8, whereas for M@r8a isomers, C18 and C24 are nearest to the alkali metal atoms. For isomers M@rc, in which all M-C bonds have same length, the interaction distance (D_{int}) is calculated among alkali metals and the center of ring (rc). The interaction distance data are summarized in Table 1.

The D_{int} data show that in the case of M@r8d, the D_{int} is 2.25 Å for Li@r8d, which increases to 2.67 Å for Na@r8d. This distance is further increased to 3.03 Å for the K@r8D isomer. Likewise, the D_{int} values, for isomers of M@r8a (M = Li, Na, K) are 2.27, 2.68, and 3.03 Å, respectively. Similarly, M@rc has a D_{int} value of 1.91 Å for Li@rc, which increases to 2.36 and 2.71 Å for Na@rc and K@rc isomers, respectively. For Li@rp, D_{int} is 2.08 Å. This trend of the D_{int} data indicates that the interaction distance between TGQD and the alkali metals shows an increases.

The thermodynamic stability is an important factor for synthetic usefulness of NLO materials. The thermodynamic



Figure 2. Optimized geometries of alkali metal doped TGQD complexes.

stability of optimized alkali metal doped TGQDs is explored by calculating their binding energies and results are summarized in Table 2.

Binding energies describe the stabilities of compounds. Therefore, a greater binding energy value represents better interaction between two components and, as a result, greater stability of the doped complexes. Selected alkali metal doped TGQD complexes have reasonably high negative values of binding energies, indicating the feasibility of doping process. The binding energy values of Li doped TGQD isomers are

Table 1. HOMO Energy $(E_{\rm H})$, LUMO Energy $(E_{\rm L})$, HOMO–LUMO Band Gap $(E_{\rm g})$, and Interaction Distance $(D_{\rm int})$ of M@ TGQD

	$E_{\rm H}~({\rm eV})$				$E_{\rm L}$ (eV)		$E_{\rm g}~({\rm eV})$		$E_{\rm g}^{\ c}$ (eV)		$D_{\rm int}$ (Å)				
TGQD:	$E_{\rm H} = -4.89 {\rm eV}$			$E_{\rm L} = -3.24 {\rm eV}$		$E_{\rm g} = 1.65 {\rm eV}$			$E_{\rm g} = 1.66 {\rm eV}$						
complex	Li	Na	K	Li	Na	K	Li	Na	Κ	Li	Na	K	Li	Na	К
M@rp	-4.19			-2.63			1.56			1.56			2.08 ^a		
M@r8d	-4.22	-4.05	-3.94	-2.62	-2.47	-2.36	1.60	1.58	1.59	1.60	1.59	1.59	2.25 ^a	2.67 ^a	3.03 ^a
M@r8a	-4.33	-4.12	-4.00	-2.64	-2.49	-2.37	1.68	1.63	1.63	1.69	1.64	1.64	2.27 ^a	2.68 ^{<i>a</i>}	3.03 ^a
M@rc	-4.08	-3.96	-3.89	-2.80	-2.60	-2.50	1.28	1.36	1.39	1.29	1.37	1.39	1.91 ^b	2.36 ^b	2.74 ^b

^{*a*}Interaction distance of the alkali metal (Li, Na, K) from the nearest carbons of TGQD. ^{*b*}Interaction distance of the alkali metal (Li, Na, K) from the center of the ring (rc) of TGQD. ^{*c*} E_g calculated at B3LYP/6-311+G(2d,p).

Table 2. Binding Energy (E_b) , NBO Charge (q) on the Alkali Metal, and Dipole N	Moment of M@TGQD
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	$E_{\rm b}~({\rm kcal~mol^{-1}})$			$E_{\rm b}^{\ a}$ (kcal mol ⁻¹)			NBO charge			μ (D)		
complex	Li	Na	K	Li	Na	K	Li	Na	K	Li	Na	К
M@rp	-39.82			-39.63			0.942			6.16		
M@r8d	-45.02	-30.92	-39.50	-45.08	-30.91	-38.97	0.941	0.965	0.971	4.67	6.97	8.93
M@r8a	-43.58	-30.05	-38.83	-43.61	-30.00	-38.26	0.940	0.965	0.972	4.23	6.66	8.70
M@rc	-36.42	-24.58	-36.12	-36.08	-24.12	-35.29	0.966	0.984	0.975	4.82	7.13	8.64
$^{a}E_{\rm b}$ calculat	E_{h} calculated at B3LYP/6-311+G(2d,p).											

larger than that of corresponding Na and K doped TGQD isomers. For instance, binding energies for Li@r8d, Na@r8d, and K@r8d are -43.58, -30.05, and -38.83 kcal mol⁻¹, respectively. Similarly, Li@r8a, Na@r8a, and K@r8a have binding energies of -43.58, -30.05, and -38.83 kcal mol⁻¹, respectively. In the case of M@rc isomers, the binding energy values are -36.42, -24.58, and -36.12 kcal mol⁻¹ for Li@rc, Na@rc, and K@rc, respectively. Hence, it can be concluded from the above discussion that Li@r8d is the most stable among all complexes. From the above discussion, it is generalized that all of these theoretically designed alkali metal doped TGQD complexes possess good thermodynamic stability. The binding energies of these newly designed complexes have also been calculated with the same functional B3LYP at a higher basis set 6-311+G(2d,p), and results are summarized in Table 2. The results imply that $E_{\rm b}$ values showed very slight variation of the second digit at a higher basis set. The trend of results found at 6-311+G(2d,p) is also consistent with the values computed at 6-311+G(d,p). For instance, the $E_{\rm b}$ values of Li doped complexes are higher than that of Na and K doped complexes in both cases. For M@r8d complexes, $E_{\rm b}$ values range from -30.91 kcal mol⁻¹ for Na@ r8d to -38.97 kcal mol⁻¹ for K@r8d and -45.08 kcal mol⁻¹ for Li@r8d.

To explore the charge transfer among alkali metal and TGQDs, the NBO charges of selected complexes are calculated. The charge analysis gives an insight into net charge transfer after doping of alkali metals.⁵¹ The results of NBO charge analysis are summarized in Table 2.

Charge analysis information obtained after the NBO analysis showed that all alkali metals carry positive NBO charges in doped complexes. This positive charge confirmed the charge transfer from alkali metal units toward TGQDs. High electropositive character of alkali metals is mainly responsible for the existence of positive charges on alkali metals. For K doped TGQDs, the NBO charge on K is 0.971, 0.972, and 0.975 e⁺ for isomers K@r8d, K@r8a, and K@rc, respectively. The maximum value of the NBO charge of 0.984 e⁺ is noted on the Na atom in Na@rc. The value of the NBO charge on alkali metals decreases for Li and the lowest value of the NBO charge 0.940 e^+ is found on Li in Li@r8a. In short, the NBO charges on alkali metals is observed in the range 0.940–0.984 e^+ . NBO analysis discloses that our computationally designed complexes possess sufficient ability to shift charge from alkali metals to TGQDs. Charge transfer has a direct relationship with NLO properties.⁴² So, this charge transfer would induce large dipole moments and polarizabilities, which in turn will aid in improvement of the NLO properties.

The dipole moment is the parameter that reveals the polarity of the system. It is a tool to determine the charge separation in the system. As the charge separation between negative and positive charges increases, the polarity of the system rises, and as a result, the dipole moment of the system also rises. The dipole moments of our considered isomers are listed in Table 2. The results obtained from the charge analysis are further supported by analysis of the dipole moment data for optimized undoped TGQD and all the optimized alkali metal doped TGQD complexes (M@TGQD). The dipole moment of the undoped TGQD is 0.013 D. Alkali metal doping resulted in a significant increase in the dipole moment of the TGQD. For instance, the dipole moments of Li@r8d, Na@r8d, and K@r8d are 4.67, 6.97, and 8.93 D, respectively. These dipole moment data are also in agreement with the charge analysis results. As the dipole moment is dependent on the extent of charges and the distance between them, a high value of charge on the K atom in the K@r8d complex is responsible for its large dipole moment. Overall, there is an increase in dipole moment after doping of alkali metals to TGQD, which is helpful in inducing adequate polarizability, and hence, an improved NLO response. Thus, our alkali metal designed complexes would show outstanding NLO response.

3.2. Molecular Electrostatic Potential (MEP) Analysis. The change in electronic properties of TGQD after doping is also supported by performing molecular electrostatic potential MEP analysis. It designates the charge distribution of a system. MEP is also helpful in linking the molecular structure to physical and chemical properties. These properties include chemical reactivity, partial charges, and the dipole mo-



Figure 3. Molecular electrostatic potential map (MEP) of undoped and M@TGQD complexes.

ment.^{46,52} Molecular electrostatic potential map of undoped as well as alkali metal doped TGQD compounds is presented in Figure 3.

Red and yellow colors indicate negative charge. Therefore, the areas showing red and yellow colors are electron rich. However, the blue color indicates the regions that are electron deficient and exhibit positive charge. The areas with green color indicate the mean potential, and hence green areas are neutral.⁴⁶ It is clear from Figure 3 that the undoped TGQDs have unequal charge distribution. All carbon atoms, especially carbons of r8c and r8d of TGQD exhibit negative charge, which is clear from the red and yellow colors in these areas of the molecular electrostatic potential map. After the alkali metals are doped, the charge distribution changes. It can be

seen in Figure 3 that in alkali metal doped TGQD complexes, metal atoms show blue color, which indicates that these metal atoms become electron deficient. This positive charge is because of the shifting of valence s electrons of the alkali metal to TGQDs. This transfer of electrons thus created diffuse excess electrons. The size of the blue area increased with the increasing size of alkali metals, which indicates more efficient charge transfer between alkali metals and TGQDs. However, TGQD complexes show uniform charge distribution. This trend of charge distribution also verifies NBO charge analysis. The NBO analysis data also indicate the presence of positive charges on alkali metals in M@TGQD complexes. In short, MEP analysis shows that our designed complexes contain potential charge distribution sites, which are appropriate for inducing significant dipole moments, which is essential for improvement of the NLO response.

3.3. Global Reactivity Descriptors. The global reactivity descriptors values for ionization potential (IP), electron affinity (EA), chemical hardness, chemical softness (s), and chemical potential of alkali metal decorated TGQD complexes computed at B3LYP/6-311+G(d,p), and results are displayed in Table 3. The global reactivity descriptors are linked with the

Table 3. Global Reactivity Descriptors (Ionization Potential, Electron Affinity, Chemical Potential, Chemical Hardness, and Chemical Softness) of M@TGQD

complex	IP (eV)	EA (eV)	EA (eV) ^a	chemical hardness (eV)	chemical softness (eV)	chemical potential (eV)				
TGQD	4.89	3.24	3.22	0.82	0.61	-4.07				
Li@rp	4.19	2.63	2.61	0.78	0.64	-3.41				
Li@r8d	4.22	2.62	2.60	0.80	0.63	-3.42				
Li@r8a	4.33	2.64	2.62	0.84	0.59	-3.49				
Li@rc	4.08	2.80	2.78	0.64	0.78	-3.44				
Na@r8d	4.05	2.47	2.45	0.79	0.63	-3.26				
Na@r8a	4.12	2.49	2.47	0.82	0.61	-3.31				
Na@rc	3.96	2.60	2.58	0.68	0.73	-3.28				
K@r8d	3.94	2.36	2.33	0.79	0.63	-3.15				
K@r8a	4.00	2.37	2.35	0.81	0.61	-3.19				
K@rc	3.89	2.50	2.48	0.69	0.72	-3.19				
'EA calculated at B3LYP/6-311+G(2d,p).										

NLO response of the materials, for example, a complex with smaller IP values exhibits a high NLO response. Similarly, an enhanced NLO response is expected from the complexes having higher softness or lower hardness values.

The HOMO and LUMO energies are directly linked with ionization potential and electron affinity, respectively. The negative of the HOMO energy is almost equal to the ionization potential and that of the LUMO energy is almost equal to the electron affinity (Koopmans approximation).53 Pure TGQD shows an ionization potential of 4.89 eV, and its electron affinity value is 3.24 eV. Doping of alkali metal to TGQD decreases the ionization potential and electron affinity values of doped compounds, as tabulated in Table 3. For instance, the ionization potential value is 4.19 eV for Li@rp, 4.22 eV for Li@r8d, 4.33 eV for Li@r8a, and 4.08 eV for Li@rc complexes. These decreasing values of IP for doped TGQD complexes indicate the ease of ionization to generate diffuse excess electrons and hence improved NLO response values. For Na@ TGQD and K@TGQD complexes, the ionization potential ranges from 3.96 to 4.12 eV and from 3.89 to 4.00 eV,

respectively. Similarly, the electron affinity, which is related to the ability of a system to gain an electron, is also modified after doping of the alkali metal atom. For example, the electron affinity ranges from 2.62 to 2.80 eV for Li@TGQD, 2.47 to 2.60 eV for Na@TGQD, and 2.36 to 2.50 eV for K@TGQD complexes. EA calculations are also executed at B3LYP/6-311+G(2d,p), and results are displayed in Table 3. The EA of undoped TGQD is found to be 3.22 eV, which is minutely lower than EA values (3.24 eV) calculated at B3LYP/6-311+G(d,p). Alkali metal doping resulted in further reduction of EA values, and these values range from 2.33 eV (K@r8d) to 2.78 eV (Li@rc). So, overall, EA values at B3LYP/6-311+G(2d,p) are marked as 0.2–0.3 eV smaller than EV values computed at B3LYP/6-311+G(d,p).

Chemical hardness is linked to the stability of a system.⁴⁶ The chemical hardness value is 0.82 eV for undoped TGQD, which is greater than values for M@TGQD complexes, indicating that undoped TGQD is more stable and less reactive and hence exhibits a smaller NLO response than doped complexes. The maximum value of chemical hardness in the case of M@r8d (M = Li, Na, K) complexes is 0.80 eV for Li@r8d, which is the most stable complex among all three. Similarly, for M@r8a complexes, Li@r8a is the most stable complex, with a chemical hardness of 0.84 eV. Chemical hardness values for Li@rc, Na@rc, and K@rc are 0.64, 0.68, and 0.69 eV, respectively. Li@rp exhibits a chemical hardness value of 0.78 eV. The chemical softness value is directly related to the NLO response, and an increase in softness is usually linked with an increase in the NLO response.⁵⁴ The chemical softness of pure TGQD is 0.61 eV, which increases after doping, and maximum chemical softness among the doped complexes is 0.78 eV for Li@rc.

The chemical potential value is -4.07 eV for undoped TGQD, which decrease monotonically from Li to K doped complexes. The chemical potential is -3.41 eV for Li@rp, whereas it is -3.49 eV for Li@r8a, -3.31 eV for Na@r8a, and -3.19 eV for K@r8a. A similar trend of chemical potential is observed for M@r8d and M@rc (M = Li, Na, K) complexes. Chemical potential values of M@TGQD complexes are lesser than that of undoped TGQD, indicating these systems to be less stable and more reactive, which leads to an enhanced NLO response.¹⁶

3.4. Electronic Properties. Frontier Molecular Orbitals (FMOs) Analysis. The information about frontier molecular orbitals (HOMO and LUMO orbitals) of a system is essential to investigate its electronic properties. The analysis of the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) of a system helps to discover the interaction between two components in a system, based on the HOMO-LUMO band gap E_{g} . According to Koopman's theorem, the HOMO energies with a negative sign can be considered as the ionization potential whereas that of LUMO can be described as the electronic affinity of a system.⁵³ That is why we have computationally carried out the frontier molecular orbitals analysis (FMO) of all the isomers of alkali metal doped TGQDs. The FMO analysis results of pure TGQD reveal that TGQD already has a small HOMO-LUMO band gap, that is, 1.65 eV. This small band gap is likely to narrow further as a consequence of doping alkali metals on TGQD. The results of this analysis disclosed that alkali metal doping has affected the energy gap (between HOMO and LUMO orbitals) in all selected isomers of alkali metal doped TGQD complexes. Doping of alkali metals caused an increase



Figure 4. continued



Figure 4. Shapes of HOMO-1, HOMO, LUMO, and LUMO+1 orbitals, HOMO-LUMO gap (E_g) and HOMO-1-LUMO+1 gap (E_g') of undoped and alkali metal doped TGQD complexes.

in energy of HOMO orbitals, because of the existence of excess electrons. Because of these excess electrons, new HOMOs are generated, and as a result, excess electrons reside in new HOMOs.

The HOMO-LUMO gap of Li@r8d, Na@r8d, and K@r8d are 1.60, 1.58, and 1.59 eV, respectively. The most significant reduction in the band gap E_{g} is observed for M@rc complexes, where E_g values are found to be 1.28, 1.36, and 1.39 eV for Li@rc, Na@rc, and K@rc, respectively. Na@r8a and K@r8a both have band gaps of 1.63 eV. The lowest HOMO-LUMO gap is 1.28 eV for the Li@rc complex. E_g for Li@rp is found to be 1.56 eV. The HOMO-LUMO gap is also explored at B3LYP/6-311+G(2d,p), and the data are presented in Table 1. The HOMO-LUMO gap E_{g} values were found to be consistent with that observed at B3LYP/6-311+G(d,p). The results obtained at B3LYP/6-311+G(2d,p) showed only a minute second digit difference; for example, the E_{g} value is 1.66 eV for undoped TGQD, which was 1.65 eV at B3LYP/6-311+G(d,p). Delocalized π electrons of TGQDs influenced the valence s electron of alkali metals, and as a result, a diffuse excess electron system is generated, resulting in the increased energy of HOMO orbitals and consequent lessening of the HOMO-LUMO energy gap. The shapes of HOMO orbitals of alkali metal decorated TGQD compounds have shown that the electron density mostly resides on TGQD. The shapes and positions of HOMO and LUMO orbitals are represented in Figure 4.

It is clear from these images that the density in HOMOs exists mostly on peripheral atoms of TGQDs for undoped as well as alkali metal doped TGQD complexes.

TDOS and PDOS Analysis. We have plotted PDOS (partial/ projected density of states) and TDOS (total density of states) for alkali metal doped TGQDs, which further elaborated the outcome of alkali metals doping on TGQDs. These spectra also indicate that both TGQD and the alkali metal atom contributed in formation of new HOMO orbitals. These new HOMO orbitals have higher energies and are located between original HOMO and LUMO orbitals of TGQD. DOS spectra of alkali metals decorated TGQD complexes are given in Figure 5.

3.5. Polarizability and First Hyperpolarizability Analysis. It has been well testified by findings of previous

workers that the NLO properties of a system can be improved to a greater extent by introducing excess electrons into the system. These excess electrons generate new HOMO orbitals, which are higher in energy, and as a result, the HOMO– LUMO gap is decreased. These excess electrons also increase the polarizability and first-order hyperpolarizability values of the system. Therefore, we have computed polarizabilities and hyperpolarizabilities of selected alkali metal doped TGQD complexes to explore their nonlinear optical response and have listed the data in Table 4.

For undoped TGQD, the calculated polarizability is 420 au. The alkali metal decorated TGQD complexes show enhanced polarizability values. The K atom doped TGQD complexes exhibit relatively better polarizabilities. The highest polarizability is computed to be 476 au for K@r8a. Isomers K@r8d and K@rc have polarizabilities of 475 and 474 au, respectively. Theoretically calculated polarizabilities for Na@r8d, Na@r8a, and Na@rc isomers are 470, 471, and 471 au, respectively. Li@ TGQD complexes show comparatively lower polarizabilities of 470, 465, 467, and 470 au for isomers Li@rp, Li@r8d, Li@r8a, and Li@rc, respectively.

The hyperpolarizability β_o data reveal that undoped TGQD has a hyperpolarizability of 0.14 au. This value of β_o is dramatically increased after doping of alkali metals. Li@r8a has a higher β_o than Na and K doped complexes. However, Li@ r8d and Li@rc have lower hyperpolarizability values than Na and K doped at r8d and rc positions.

The hyperpolarizability β_{o} values of alkali metal doped TGQD complexes are given in Table 5.

The β_{o} value for Li@rp is 7.8 × 10³. The Li@r8d complex has a hyperpolarizability β_{o} value of 9.9 × 10² au, which increases to 2.7 × 10³ and 5.6 × 10³ au for Na@r8d and K@ r8d complexes, respectively. Similarly, for M@rc (M = Li, Na, K), hyperpolarizabilities of 2.2 × 10², 2.5 × 10², and 4.3 × 10² au are observed, respectively. Comparison of the hyperpolarizabilities of alkali metal doped TGQD complexes revealed that the highest β_{o} value exhibited by Li@r8a is 5.2 × 10⁵ au, Na@r8a is 3.7 × 10⁴ au, and K@r8a it is 2.74 × 10⁴ au. The β_{o} value of Li@r8a is greater than previously reported values of alkali metal doped NLO compounds, such as Li doped graphdiyne Li@GDY showed a β_{o} value of 8.57 × 10⁴



Figure 5. continued



Figure 5. TDOS and PDOS of undoped TGQD and alkali metal doped TGQD complexes.

Table 7. I blatizability and vertical formzation i btential of Migwi GQD	Т	able	4.	Polarizabilit	y and	Vertical	Ionization	Potential	of M@TGQD
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		α (au)			VIP (eV)		VIP (eV) ^a		
TGQD:	α = 420 au				VIP = 6.15 eV		$VIP = 6.14 \text{ eV}^{a}$		
complex	Li	Na	K	Li	Na	K	Li	Na	К
M@rp	470			5.43			5.40		
M@r8d	465	470	475	5.46	5.29	5.18	5.44	5.27	5.16
M@r8a	467	471	476	5.56	5.35	5.23	5.54	5.34	5.21
M@rc	470	471	474	5.32	5.20	5.12	5.30	5.19	5.11
^{<i>a</i>} VIP calculated	at B3LYP/6-3	311+G(2d.p)							

Table 5. Static First Hyperpolarizabilities of M@TGQD

	$\beta_{\rm o}$ (au) CAM-B3LYP/6-311+0	G(d,p)	β_{o} (au) CAM-B3LYP/6-311+G(2d,p)			
TGQD:		$\beta_{\rm o}$ = 0.14 au			$\beta_{\rm o}$ = 0.19 au		
complex	Li	Na	K	Li	Na	K	
M@rp	7.8×10^{3}			7.6×10^{3}			
M@r8d	9.9×10^{2}	2.7×10^{3}	5.6×10^{3}	2.9×10^{2}	1.6×10^{3}	3.9×10^{3}	
M@r8a	5.2×10^{5}	3.7×10^{4}	2.7×10^{4}	3.9×10^{5}	3.9×10^{4}	2.8×10^{4}	
M@rc	2.2×10^{2}	2.5×10^{2}	4.3×10^{2}	2.1×10^{2}	2.5×10^{2}	4.4×10^{2}	

than previously reported potassium doped calix[4]pyrrole having a β_o value of 17304 au.⁴⁵ Nazir et al. reported Li@Cora 1N exhibited a 7.36 × 10³ au β_o value.⁴⁶ Yaqoob et al. recently designed K@SiCNs-III, exhibiting a β_o value of 7.7 × 10⁴ au.⁵⁵ Our Li@r8a isomer possesses a greater NLO response than all mentioned compounds, which suggests it is a more efficient NLO material for optics and optoelectronics applications. The hyperpolarizability β_o values are also calculated at CAM-B3LYP/6-311+G(2d,p) and results are tabulated in Table 5. The β_o value followed the same trend at CAM- B3LYP/6-311+G(d,p) as shown by B3LYP/6-311+G(d,p). For example, among M@r8a complexes, Li@r8a showed the highest NLO response, which decreases for Na@r8a and K@r8a.

For these complexes, vertical ionization potential data are also in line with hyperpolarizability β_0 results. VIP decreases as a result of doping.³⁸ The vertical ionization potential of pure TGQD is 6.15 eV, which decreases from 5.46 eV for Li@r8d to 5.29 and 5.18 eV for Na@r8d and K@r8d, with an increase in their hyperpolarizabilities. VIP data calculated at B3LYP/6-311+G(2d,p) also show the same trend as calculated at B3LYP/6-311+G(d,p); undoped TGQD showed a 6.14 eV VIP value that decreases for alkali metal doped complexes as a result of doping. The vertical ionization potential results are summarized in Table 4.

Tuning of $\beta_{\rm o}$ values can be explained by employing a two-level expression, given as 39

$$\beta_{\rm o} \approx \frac{\Delta \mu f_{\rm o}}{\Delta E^3} \tag{11}$$

According to this formula β_o is directly linked to the transition dipole moment $\Delta \mu$ and oscillator strength f_o and inversely linked to the third power of the transition energy ΔE , so ΔE becomes a major factor in deciding β_o values.⁴¹

According to the two-level formula, it is well demonstrated in the literature that a decrease in the transition energy leads to an increase in the NLO response.⁵⁶ Therefore, we have also calculated crucial transition energies of undoped as well as alkali metal doped TGQD complexes, and results are summarized in Table 7. The transition energy for undoped TGQD is 2.2701 eV, which is expected to decrease for alkali metal doped complexes because of the creation of new energy levels as a result of doping. Results of alkali metal doped complexes reveal a decrease in the transition energy after doping. For example, Li@r8d, Na@r8d, and K@r8d have

Table 6. Frequency Dependent First Hyperpolarizabilities of M@TGQD Complexes

			I	Electro-Optical Po	ockels Effect (EC	DPE)			
	$\beta(-a)$	o;w,0) (au) at 80	00 nm	$\beta(-\omega$; <i>w</i> ,0) (au) at 10	64 nm	$\beta(-\omega;\omega,0)$ (au) at 1900 nm		
TGQD:	β($-\omega;\omega,0) = 0.11$	au	β($-\omega;\omega,0) = 0.11$	au	$\beta(-\omega;\omega,0) = 0.08$ au		
complex	Li	Na	K	Li	Na	K	Li	Li	Li
M@rp	8.6×10^{3}			1.8×10^{6}			1.1×10^{4}		
M@r8d	3.0×10^{3}	1.3×10^{3}	8.8×10^{2}	6.3×10^{4}	1.6×10^{6}	3.4×10^{4}	4.0×10^{3}	4.9×10^{3}	5.8×10^{3}
M@r8a	7.9×10^{4}	1.3×10^{5}	7.6×10^{5}	6.7×10^{4}	7.4×10^{4}	1.8×10^{5}	1.9×10^{4}	1.2×10^{4}	1.3×10^{4}
M@rc	2.3×10^{3}	6.5×10^{4}	1.1×10^{5}	1.1×10^{3}	1.4×10^{3}	1.5×10^{3}	3.1×10^{2}	2.7×10^{2}	7.2×10^{2}
			:	Second Harmoni	c Generation (SI	HG)			
	$eta(-2\omega;\omega,\omega)$ (au) at 800 nm			$\beta(-2a)$	(ω,ω) (au) at 10	064 nm	$\beta(-2\omega;\omega,\omega)$ (au) at 1900 nm		
TGQD:	β(-	$-2\omega;\omega,\omega) = 11.9$) au	β(-	$-2\omega;\omega,\omega) = 1.14$	au	$\beta(-2\omega;\omega,\omega) = 0.12$ au		
complex	Li	Na	K	Li	Na	K	Li	Na	K
M@rp	4.9×10^{5}			2.6×10^{6}			1.9×10^{4}		
M@r8d	8.5×10^{4}	4.0×10^{4}	3.7×10^{4}	2.9×10^{5}	2.7×10^{6}	8.7×10^{4}	4.2×10^{4}	4.2×10^{4}	1.9×10^{4}
M@r8a	3.9×10^{4}	7.2×10^{5}	2.1×10^{6}	2.4×10^{4}	4.6×10^{4}	1.1×10^{5}	5.4×10^{3}	5.8×10^{3}	7.5×10^{3}
M@rc	3.1×10^{3}	6.8×10^{3}	1.5×10^{4}	6.2×10^{2}	2.2×10^{2}	2.0×10^{3}	5.6×10^{1}	4.9×10^{1}	4.9×10^{2}

Table 7. TD-DFT Data, Transition Wavelength (λ_{max}), Highest Oscillator Strength (f_o), Crucial Transition Energies (ΔE) of M@TGQD Calculated at CAM-B3LYP/6-311+G(d,p) and CAM-B3LYP/6-311+G(2d,p)

	CAM-B3LYP/6-311+G(d,p)											
		λ_{\max} (nm)			f_{o}		ΔE (eV)					
TGQD:	2	max = 546.15 nm	n		$f_{\rm o} = 0.0199$		$\Delta E = 2.2701 \text{ eV}$					
complex	Li	Na	K	Li	Na	K	Li	Na	K			
M@rp	1046			0.0197			1.2119					
M@r8d	1018	1068	1096	0.0523	0.0391	0.0599	1.2177	1.1605	1.1312			
M@r8a	959	769	759	0.0062	0.0079	0.02	0.1190	0.2162	0.2416			
M@rc	1429	1356	1355	0.0417	0.0585	0.0579	0.8678	0.9144	0.9148			
CAM-B3LYP/6-311+G(2d,p)												
	λ_{\max} (nm)				fo			ΔE (eV)				
TGQD:		$\lambda_{\rm max} = 549 \ {\rm nm}$			$f_{\rm o} = 0.0185$			$\Delta E = 2.2574 \text{ eV}$				
complex	Li	Na	K	Li	Na	K	Li	Na	K			
M@rp	1051			0.0197			1.1790					
M@r8d	1029	1080	1110	0.0535	0.0400	0.0598	1.2045	1.1480	1.1164			
M@r8a	961	770	787	0.0062	0.0074	0.0196	1.2903	1.6103	1.5754			
M@rc	1429	1364	1362	0.0427	0.0583	0.058	0.8674	0.9086	0.9098			

transition energy values of 1.2177, 1.1605, and 1.1312 eV, respectively. Similarly, M@r8a shows 0.1190, 0.2162, and 0.2416 eV for crucial transition energy values of the Li@r8a, Na@r8a, and K@r8a complexes, respectively. For M@rc, crucial transition energies are in the range 0.8678–0.9148 eV.

When the external frequencies are imposed on designed complexes, the phenomena of the electro-optical pockels effect (EOPE) and second harmonic generation (SHG) are observed. Therefore, the effect of external frequencies on hyperpolarizabilities of designed complexes has also been explored at 800, 1064, and 1900 nm, and the values of EOPE $\beta(-\omega;\omega,0)$ as well as SHG $\beta(-2\omega;\omega,\omega)$ are listed in Table 6. These results computed at wavelengths of 800 and 1064 nm indicated that most of complexes showed an increase in values of EOPE and SHG as compared to β_0 . However, some exceptions are also there, such as for Li@r8a, where both $\beta(-\omega;\omega,0)$ and $\beta(-2\omega;\omega,\omega)$ values are decreased as compared to that of β_{o} when incident wavelengths of 800 and 1064 nm are imposed on these complexes. The maximum values of $\beta(-\omega;\omega,0)$, 1.8 × 10⁶ au, and $\beta(-2\omega;\omega,\omega)$, 2.6 × 10⁶ au, are exhibited by Li@rp at the wavelength of 1064 nm. At a wavelength of 1900 nm, most of the complexes showed a decline in EOPE and SHG values as compared to values of static hyperpolarizabilities.

There are many factors considered for determining the hyperpolarizability β_0 of a system. The first factor is the ionization potential of the alkali metal, and the second is the interaction distance between the alkali metal and the system of interest. If the ionization potential is the sole parameter, which affects β_{o} values, then it is expected that β_{o} increases in a monotonic way with the increasing atomic number of the alkali metals. The ionization potential values of alkali metals decrease from Li to K. Li has an ionization potential of 520.2 kJ mol⁻¹, which decreases to 495.8 and 418.8 kJ mol⁻¹ for Na and K, respectively.⁵⁷ This decreasing ionization potential value with increasing atomic size indicates that the valence s electron of the higher alkali metal (K) is easy to push out, and as a result, a diffuse electron system is generated easily. Therefore, the systems with heavier alkali metals can probably show higher hyperpolarizability values. Such behavior of increasing hyperpolarizability β_0 with increasing atomic size is well documented in previous works, for example, Na and K doped calix[4]pyrrole complex⁴⁵ and alkali metal decorated hexalithioben-



Figure 6. UV-visible absorption spectra of undoped and alkali metal doped TGQD complexes calculated at (a) CAM-B3LYP/6-311+G(d,p) and (b) CAM-B3LYP/6-311+G(2d,p).

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-0.005

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0.020 0.015

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0.000

-0.005

-0.010

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-0.020

-0.025

-0.030 -0.035

0.020

0.015

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0.005

0.000

-0.005

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0.05

0.04

0.04

0.04

0.04

0.05



Figure 7. continued



Figure 7. continued





zene.⁴¹ We observed this behavior in the case of our M@r8d and M@rc (M = Li, Na, K) complexes.

The second important factor affecting the hyperpolarizability β_{o} is the interaction distance between the alkali metal and the system. A shorter distance between the alkali metal and the system ensures a stronger interaction, resulting in a higher hyperpolarizability. However, the longer the distance between the alkali metal and the system, the weaker the interaction, leading to a lower hyperpolarizability. The interaction distances between alkali metals and the system increase from lithium to potassium. Hence, if it depends solely on the interaction distance, it is expected that the hyperpolarizability would decrease monotonically with an increase in the atomic number of the alkali metal. This type of monotonic decrease in hyperpolarizability is also well reported in the literature, for

example, $M@Al_{12}P_{12}$ nanocages (M = Li, Na, K)⁵³ and $M_2@$ b₆₆ isomers of bi-alkali metal doped $B_{12}P_{12}$ nanocages.⁴⁴ In our study, M@r8a (M = Li, Na, K) complexes have revealed this monotonic decrease in the hyperpolarizability β_0 .

3.6. UV–Visible Analysis. The NLO materials exhibiting high values of static first hyperpolarizability are utilized for frequency doubling through the phenomenon of second harmonic generation (SHG).⁴³ Hence, along with the high first hyperpolarizability value, the NLO material should be transparent for used lasers.⁵⁸ For this purpose, UV–visible absorption spectra of undoped as well as alkali metal doped TGQD compounds have been evaluated by performing time dependent DFT (TD-DFT) calculations at CAM-B3LYP/6-311+G(d,p). The results of the transition wavelength (λ_{max}),

the highest oscillator strength (f_o), and the crucial transition energy (ΔE) are displayed in Table 7.

The UV-visible data disclose that absorption spectra of alkali metal decorated TGQD compounds have shown a red shift (bathochromic shift) in comparison to that of undoped TGQD. Alkali metal doped TGQD complexes show absorption peaks mostly in the near-IR region, whereas undoped TGQD showed absorption in the visible region. Li@rp exhibited an absorption peak at 1046 nm. For M@r8d complexes, the value of maximum absorption shows an increasing trend. Li@r8d has a transition wavelength value of 1018 nm, which increases to 1068 and 1096 nm for Na@r8d and K@r8d, respectively. However, the transition wavelength for M@r8a (M = Li, Na, K) follows a decreasing order. The highest value of the transition wavelength in the case of the M@r8a series is computed for Li@r8a (959 nm); Na@r8a (769 nm) and K@r8a have lowest value in the series with an absorption at 759 nm. Similarly, M@rc complexes also show a decrease in the transition wavelength value on moving from Li to K. Maximum absorptions are 1429, 1356, and 1355 nm for Li@rc, Na@rc, and K@rc, respectively. These results indicate that the Li@rc complex has shown a maximum transition wavelength value (1429 nm) among all alkali metal doped TGQD complexes, which can be accredited to the lowest HOMO-LUMO gap of the mentioned complex.⁴⁴

Hence, all the alkali metal doped TGQD complexes are transparent in the visible region. Furthermore, these complexes are completely transparent for the UV region (less than 400 nm) and can be considered as potential candidates for utilization as NLO materials in the UV–vis region. UV–vis graphs for all complexes are given in Figure 6.

TD-DFT data, i.e., the transition wavelength λ_{max} the highest oscillator strength f_o , and crucial transition energies ΔE , of M@TGQD as well as UV-vis absorption spectra have also been calculated at CAM-B3LYP/6-311+G(2d,p) and results are displayed in Table 7 and Figure 6, respectively. These results indicated that λ_{max} is slightly shifted to longer wavelengths at this basis set. For example, for M@r8d, λ_{max} increases to 1029, 1080, and 1110 nm for Li, Na, and K doped complexes, respectively.

3.7. NCI-RDG Analysis. Noncovalent interaction analysis has been performed, to have a deep understanding of the nature of various types of intermolecular forces (binding interactions) in our newly designed alkali metal doped TGQD complexes. NCI analysis is helpful to differentiate the areas of steric repulsions, hydrogen bonding, and van der Waals interactions.^{59,60}

The three-dimensional NCI isosurfaces of alkali metal doped TGQD isomers are presented in Figure 7. On these isosurfaces, different colors are used to represent various types of interactions. For example, red shows steric repulsion, whereas green and yellow spots represent van der Waals forces. Strong bonding forces are denoted by blue spots.

In the case of Li decorated TGQD complexes, Li@r8d and Li@r8a complexes show green patches between the Li atom and TGQD, indicating Van Der Waals interactions in these systems. However, in the case of Li@rc, a blue patch is present between Li and TGQD, indicating a trend toward strong covalent interactions. Each Na and K decorated TGQD complex shows a green patch between the dopant and TGQD, which is indicative of Van Dr Waals interactions in these complexes.

Along with 3D images (isosurfaces), the outcomes of NCI analysis are also presented as two-dimensional RDG (reduced density gradient) plots. The NCI graphs are plotted between RDGs (reduced density gradients) and (sign $\lambda 2$) ρ . The value of (sign $\lambda 2$) ρ is less than zero for attractive forces, whereas a value of (sign $\lambda 2$) ρ greater than zero indicates repulsions. RDG plots and 3D isosurfaces for alkali metal doped TGQD are presented in Figure 7. As mentioned above, all the alkali metal doped TGQD complexes, except Li@rc, have shown green patches in their 3D images, indicating Van Der Waals interactions is also verified by respective NCI plots, which show green peaks of high density between -0.01 and -0.03 au.

4. CONCLUSION

In the present work, ten novel alkali metal doped TGQD complexes are designed theoretically through the density functional theory calculations. Analysis of geometric parameters of these complexes shows that lithium is doped at a minimum distance from the system of interest (TGQDs), whereas the potassium atom is doped at a maximum distance from the TGQDs. The binding energy calculations reveal the thermodynamic stability of these newly designed complexes. Li@r8d is found to be most stable with an $E_{\rm b}$ value of -45.02 kcal mol⁻¹. The doping of alkali metals on TGQDs causes a dramatic change in their electronic and nonlinear optical properties. The highest static first-order hyperpolarizability β_{0} value calculated for Li@r8a is 5.2×10^5 au. This value is several orders of magnitude higher than that of undoped TGQD and is comparable to values for previously reported best NLO compounds. This extraordinarily high NLO response is rationalized on the basis of HOMO and LUMO energies, TDOS, PDOS, and transition energy analysis. The β_{0} value of Li@r8a is mainly attributed to the lowest interaction distance between the Li atom and TGQD. Moreover, frequency dependent hyperpolarizabilities $\beta(-\omega;\omega,0)$ and $\beta(-2\omega;\omega,\omega)$ are calculated at 800, 1064, and 1900 nm. Maximum $\beta(-\omega;\omega,0)$ and $\beta(-2\omega;\omega,\omega)$ values of 1.6×10^6 and 2.6 \times 10⁶, respectively, are exhibited by the Na@r8d complex. The NCI analysis discloses that noncovalent interactions are mainly responsible for adsorption of alkali metals on TGQD. The UV-visible spectra of these alkali metals decorated complexes are also evaluated for guidance of future studies, which indicated the absorption ranges from 769 to 1429 nm. Finally, this study furnishes a theoretical base, which would be helpful to practically synthesize the novel materials with exceptional NLO response.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01746.

Bond lengths of all bonds of TGQD (PDF)

AUTHOR INFORMATION

Corresponding Author

Muhammad Usman Khan – Department of Chemistry, University of Okara, Okara 56300, Pakistan; • orcid.org/ 0000-0003-1900-8136; Phone: +923216967887; Email: usman.chemistry@gmail.com, usmankhan@ uo.edu.pk

Authors

- Saadia Sarwar Department of Chemistry, University of Okara, Okara 56300, Pakistan
- Junaid Yaqoob Department of Chemistry, University of Okara, Okara 56300, Pakistan; Department of Chemistry, COMSATS University Islamabad, Lahore 54600, Pakistan
- Riaz Hussain Department of Chemistry, University of Okara, Okara 56300, Pakistan; Occid.org/0000-0003-4304-0451
- Sobia Zulfiqar Department of Botany, University of Okara, Okara 56300, Pakistan
- Abida Anwar Department of Chemistry, University of Okara, Okara 56300, Pakistan
- Mohammed A. Assiri Department of Chemistry, Faculty of Science, King Khalid University, Abha 61413, Saudi Arabia
- Muhammad Imran Department of Chemistry, Faculty of Science, King Khalid University, Abha 61413, Saudi Arabia
- Mohamed M. Ibrahim Department of Chemistry, College of Science, Taif University, Taif 21944, Saudi Arabia
- Gaber A. M. Mersal Department of Chemistry, College of Science, Taif University, Taif 21944, Saudi Arabia
- Ashraf Y. Elnaggar Department of Food Science and Nutrition, College of Science, Taif University, Taif 21944, Saudi Arabia

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c01746

Notes

The authors declare no competing financial interest.

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