Exploration of nonlinear optical enhancement and interesting optical behavior with pyrene moiety as the conjugated donor and efficient modification in acceptor moieties

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Received: 20 August 2021 / Accepted: 28 April 2022 / Published online: 6 June 2022 © The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2022

Abstract
Herein, a series of new pyrene based hexylcyanoacetate derivatives (HPPC1–HPPC8) with A–π–D–π–D configuration were designed by end-capped modeling of non-fullerene acceptors on the structure of reference compound named dihexyl 3,3′-(pyrene-1,6-diylbis(4,1-phenylene))(2E,2′E)-bis(2-cyanoacrylate) HPPCR. Quantum chemical calculations of HPPCR and HPPC1–HPPC8 were accomplished at M06/6-31G(d, p) level. The stability of molecules due to the strongest hyper conjugative interactions in HPPCR and HPPC1–HPPC8 was estimated through NBO study. Interestingly, HOMO–LUMO band-gap of HPPC1–HPPC8 was found smaller than HPPCR which resulted in large NLO response. Among all the investigated compounds, HPPC7 showed the larger NLO response due to the presence of four cyanide (CN) groups which strengthens the bridge conjugation, and its band gap was found to be 2.11 eV, smaller as compared to band gap of HPPCR (3.225 eV). The absorption spectra of HPPC1–HPPC8 compounds showed maximum absorption wavelengths (483–707 nm) than HPPCR (471.764 nm). The designed compounds showed high NLO response than HPPCR. Amazingly, highest amplitude of linear polarizability (\( <\alpha > \)), first hyperpolarizability (\( \beta_{\text{total}} \)) and second hyperpolarizability (\( <\gamma > \) for...
HPPC\textsuperscript{7} were achieved to be $1331.191$, $200,112.2$ and $4.131 \times 10^7$ (a.u), respectively. NLO response showed that the HPPC\textsuperscript{1}–HPPC\textsuperscript{8} might be potential candidates for NLO applications.

Graphical abstract

**Keywords** Linear polarizability · First hyperpolarizability · Second hyperpolarizability · UV–Vis · FMO · End-capped moieties · Non-fullerene acceptors

1 Introduction

In recent era, it has become essential to turn our attention from electrons usage towards photon usage for ultra-fast technologies. Therefore, broad-spectrum investigations are carried out in several technological grounds including optical computing, data storage, optical switching and telecommunication (Thukral et al. 2017). Nowadays, photons are considered with great preference for the transfer of information (Northup and Blatt 2014). The non-linear optics (NLO) have attracted significant interest, especially during the last era due to the progression in experimental communities and molecular modelling (Jawaria et al. 2022; Concepcion et al. 2021; Adeel et al. 2021; Khalid et al. 2021; Ali et al. 2021). Molecules with large NLO response have gained notable significance (Garmire 2013; Guo et al. 2017). As a result, diverse efforts have been made to model innovative NLO materials have increased rapidly (Kanis et al. 1994). Organic NLO materials are preferred over the inorganic NLO materials due to their lower production costs, smaller dielectric constants, fast NLO response, higher second and third order hyperpolarizabilities and design flexibility (Khalid et al. 2020; Chemla 2012; Fuchs et al. 1989). NLO characteristics of conjugated organic materials can be efficiently enhanced via structural tailoring and doped with fullerene acceptors (Kamanina et al. 2012). Fullerene derivatives with greater photoinduced electron transfer and suitable charge separation property have been extensively used as electron acceptors for many years (Li et al. 2017a). Unfortunately, there are certain intrinsic drawbacks associated with fullerene acceptors; for example poor accepting power, visible range weak light absorption, and limited guideline on their molecular energy levels.
(Speller et al. 2019). Compared with fullerene derivatives, non-fullerene acceptors (NFAs) have exclusive benefits, such as transparency, easily-tuned energy levels, efficient light absorption, easy in fabrication, diverse chemical structures and flexibility (McAfee et al. 2015; Nielsen et al. 2015; Li et al. 2017b; Hou et al. 2018; Yang et al. 2016).

Literature study reveals that organic NFAs are used in organic solar cells but their usage in NLO materials has not been reported yet. We identified a compound HPPCR from literature (Nan et al. 2020) as reference compound and to the best of our knowledge, no systematic NLO study of HPPCR has been published yet. HPPCR is non-fullerene based (A-π-D-π-A) type compound which comprises of hexyl 2-cyanoacrylate as first and second acceptor, phenyl as first and second π-linker and pyrene core as a donor moiety. The literature survey revealed different types of donor acceptor moieties including donor–acceptor, donor-π-acceptor, donor-π-π-acceptor, donor–acceptor-π-acceptor, donor-donor-π-acceptor, donor-π-acceptor-π-donor and acceptor-π-donor-π-donor (Wielopolski et al. 2013; Katono et al. 2014; Panneerselvam et al. 2017; Namuangruk et al. 2012). Frequently, a push–pull model is used for designing of A-π-D-π-D type organic compounds. The NLO compounds with push pull schemes have drawn abundant attention for researchers because of remarkable NLO results (Khan et al. 2018, 2019a, 2019b, 2019c).

In the current study, we considered HPPCR as prototype and designed eight compounds (HPPC1–HPPC8) containing A–π–D–π–D architecture by structural tailoring with various halogenated non-fullerene-based acceptors. The donor and π-linker are kept preserved during the course of the designing while acceptor groups are modified. Different parameters, such as electronic properties, NBO analysis, absorption maximum, second and third order NLO, linear polarizability and dipole moment for all investigated compounds (HPPC1–HPPC8) and the reference compound HPPCR were computed to estimate the performance of the new engineered compounds as effective NLO materials. These findings will provide information for designing A–π–D–π–D configuration-based novel non fullerene organic entities and trigger experimental researchers for the synthesis of these molecules having exceptional NLO features.

2 Computational procedure

Entire calculations regarding computational analyses are carried out with aid of Gaussian 16 program (Frisch et al. 2016). The computations input files were developed using the Gauss View 6.0 program (Dennington et al. 2016). Geometrical optimization without symmetry restrictions of reference HPPCR molecule and HPPC1–HPPC8 are performed at DFT/M06/6-31G (d,p) level of theory. The same functional was utilized to investigate NBO and NLO properties. TD-DFT with aforesaid level was performed to investigate FMO and UV–Vis spectra of pyrene based compounds (HPPC1–HPPC8). The solvent (DCM) effect was calculated by means of conductor-like polarizable continuum (CPCM) model in all computational analyses (Barone and Cossi 1998). For interpretation of results from output files, Avogadro (Hanwell et al. 2012) and Chemcraft (Zhurko and Chemcraft 2014) were employed. Entire computational support is provided by A.A.C.B from IQ-USP Brazile.

Dipole moment was determined by using Eq. (1) (Valverde et al. 2018).

\[ \mu = \left( \mu_x^2 + \mu_y^2 + \mu_z^2 \right)^{1/2} \]
Average polarizability $<\alpha>$ determined with Eq. (2) (Barone and Cossi 1998).

\[
<\alpha> = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})
\]

(2)

The magnitude of total first hyperpolarizability ($\beta_{tot}$) was calculated via Eq. (3) (Barone and Cossi 1998).

\[
\beta_{total} = \left[ (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{xyz})^2 \right]^{1/2}
\]

(3)

The second hyperpolarizability was determined by using the Eq. (4) (Valverde et al. 2018).

\[
<\gamma> = \frac{1}{5}\left[ \gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz}) \right]
\]

(4)

3 Results and discussion

Herein, the experimentally reported compound is taken as the reference HPPCR. The reference HPPCR compound consists of A–π–D–π–A configuration as shown in Fig. 1. The pyrene ring in reference compound is acting as a donor moiety which has electronic donating ability. Whereas, hexylcyanoacetate parts located at both ends consisting of electron
withdrawing capability regarded as acceptors. The pyrene ring and hexylcyanoacetate parts are coupled via phenyl \( \pi \)-linker. We exchanged the first acceptor moiety of the \textit{HPPCR} compound with various halogenated non-fullerene acceptors and second acceptor with the pyrene donor and also incorporated the thienyl with the second \( \pi \)-linker. By carrying out these modifications in the reference (\textit{HPPCR}) compound, we designed eight derivatives (\textit{HPPC1–HPPC8}) having A–\( \pi \)-D–\( \pi \)-D architecture as shown in Fig. 2. The aim of our current investigation is to design the innovative non-fullerene-based acceptor materials with notable optoelectronic properties. The detailed computations were achieved to reveal that how \( \pi \)-linkers and numerous accepters affect the HOMO/LUMO band gaps, ICT, absorption spectra, electronic properties, linear polarizability \( \langle \alpha \rangle \), first hyperpolarizability \( \langle \beta \rangle \) and second hyperpolarizability \( \langle \gamma \rangle \) as well as NBO investigation.

### 4 Electronic structures

The frontier molecular orbital (FMO) investigation is considered as vital tool in explaining UV–Vis analysis, kinetic stability, chemical reactions, optical and electronic properties of the molecule (Risser et al. 1993; Solomon et al. 2012). The LUMO, HOMO and their energy difference are essential pointers which are used to enhance and adjust the NLO characteristics of the molecule (Albayrak and Frank 2010). The band gap \( (E_g) \) is a quite essential parameter to analyze the softness, hardness and intramolecular charge transfer (ICT) from end-capped donor moiety towards the electron-acceptor units via \( \pi \)-conjugated linker of the molecules (Solomon et al. 2012; Almutairi et al. 2017; Sajan et al. 2010). The molecules having larger band gap are considered hard and those with smaller band gap are called soft molecules. Hard compounds are less reactive, stable and having a lower polarizability (Maidur et al. 2017). On the other hand, soft molecules are highly reactive, unstable and more polarizable because they need less energy for excitation (Prasad et al. 2016). Generally, promising NLO response is originated with smaller energy gaps. Therefore, qualitative estimation for the NLO response of compounds is done from FMO band gap (Katariya et al. 2017). The FMO band gap of reference \textit{HPPCR} and designed compounds \textit{HPPC1–HPPC8} are tabulated in the Table 1.

Table 1 shows the HOMO/LUMO calculated values of reference compound is \(-5.755/-2.530 \text{ eV}\), which is very close to experimentally determined values \(-5.82/2.86 \text{ eV}\) (Nan et al. 2020) respectively. These results indicated that the implemented computational procedure was suitable to investigate \textit{HPPC1–HPPC8} compounds. All the investigated \textit{HPPC1–HPPC8} compounds exhibited smaller HOMO and LUMO values in 2.118–3.098 eV span in contrast to \textit{HPPCR} (3.225 eV) which might be owing to the extended conjugation factor. This energy gap value decreased to 3.098 eV in \textit{HPPC1} because of the replacement of second acceptor with pyrene donor, along with the incorporation of thienyl with second linker, which enhances the electron donating ability of donor group towards the acceptor group by generating push pull mechanism. This energy gap is further reduced in \textit{HPPC2} due to the substitution of non-fullerene acceptor group 2-(2-methylene-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile. The structure of \textit{HPPC3} is designed by substitution of two fluorine groups on the acceptor unit in \textit{HPPC2} derivative. The band gap of \textit{HPPC3} is lowered owing to the two F groups substituents which enhances the electron withdrawing nature of acceptor moiety. The \textit{HPPC4} and \textit{HPPC5} have a comparable HOMO and LUMO energies as \(-5.563/-3.196 \text{ and } -5.608/-3.233 \text{ eV}\), respectively. The
structure of HPPC4 is designed by incorporating the F group in the acceptor moiety of HPPC3 derivative. Among all the halogens F is highly electronegative and it increases the electron withdrawing capacity of acceptor group which might be the reason for

Fig. 2 Structure of (HPPCR) and designed compounds (HPPC1–HPPC8)
The reduction in the energy gap value 2.367 eV in HPPC4. The structure of HPPC5 is designed by replacing the three F groups with the two (–Cl) groups at the end capped acceptor moiety of HPPC4 derivative. The HPPC5 shows little bit more energy gap than HPPC4 because (–Cl) is less electronegative than (–F). The structure of HPPC6 is designed by substitution of (–Cl) group at the acceptor region of HPPC5 which might be the reason for lowering the band gap. Abundant HOMO/LUMO energy gap is observed at 2.118 eV in HPPC7. In fact, HPPC7 structure is designed by the replacing three (-Cl) group with the two cyano (–CN) groups on the acceptor unit in HPPC6 derivative. In HPPC7 the energy gap is reduced because of cyano (–CN) groups substitution on the acceptor region. These (–CN) groups have excellent electron withdrawing nature and can withdraw more electrons toward the acceptor region. Thus, this thing intensifies the transfer of charge and lowers its band gap. In the same way the HPPC8 is reported with a little bit more energy gap (E_{gap} = 2.444 eV) due the effect of acceptor group 2-(2-methylene-3-oxo-2,3-dihydro-1H-cyclopenta[b]naphthalen-1-ylidene) malononitrile. Therefore, the HOMO–LUMO energy gap was remarkably reduced in all the designed molecules. The band gap increasing order: HPPC7 < HPPC6 < HPPC4 < HPPC5 < HPPC3 < HPPC8 < HPPC2 < HPPC1 < HPPC8. This order shows that the incorporating various electronegative substituent in the designed compounds would be an outstanding feature to reduce the band gap results, hence, significant the NLO behavior (Fig. 3).

In the HPPC8 and HPPC1-HPPC8 charge distribution pattern depicted in the Fig. 4. The charge transfer phenomena indicated by electron density distribution pattern proved that investigated compounds would be the outstanding NLO material. In the reference compound, HPPC8 charge density is mostly situated over the donor region. While in LUMO, it is located above π-linker and minutely over donor segment. In the HOMO of HPPC7, charge density is mainly obtained above donor and π-spacers fragment, whereas the LUMO charge density spread over acceptor and π-spacer. In the designed compounds HPPC1–HPPC8, the large component of HOMOs was situated over donor portion while, small part on the π-spacers. Though, LUMOs are generally placed over the acceptor portion and partially over π-spacers. This shows that donor and acceptor units are linked with each other with the help of π-spacers, donor donates electron towards acceptor and π-spacers facilitate this transfer. This charge transfer

| Compounds  | E_{HOMO}  | E_{LUMO}  | Band gap |
|------------|-----------|-----------|----------|
| HPPC8      | −5.590    | −3.146    | 2.444    |
| HPPC7      | −5.647    | −3.529    | 2.118    |
| HPPC6      | −5.597    | −3.310    | 2.287    |
| HPPC5      | −5.608    | −3.233    | 2.375    |
| HPPC4      | −5.563    | −3.196    | 2.367    |
| HPPC3      | −5.560    | −3.123    | 2.437    |
| HPPC2      | −5.595    | −3.084    | 2.511    |
| HPPC1      | −5.593    | −2.495    | 3.098    |
| HPPC8      | −5.755    | −2.530    | 3.225    |

Units in eV
phenomena reveals that all the studied compounds might be considered as impressive NLO constituents.

5 Global reactivity depicters

The global reactivity depicters are very useful tool for measuring the reactivity and stability of designed molecules HPPC1–HPPC8 (Dheivamalar et al. 2018). Global chemical reactivity descriptors, such as chemical potential (µ), global hardness (η), global softness (S), electronegativity (χ), electrophilicity (ω), ionization potential (IP) and electron affinity (EA) have been determined by utilizing the HOMO–LUMO band gap of designed compounds (Yousif and Fadhil 2021). The \( IP \) denotes the energy required for removal of electron from HOMO and \( EA \) describe the energy required to add an electron to the LUMO (Dheivamalar et al. 2018). \( IP \) and \( EA \) are calculated by using the Koopman’s equation (Koopmans 1933).

\[
IP = -E_{\text{HOMO}}
\]
Atoms and molecules chemical reactivity is depicted by ionization energy. High ionization energy means high stability, chemical inertness and vice versa. $EA$ refers to the capability of acceptor group to accept electron from a donor (Meenakshi 2017). Table 2 reveals that $IP$ values of designed compound are smaller and $EA$ values are greater than the reference compound. These results showed that the HPPC1–HPPC8 might be soft, unstable and highly reactive compounds.

Global hardness ($\eta$) and global softness ($\sigma$) are calculated by using following equations (Pearson 1997).

$$EA = -E_{\text{LUMO}}$$ (6)

Fig. 4 HOMOs and LUMOs of (HPPCR) and designed molecules (HPPC1–HPPC8)
From Table 2, values of softness and hardness reveals that all the investigated compounds \textbf{HPPC1–HPPC8} are the reactive, soft and polarizable compounds relative to the reference compound. Amongst all designed compounds, \textbf{HPPC7} has lowest hardness value found to be 0.038 and highest softness value 12.845. Global hardness is decreased because of the substitution of (–CN) unit on end-capped moiety. These (–CN) groups enhance the electron withdrawing capacity of acceptor part and create a strong push pull mechanism within the compound, which in turn effects the stability of the compound and reduces its hardness.

The electronegativity of molecule is estimated by using the following equation (Pritchard and Skinner 1955).

\[
\eta = \frac{IP - EA}{2} = -\frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \tag{7}
\]

\[
\sigma = \frac{1}{2\eta} \tag{8}
\]

From Table 2, values of softness and hardness reveals that all the investigated compounds \textbf{HPPC1–HPPC8} are the reactive, soft and polarizable compounds relative to the reference compound. Amongst all designed compounds, \textbf{HPPC7} has lowest hardness value found to be 0.038 and highest softness value 12.845. Global hardness is decreased because of the substitution of (–CN) unit on end-capped moiety. These (–CN) groups enhance the electron withdrawing capacity of acceptor part and create a strong push pull mechanism within the compound, which in turn effects the stability of the compound and reduces its hardness.

The electronegativity of molecule is estimated by using the following equation (Pritchard and Skinner 1955).

\[
X = \frac{IP + EA}{2} = -\frac{E_{\text{LUMO}} + E_{\text{HOMO}}}{2} \tag{5}
\]

The electronegativity index signifies the electrons attraction by the functional group and atom, which results in the electronic transitions from lower to higher electronegative part of the molecule (Yousif and Fadhil 2021). The \( \mu \) is the opposite of \( \chi \). It is calculated by using the following equation (Parr et al. 1978).

\[
\mu = \frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2} \tag{6}
\]

More reactive compounds are those having larger chemical potential values. The electrophilicity index is described as a structural depicter for the analysis of the chemical reactivity of molecules. It measures the tendency of the species to accept electrons. A good, more reactive, nucleophile has a lower value of (\( \omega \)), in opposite a good electrophile has a high value of (\( \omega \)). The electrophilicity index values are calculated by equation (Maynard et al. 1998; Parr et al. 1999).

| Compounds | \( IP \) | \( EA \) | \( X \) | \( \eta \) | \( \mu \) | \( \omega \) | \( \sigma \) |
|-----------|---------|---------|-------|-------|-------|-------|-------|
| HPPCR     | 0.211   | 0.092   | 0.152 | 0.059 | -0.152| 0.195 | 8.438 |
| HPPC1     | 0.205   | 0.091   | 0.148 | 0.056 | -0.148| 0.193 | 8.781 |
| HPPC2     | 0.205   | 0.113   | 0.159 | 0.046 | -0.159| 0.275 | 10.836|
| HPPC3     | 0.204   | 0.114   | 0.159 | 0.044 | -0.159| 0.284 | 11.169|
| HPPC4     | 0.204   | 0.117   | 0.160 | 0.043 | -0.160| 0.297 | 11.497|
| HPPC5     | 0.206   | 0.118   | 0.162 | 0.043 | -0.162| 0.302 | 11.460|
| HPPC6     | 0.205   | 0.121   | 0.163 | 0.042 | -0.163| 0.318 | 11.896|
| HPPC7     | 0.207   | 0.129   | 0.168 | 0.038 | -0.168| 0.365 | 12.845|
| HPPC8     | 0.205   | 0.115   | 0.160 | 0.044 | -0.160| 0.286 | 11.136|
\[ \omega = \frac{\mu^2}{2\eta} \]  

(7)

Table 2 reveals all the investigated compound has higher electrophilicity index. Electrophilicity is considered to be good if \( \eta \) is low and \( \mu \) value is high (Kumar et al. 2017).

Consequently, HPPC1–HPPC8 may hold potential NLO findings. Furthermore, these findings of the proposed compounds are linked with the energy gap values. Compounds with lower energy gap showed smaller values of hardness, chemical potential and larger value of softness hence, more reactive and vice versa. Consequently, this entire information illustrates that the compounds may be logically active and has noteworthy NLO characteristics.

### 6 UV–Vis analysis

In order to comprehend the different substituents effect on end-capped acceptor moiety, observed spectral properties of designed compounds have been calculated through TD-DFT/M06/6-311G(d,p) functional. These calculations were performed in DCM (dichloromethane) solvent for the approximation of six lowest singlet–singlet transitions. The computed absorption wavelengths (\( \lambda \)) are function of electron availability, oscillator strengths (\( f \)) and excitation energies (\( E \)) were also calculated for the same solvent of compounds (HPPCR) and (HPPC1–HPPC8) are presented in Table S23, while major values are collected in Table 3.

The \( \lambda_{\text{max}} \) of all the designed derivatives are observed in the range of 483–707 nm. The computed results revealed that the strong electron withdrawing end-capped moieties having more extended conjugation, resulting in a greater red shift in the \( \lambda_{\text{max}} \). The designed compounds have higher red shifted compared with reference HPPCR (\( \lambda_{\text{max}} = 471 \) nm) as can be seen in Table 3. The decreasing order of absorption wavelengths for all investigated compounds along with the reference compound are found to be HPPC7 > HPPC6 > HPPC4 > HPPC5 > HPPC3 > HPPC8 > HPPC2 > HPPC1 > HPPCR.

The decreasing order of absorption wavelengths and energy gap is obtained to be the same for all the studied molecules. In fact, these compounds (HPPCR–HPPC7) have low

| Compounds | \( \lambda \) (nm) | E (eV) | \( f \) | MO contributions |
|-----------|-----------------|-------|------|-----------------|
| HPPCR     | 471.764 (405) nm | 2.628 | 1.085 | H \( \rightarrow \) L (97%) |
| HPPC1     | 483.727          | 2.563 | 0.978 | H \( \rightarrow \) L (92%), H-2 \( \rightarrow \) L (5%) |
| HPPC2     | 594.334          | 2.086 | 0.609 | H \( \rightarrow \) L (92%), H-2 \( \rightarrow \) L (5%) |
| HPPC3     | 620.138          | 1.999 | 0.169 | H \( \rightarrow \) L (92%), H-2 \( \rightarrow \) L (5%) |
| HPPC4     | 641.408          | 1.933 | 0.218 | H \( \rightarrow \) L (92%), H-2 \( \rightarrow \) L (6%) |
| HPPC5     | 631.252          | 1.964 | 0.595 | H \( \rightarrow \) L (92%), H-2 \( \rightarrow \) L (5%) |
| HPPC6     | 654.996          | 1.893 | 0.530 | H \( \rightarrow \) L (92%), H-2 \( \rightarrow \) L (6%) |
| HPPC7     | 707.996          | 1.751 | 0.435 | H \( \rightarrow \) L (92%), H-2 \( \rightarrow \) L (5%) |
| HPPC8     | 613.753          | 2.020 | 0.695 | H \( \rightarrow \) L (92%), H-2 \( \rightarrow \) L (5%) |

Values in parenthesis are experimental, (Nan et al. 2020) H = HOMO, H-2 = HOMO-2, L = LUMO, L-1 = LUMO-1
energy gaps and demands small energy for the electronic transitions. Indeed, red shifted absorption wavelengths were found in HPPCR–HPPC7 due to low energy transitions. Interestingly, HPPCR–HPPC7 are also found in the range of environment friendly compounds owing to absorbance in the UV region (Tomkinson et al. 2009; Bechtold and Mus-sak xxxx). It is expected that these compounds will immensely play a positive role in lowering the current global warming situation of the world. Moreover, the transition energy of all of the investigated compounds is obtained in the range of 2.628–1.751 eV. The lower transition energy is seen in HPPC7, due to the effect of strong end-capped acceptor unit. The increasing order of transition energies are such as HPPC7 < HPPC6 < HPPC4 < HPPC5 < HPPC3 < HPPC8 < HPPC2 < HPPC1 < HPPCR that is alike with oscillator strength. The molecular orbital calculations reveal that the visible region absorption maxima of studied compounds relate to the transition of electrons from HOMO to LUMO. Major contribution in these molecular orbital transitions belongs to H → L (92%). The molecular orbital transition reveals that maximum absorption spectra correlate with the transition from HUMO to LUMO. Furthermore, higher HOMO–LUMO compound shows deprived NLO response, while lowest HOMO–LUMO band gap compound HPPC7 establish maximum NLO response.

For the designing of NLO active materials with outstanding NLO response involves strong electronic coupling between donor and acceptor. Based on above discussion, (a) absorption spectra, (b) transition energy and (c) oscillator strength of designed compounds (HPPC1–HPPC8) are much better than the reference compound HPPCR. These results proposed that, these type (A–π–D–π–D) of designed compounds have marvelous NLO properties. The usage of the substituents has (–I) effect on acceptor moiety is a substantial approach. We anticipate that the effect of these non-fullerene acceptor units on NLO materials will be applied to design the NLO materials which performs a vital role in applied sciences.

7 NBO analysis

The natural bond orbital analysis was achieved by utilizing Gaussian NBO 6.0 program package (Glendening et al. 2013) and M06/6-31G(d,p) level of theory. NBO analysis allows us to evaluate: (i) the interaction between donor unit (D) and acceptor unit (A); (ii) the electronic excitation; and (iii) the electron delocalization (Ans et al. 2018). The studied compounds are divided into D, π (linker group) and A parts, although NBO analysis explains the transfer of charge density from donor(i) to acceptor (j) and π-linker acts as a conveyor for ICT charge transfer (Bribes et al. 1991). The stabilization energy $E^{(2)}$ for delocalization can be attained by Eq. 12:

$$E^{(2)} = q_I \left( \frac{F_{ij}}{\epsilon_j - \epsilon_i} \right)^2$$

whereas $q_i$ is donor orbital occupancy, $\epsilon_j$ and $\epsilon_i$ are off-diagonal and $F_{ij}$ is diagonal NBO Fock matrix elements (Liu et al. 2005). The NBO analysis offers useful understandings for analyzing the inter and intra-molecular hydrogen bonding, hyper conjugative interactions, charge transference between D and A units (Ans et al. 2018; Liu et al. 2005). The designed compounds NBO analysis parameters are listed in the Table S11-S19 while major values are put in Table 4.
| Compounds | Donor(i) | Type | Acceptor(j) | Type | E(2)\(^a\) | E(J)E(i)\(^b\) | F(i,j)\(^c\) |
|-----------|----------|------|-------------|------|-----------|----------------|--------------|
| **HPPCR** |          |      |             |      |           |                 |              |
| C25–C26   | π        | C28–C32 | π*          |      | 27.13     | 0.29           | 0.079        |
| C77–O78   | π        | C77–O78 | π*          |      | 0.71      | 0.43           | 0.017        |
| C72–H73   | σ        | C74–C77 | σ*          |      | 7.41      | 0.96           | 0.076        |
| C90–C93   | σ        | C93–H97 | σ*          |      | 0.50      | 1.04           | 0.020        |
| O79       | LP(2)    | C77–O78 | π*          |      | 52.51     | 0.36           | 0.124        |
| O79       | LP(2)    | C63–C65 | π*          |      | 0.54      | 0.38           | 0.013        |
| **HPPC1** |          |      |             |      |           |                 |              |
| C2–C3     | π        | C1–C6  | π*          |      | 23.77     | 0.29           | 0.075        |
| C35–C37   | π        | C35–C37| π*          |      | 1.70      | 0.33           | 0.021        |
| C92–H103  | σ        | C86–C93| σ*          |      | 4.70      | 1.10           | 0.064        |
| C95–H96   | σ        | C83–C95| σ*          |      | 0.66      | 1.07           | 0.024        |
| O42       | LP(2)    | C40–O41| σ*          |      | 52.15     | 0.36           | 0.124        |
| O42       | LP(1)    | C43–H46| σ*          |      | 0.93      | 1.01           | 0.027        |
| **HPPC2** |          |      |             |      |           |                 |              |
| C92–C94   | π        | C23–C73| π*          |      | 25.81     | 0.29           | 0.081        |
| C82–N83   | π        | C84–N85| π*          |      | 0.78      | 0.47           | 0.017        |
| C23–C79   | σ        | C73–C74| σ*          |      | 7.98      | 0.98           | 0.080        |
| C92–H96   | σ        | C23–C79| σ*          |      | 0.67      | 0.96           | 0.023        |
| S36       | LP(2)    | C37–C39| π*          |      | 23.31     | 0.29           | 0.073        |
| O86       | LP(1)    | C67–C74| σ*          |      | 1.35      | 1.19           | 0.036        |
| **HPPC3** |          |      |             |      |           |                 |              |
| C24–C25   | π        | C27–C30| π*          |      | 25.84     | 0.29           | 0.077        |
| C91–N92   | π        | C89–N90| π*          |      | 0.59      | 0.47           | 0.015        |
| C89–N90   | σ        | C88–C89| σ*          |      | 6.30      | 1.57           | 0.089        |
| C89–N90   | σ        | C84–C88| σ*          |      | 0.52      | 1.64           | 0.026        |
| S46       | LP(2)    | C47–C49| π*          |      | 23.31     | 0.29           | 0.073        |
| O93       | LP(2)    | C33–H87| σ*          |      | 0.59      | 0.70           | 0.019        |
| **HPPC4** |          |      |             |      |           |                 |              |
| C24–C26   | π        | C29–C30| π*          |      | 26.23     | 0.29           | 0.077        |
| C90–N91   | π        | C88–N89| π*          |      | 0.57      | 0.47           | 0.015        |
| C33–H86   | σ        | C83–C84| σ*          |      | 9.50      | 1.01           | 0.088        |
| C3–C7     | σ        | C7–CH18| σ*          |      | 0.80      | 1.13           | 0.027        |
| O92       | LP(2)    | C76–C82| σ*          |      | 23.67     | 0.74           | 0.120        |
| F95       | LP(2)    | C80–C81| σ*          |      | 0.51      | 0.98           | 0.020        |
| **HPPC5** |          |      |             |      |           |                 |              |
| C78–C80   | π        | C83–C85| π*          |      | 28.83     | 0.28           | 0.080        |
| C93–N94   | π        | C91–N92| π*          |      | 0.71      | 0.46           | 0.016        |
| C34–H37   | σ        | C33–S35| σ*          |      | 5.26      | 0.75           | 0.056        |
| C3–C6     | σ        | C6–H17 | σ*          |      | 0.80      | 1.13           | 0.027        |
| S35       | LP(2)    | C33–C34| π*          |      | 23.32     | 0.29           | 0.073        |
| C176      | LP(2)    | C65–C70| σ*          |      | 0.55      | 0.91           | 0.020        |
| **HPPC6** |          |      |             |      |           |                 |              |
| C78–C80   | π        | C83–C85| π*          |      | 29.12     | 0.28           | 0.081        |
| C91–N92   | π        | C93–N94| π*          |      | 0.78      | 0.46           | 0.017        |
| C93–N94   | σ        | C89–C93| σ*          |      | 6.27      | 1.57           | 0.089        |
| C3–C6     | σ        | C3–H17 | σ*          |      | 0.80      | 1.13           | 0.027        |
| O90       | LP(2)    | C66–C73| σ*          |      | 23.57     | 0.74           | 0.119        |
| C176      | LP(2)    | C65–C70| σ*          |      | 0.57      | 0.91           | 0.020        |
Typically, remarkable four types of molecular transitions were noticed; $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, LP$\rightarrow \sigma^*$ and LP$\rightarrow \pi^*$. Transitions $\pi \rightarrow \pi^*$ was considered most significant, $\sigma \rightarrow \sigma^*$ was considered slightest and LP$\rightarrow \sigma^*/$LP$\rightarrow \pi^*$ were considered a little dominating transition. The extended conjugation and charge transfer in the designed molecules can be explained with $/u1D70B\rightarrow /u1D70B^*$ transitions. The most noteworthy electronic interactions in terms of $\pi \rightarrow \pi^*$ such as $\pi$(C25–C26)$\rightarrow \pi^*(C25–C28)$, $\pi$(C93–N94)$\rightarrow \pi^*(C91–N92)$, $\pi$(C35–H88)$\rightarrow \pi^*(C85–C86)$, $\pi$(C24–C26)$\rightarrow \pi^*(C29–C30)$, $\pi$(C24–C25)$\rightarrow \pi^*(C27–C30)$, $\pi$(C25–C27)$\rightarrow \pi^*(C25–C28)$, $\pi$(C24–C26)$\rightarrow \pi^*(C29–C30)$, $\pi$(C72–H73)$\rightarrow \pi^*(C74–C77)$, $\pi$(C90–N91)$\rightarrow \pi^*(C88–N89)$, $\pi$(C92–H96)$\rightarrow \pi^*(C93–H97)$, $\pi$(C92–H96)$\rightarrow \pi^*(C23–C79)$, $\pi$(C89–N90)$\rightarrow \pi^*(C84–C88)$, $\pi$(C3–C7)$\rightarrow \pi^*(C7–C18)$, $\pi$(C3–C6)$\rightarrow \pi^*(C6–C17)$, $\pi$(C3–C6)$\rightarrow \pi^*(C3–H17)$, $\pi$(C5–C16)$\rightarrow \sigma^*(C16–H17)$, and $\pi$(C5–C16)$\rightarrow \sigma^*(C16–H17)$. $\pi$(C3–C6)$\rightarrow \pi^*(C6–C17)$, $\pi$(C3–C6)$\rightarrow \pi^*(C3–H17)$, $\pi$(C5–C16)$\rightarrow \sigma^*(C16–H17)$, and $\pi$(C5–C16)$\rightarrow \sigma^*(C16–H17)$.

Table 4 (continued)

| Compounds | Donor(i) | Type | Acceptor(j) | Type | $E(2)^a$ | $E(J)$ | $E(i)^b$ | $F(i,j)^c$ |
|-----------|----------|------|-------------|------|----------|--------|----------|----------|
| HPPC7     | C25–C27  | $\pi$ | C25–C28     | $\pi^*$| 29.59    | 0.28   | 0.081    |
|           | C93–N94  | $\pi$ | C91–N92     | $\pi^*$| 0.73     | 0.46   | 0.016    |
|           | C35–H88  | $\sigma$| C85–C86    | $\sigma^*$| 7.86    | 0.98   | 0.079    |
|           | C5–C16   | $\sigma$| C16–H17    | $\sigma^*$| 0.93    | 1.13   | 0.029    |
| S48       | LP(2)    |       | C46–C47     | $\pi^*$| 23.24    | 0.29   | 0.073    |
|           | O89      | LP(1) | C79–C86     | $\sigma^*$| 1.39    | 1.17   | 0.036    |
| HPPC8     | C24–C26  | $\pi$ | C29–C30     | $\pi^*$| 28.45    | 0.28   | 0.080    |
|           | C90–N91  | $\pi$ | C88–N89     | $\pi^*$| 0.73     | 0.46   | 0.016    |
|           | C47–H50  | $\sigma$| S46–C49    | $\sigma^*$| 5.28    | 0.75   | 0.056    |
|           | C3–C7    | $\sigma$| C7–H18     | $\sigma^*$| 0.80    | 1.13   | 0.027    |
|           | S46      | LP(2) | C47–C49     | $\pi^*$| 23.26    | 0.29   | 0.073    |
|           | O86      | LP(1) | C77–C83     | $\sigma^*$| 1.44    | 1.19   | 0.037    |

$aE(2)$ means energy of hyper conjugative interaction (stabilization energy in kcal/mol). $^b$Energy difference between donor and acceptor $i$ and $j$ NBO orbitals, $^c$F$(i,j)$ is the Fock matrix element between $i$ and $j$ NBO orbitals.
σ(C3–C7) → σ*(C7–H18) with 0.50, 0.66, 0.67, 0.52, 0.80, 0.80, 0.93, and 0.80 kcal/mol stabilization energies were found least values among all σ → σ* transitions in HPPCR and HPPC1–HPPC8, respectively.

Furthermore, some important interactions were observed like LP2 (O79) → π*(C77–O78), LP2(O42) → π*(C40–O41), LP2(S36) → π*(C37–C39), LP2(S46) → π*(C47–C49), LP2 (O92) → σ*(C76–C82), LP2(S35) → π*(C33–C34), LP2(O90) → σ*(C66–C73) LP2(S48) → π*(C46–C47), and LP2(S46) → π*(C47–C49) contained 52.51,52.15, 23.31, 23.31, 23.67, 23.32,23.57,23.24 and 23.26 kcal/mol in HPPCR and HPPC1–HPPC8, respectively. Furthermore, some important interactions were observed like LP2 (O79) → π*(C77–O78), LP2(O42) → π*(C40–O41), LP2(S36) → π*(C37–C39), LP2(S46) → π*(C47–C49), LP2 (O92) → σ*(C76–C82), LP2(S35) → π*(C33–C34), LP2(O90) → σ*(C66–C73) LP2(S48) → π*(C46–C47), and LP2(S46) → π*(C47–C49) contained 52.51,52.15, 23.31, 23.31, 23.67, 23.32,23.57,23.24 and 23.26 kcal/mol in HPPCR and HPPC1–HPPC8, respectively.

These LP → π* were collected as highest values among all of LP → π* transitions. On the other hand, LP2 (O79) → σ* (C63–C65), LP1(O42) → σ* (C43–H46), LP1(O86) → σ* (C67–C74), LP2(O93) → σ* (C33–H87), LP2(F95) → σ*(C80–C81), LP2(C176) → σ*(C65–C70), LP2(C176) → σ*(C65–C70),LP1(O89) → σ* (C79–C86), and LP1(O86) → σ* (C77–C83) contained 0.54, 0.93, 1.35, 0.59, 0.51, 0.55, 0.57, 1.39 and 1.44 kcal/mol in HPPCR and HPPC1–HPPC8, respectively. These LP → π* were collected as least values in terms of magnitudes among all of LP → π* transitions. The NBO results show the conjugation, hyperconjugation and intramolecular charge transfer (ICT) phenomena is found in our HPPCR and HPPC1–HPPC8. Moreover, these NBO results also support NLO responses of the studied molecules (Khan et al. 2020).

8 Nonlinear optical properties

Nonlinear materials along their investigations are gathering significance in various scientific aspects because of their huge role in an extensive diversity of applications ranging from lasers to signal processing and optical sensing devices (Muthu and Maheswari 2012; Govindarasu and Kavitha 2014a; Govindarasu et al. 2014). We have computed the dipole moment (µtotal), linear polarizability (α), first (β), and second (γ) hyperpolarizabilities of the designed compounds HPPC1–HPPC8 at M06/6-311 g(d, p). These are the important parameters which indicate their usefulness as NLO active materials (Govindarasu and Kavitha 2014b). They are theoretically calculated by employing x, y, z tensors presented in Eqs. (1–4). The strength of the optical response correlate directly with the electronic properties and these properties are in good agreement. The computed µ, α, β and γ values exhibited in Table 5, and their contributing tensors are mentioned in Tables S20-S22.

At molecular level, the dipole moment is an important parameter to determine the role of acceptor group and also used to quantify the response of an isolate compound in an

| Compounds | µtotal | <α> | βtotal | <γ> × 10.7 |
|-----------|--------|------|--------|------------|
| HPPCR     | 4.275  | 854.100 | 8501.7 | 0.555 |
| HPPC1     | 3.537  | 1089.330 | 37,856.5 | 0.796 |
| HPPC2     | 2.687  | 1230.656 | 98,320.3 | 1.955 |
| HPPC3     | 1.955  | 1161.027 | 38,409.2 | 1.050 |
| HPPC4     | 2.006  | 1177.857 | 56,003.9 | 1.364 |
| HPPC5     | 3.308  | 1296.011 | 127,270.7 | 2.656 |
| HPPC6     | 2.942  | 1323.223 | 141,902.9 | 3.033 |
| HPPC7     | 5.666  | 1331.191 | 200,112.2 | 4.131 |
| HPPC8     | 2.842  | 1344.056 | 120,047.7 | 2.653 |

Table 5 Dipole polarizability (µtotal), average polarizability < α > , first hyperpolarizability (βtotal), and second hyperpolarizability < γ > of the studied compounds
applied electric field. The non-zero values of $\mu_{\text{total}}$ depicts the dipolar character of investigated compounds. There are three tensors of the dipole polarizability (µ) along the directions of x, y and z axes. Table S20 reveals that $\mu_x$ tensor of HPPCR, HPPC1–HPPC4 and HPPC8 consisting of most significant values. Moreover, HPPC5–HPPC7 consist of most significant values of $\mu_x$. However, all HPPCR and HPPC1–HPPC8 molecules comprise of lowest value of $\mu_y$. The dipole moment values of reference compound HPPCR along with the designed compounds HPPC1–HPPC8 in DCM solvent are found to be 4.275, 3.537, 2.687, 1.955, 2.006, 3.308, 2.942, 5.666 and 2.842 respectively.

Among HPPCR and HPPC1–HPPC8, HPPC7 has the highest value of $\mu_{\text{total}}$ is owing to the strong electron withdrawing effect of non-fullerene acceptor moiety. The computed dipole moment of all the designed compounds is larger as compared to HPPCR. The total dipole polarizability (µ) decreasing trend is found to be HPPC7 > HPPCR > HPPC1 > HPPC5 > HPPC6 > HPPC8 > HPPC2 > HPPC4 > HPPC3, disclosed that all the designed compounds have significantly polar behavior. Hence, it is clear from the result that larger the values of dipole moment greater will be the ICT charge transfer and therefore greater electron mobility. Therefore, all our studied compounds are enriched in this aspect. Linear polarizability (α) has three tensors in the directions of x, y and z axes. Table S20 reveals that $\alpha_{xx}$ tensor of HPPCR, HPPC1–HPPC8 consist of most significant values. However, all HPPC1–HPPC8 molecules comprise of the lowest values of $\mu_{xx}$ and HPPCR comprise of lowest values of $\mu_{yy}$. The HPPCR (α) value was found to be 854.10(a.u) and designed HPPC1–HPPC8 compounds have values: 1089.330, 1230.656, 1161.027, 1177.857, 1296.011, 1323.223, 1331.191 and 1344.056 a.u respectively. Linear polarizability trend was found to be HPPC8 > HPPC7 > HPPC6 > HPPC5 > HPPC2 > HPPC4 > HPPC3 > HPPC1 > HPPCR, revealed that all the designed compounds are more effective than the reference compound in terms of linear polarizability (α) responses.

The first hyperpolarizability is represented by a third rank tensor by characterizing the response of a system in an applied electric field (Kleinman 1962). Table S21 reveals that $\beta_{xxx}$ tensor of HPPCR, HPPC1–HPPC8 consist of most significant values. Moreover, $\beta_{xyy}$ also consist of significant values but less than $\beta_{xxx}$. Therefore, main charge transfers in HPPCR, HPPC1–HPPC8 are found in the direction of x-axis. Moreover, Table S21, all HPPC1–HPPC8 have significant values of second order polarizability tensors as compared to HPPCR. This data suggests that the studied systems (HPPC1–HPPC8), other than reference system (HPPCR), have strong second-order polarizability responses. Second-order polarizabilities (β) exemplify the NLO responses in which HPPC7 exhibited highest 200,112.2 a.u and found least as 8501 a.u by HPPCR. In HPPC7, four CN groups on the acceptor moiety enhance the charge transfer ability by lowering the transition energy which in turn increases the NLO response of first hyperpolarizability. Large values in $\beta_{\text{total}}$ are observed to be 37,856.5, 98,320.3, 38,409.2, 56,003.9, 127,270.7, 141,902.9, 200,112.2, and 120,047.7 a.u for HPPC1–HPPC8, respectively as compared to HPPCR (8501.7). This data proved that the efficacy of strong acceptor moieties was noticed remarkably in HPPC1–HPPC8. Moreover, linear polarizability and β values of our designed compounds are found remarkably greater than urea, as a reference compound for the estimation of NLO response (Shelton and Rice 1994). The β values of HPPCR, HPPC1, HPPC2, HPPC3, HPPC4, HPPC5, HPPC6, HPPC7 and HPPC8 were 197 times, 880 times, 2286 times, 893 times, 1302 times, 2959 times, 3300 times, 4653 and 2791 times greater than urea, respectively, indicating high performance NLO active compounds. Indeed, second order NLO response correlate with the ICT in which electrons migrated through π-bridge towards the x-axis. However, higher delocalization of π-electrons decreased the band gaps, which in turn increased NLO response for the compounds (Kumar et al. 2014). The
exploration of nonlinear optical enhancement and interesting…

second hyperpolarizability ($\gamma$) is often thought as two-photon absorption (TPA) phenomenon in NLO compounds. Table S22 reveals that $\gamma_X$ tensor of HPPCR, HPPC1–HPPC8 consist of most significant values. However, $\gamma_z$ consist of lowest values for HPPCR, HPPC1–HPPC8. Therefore, main charge transfer in HPPCR–HPPC8 is found in the direction of x-axis. The amplitude of $\gamma_X$ tensor for HPPC2–HPPC8 has greater magnitude than HPPC1 and HPPCR. All the investigated molecules show high third-order NLO response as compared to HPPCR. Third-order polarizability values of reference and designed compounds are 0.555, 0.796, 1.955, 1.050, 1.364, 2.656, 3.033, 4.131 and 2.653 all values of $10^7$ a.u respectively. All designed compounds are in the following decreasing order: HPPC7 > HPPC6 > HPPC5 > HPPC8 > HPPC2 > HPPC4 > HPPC3 > HPPC1 > HPPCR.

Based on the above discussion, dipole moment, polarizability and hyperpolarizability of all the designed compounds are greater than the reference compound. This increase is owing to the incorporation of electron withdrawing groups on accepter unit. These electron loving groups attract the electrons from the donor unit through \(\pi\)-spacers by lowering the transition energy, band gap and enhance the NLO response.

The investigated NLO results are compared with reported NLO results. Mehmood et al. reported the carbazole like groups effect on the NLO properties (Mahmood et al. 2017). Our reported NLO results are found 177 times greater than their reported NLO values. The $\beta_{\text{total}}$ value of HPPC7 is found greater than the reported benzoazole based dyes with D-\(\pi\)-A-A configuration with $\beta_{\text{total}}=124,711.72$ a.u results (Janjua 2017). Overall, the designed compounds exhibited promising NLO features with respect to published experimental results and also theoretical results (Migalska-Zalas et al. 2008; Popczyk et al. 2021, 2019; Guezguez et al. 2014; Karakas et al. 2013; Mydlova et al. 2018; Ouazzani et al. 2011). So, we conclude that the designed compounds show promising NLO properties which provides basis for future studies.

9 Conclusion

In this work, the structural tailoring with acceptor groups remarkably affects the NLO properties of compounds has been reported. A series of chromophores (HPPC1–HPPC8) with A–\(\pi\)–D–\(\pi\)–D architecture have been designed via different end-capped acceptor moieties, where pyrene ring acts as a donor unit and phenyl as well as thienyl act as \(\pi\)-bridges. The computed data for excitation energies reveals that all the investigated compounds have extensive electron delocalization as compared to the HPPCR. The band gap is ascertained in the range of 3.225–2.118 eV for HPPC1–HPPC8. This energy difference communicated a clue about the stability and chemical reactivity of designed molecules. NBO result illustrates the charge transfer phenomena anticipated in HPPC1–HPPC8. In dichloromethane (DCM), the maximum bathochromic shift is observed as 707.996 nm for HPPC7 and has the smallest band gap is established as 2.118 eV. Consequently, HPPC7 has a more promising NLO than HPPCR and HPPC1–HPPC8. The total dipole polarizability ($\mu$) trend is found to be HPPC7 > HPPCR > HPPC1 > HPPC5 > HPPC6 > HPPC8 > HPPC2 > HPPC4 > HPPC3, disclosed that all the designed compounds have significantly polar behavior. Trend of linear polarizability ($\alpha$) and first hyperpolarizability ($\beta$) was found to be HPPC8 > HPPC7 > HPPC6 > HPPC5 > HPPC2 > HPPC4 > HPPC3 > HPPC1 > HPPCR. All designed molecules are in the following decreasing order of second hyperpolarizability ($\gamma$): HPPC7 > HPPC6 > HPPC5 > HPPC8 > HPPC2 > HPPC4 > HPPC3 > HPPC1.
HPPCR. Overall, all investigated compounds (HPPC1–HPPC8) have shown marvelous NLO response in the range of 37,856–200,112 a.u as compared to HPPCR ($\beta_{\text{total}} = 8501$ a.u). Overall, proposed compound HPPC7 displayed highest first and second order NLO response values 200,112 a.u and $0.555 \times 10^7$ respectively. The proposed compounds are recommended for future NLO applications in optical computing, data storage, optical switching and telecommunication.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11082-022-03782-w.

Acknowledgements This project was funded by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under Grant No. (D-246-130-1443). The authors, therefore, gratefully acknowledge DSR technical and financial support.

Funding The funding was provided by Muhammad Nadeem Arshad, Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, Grant No. D-246-130-1443.

Declarations

Conflict of interest The authors have not disclosed any conflict of interest.

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