First principles study of electronic and nonlinear optical properties of A–D–π–A and D–A–D–π–A configured compounds containing novel quinoline–carbazole derivatives†

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Materials with nonlinear optical (NLO) properties have significant applications in different fields, including nuclear science, biophysics, medicine, chemical dynamics, solid physics, materials science and surface interface applications. Quinoline and carbazole, owing to their electron-deficient and electron-rich character respectively, play a role in charge transfer applications in optoelectronics. Therefore, an attempt has been made herein to explore quinoline–carbazole based novel materials with highly nonlinear optical properties. Structural tailoring has been made at the donor and acceptor units of two recently synthesized quinoline–carbazole molecules (Q1, Q2) and acceptor–donor–π–acceptor (A–D–π–A) and donor–acceptor–donor–π–acceptor (D–A–D–π–A) type novel molecules Q1D1–Q1D3 and Q2D2–Q2D3 have been quantum chemically designed, respectively. Density functional theory (DFT) and time-dependent density functional theory (TDDFT) computations are performed to process the impact of acceptor and donor units on photophysical, electronic and NLO properties of selected molecules. The \( \lambda_{\text{max}} \) values (321 and 319 nm) for Q1 and Q2 in DMSO were in good agreement with the experimental values (326 and 323 nm). The largest shift in absorption maximum is displayed by Q1D2 (436 nm). The designed compounds (Q1D3–Q2D3) express absorption spectra with an increased border and with a reduced band gap compared to the parent compounds (Q1 and Q2). Natural bond orbital (NBO) investigations showed that the extended hyper conjugation and strong intramolecular interaction play significant roles in stabilising these systems. All molecules expressed significant NLO responses. A large value of \( \beta_{\text{max}} \) was elevated in Q1D2 (23 885.90 a.u.). This theoretical framework reveals the NLO response properties of novel quinoline–carbazole derivatives that can be significant for their use in advanced applications.

Introduction

The development of nonlinear optical (NLO) materials has attracted significant interest in fundamental and applied research.1 Both theoretical and experimental communities2−4 have largely been investigating NLO materials due to their promising applications in different fields, including nuclear science, medicine, chemical dynamics, solid-state physics, materials science, surface interface studies and biophysics.5 Moreover, NLO materials have also gained notable significance in different technologies, such as optical computing, dynamic image processing and optical communication.6−8 Therefore, different attempts are being made to model various materials which show NLO properties, such as natural and fabricated nanomaterials, organic and inorganic semiconductors, polymer frameworks and molecular dyes.9−13 Organic NLO materials can offer low production costs, low dielectric constants, high photoelectric coefficients and design flexibility. Usually, macroscopic NLO material properties originate from the hyperpolarizability of the NLO chromophore. Therefore, NLO molecules consist of donor (D)–acceptor (A) pairs which are linked to each other through π-conjugated electron bridges (D–π–A). To develop D–π–A chromophores, the nature of the donor and acceptor moieties and conjugated length have been
considered.\textsuperscript{14-19} Usually, electronic charge is delocalized in the π-bond framework of NLO organic materials. The first hyperpolarizability ($\beta_{\text{tot}}$) is associated with intramolecular charge transfer from the electron-donating moiety (D) via the π-conjugated spacers towards the electron-accepting moiety (A).\textsuperscript{20,21}

Several framework types have been reported in the literature, including D–A, D–π–A, D–π–π–A, D–A–π–A, D–D–π–A, D–π–A–π–D and A–π–D–π–A.\textsuperscript{22-26} The nature of both D and A moieties plays a critical role in developing a good NLO response and the literature is replete with a huge variety of π-linkers. Through assimilation of suitable D, π-conjugation spacers and A, a push–pull architecture has been built for designing A–D–π–π–A and D–A–D–π–π–A organic compounds. These push–pull arrangements decrease the recombination of charges, influence charge detachment, deepen the penetration range within higher wavelengths, magnify the asymmetric electronic distribution and decrease the HOMO–LUMO band gap, hence elevating the NLO response.\textsuperscript{26-32}

Quinoline and its derivatives have been widely studied in various areas, exhibiting a variety of practical applications: e.g., such compounds are used in optoelectronics due to their chemical and thermal stability, fluorescence and electron transporting capabilities and the possibility of their chemical modification.\textsuperscript{33} Quinoline has the ability to attract electrons and is a good candidate for an organic acceptor moiety. Carbazole derivatives are electron-rich (D) making them suitable for organic donor moieties and are frequently used in optoelectronics, especially in solar cell technologies, and as hole-transporter materials in organic light emitting diode (OLED) devices.\textsuperscript{34} In addition, the carbazole moiety can easily be modified by substitution at the 9-position, modifying the overall solubility and photophysical properties of the NLO molecule.\textsuperscript{35} In view of the acceptor and donor properties of these moieties, we have taken frameworks from two quinoline–carbazole based compounds (Q1 and Q2) recently synthesized by Slodek et al.\textsuperscript{36} and have built upon them to develop new compounds (Q1D1, Q1D2, Q1D3, Q2D1, Q2D2 and Q2D3) to study and explore the NLO response properties of quinoline–carbazole systems. We hope that this study will serve as a springboard for experimental chemists and physicists for the synthesis of compounds with excellent NLO response properties.

\section*{Computational procedure}

In the present analysis, the absorption spectra, natural bond orbital (NBO) analysis, electronic properties and $\beta$ results of Q1, Q2 and their derivatives were obtained by performing time-dependent density functional theory (TDDFT) and density functional theory (DFT) calculations. All computations were done using the Gaussian 09 program.\textsuperscript{37} Geometric optimization was performed in gas and dimethylsulfoxide (DSMO) as a solvent and without symmetry restriction at the 6-311G(d,p) basis set in combination with the CAM-B3LYP\textsuperscript{38} level of theory.\textsuperscript{39,40} For the confirmation of stable geometries and a stationary nature at the minimum energy, vibrational frequency analyses were carried out by applying identical functionals.\textsuperscript{41,42} Frontier molecular orbital (FMO) examination was performed with the CAM-B3LYP/6-311G(d,p) functional to calculate the energies of HOMO and LUMO and the energy difference between them. The natural bond orbital (NBO) investigation was performed using the same functionals for the approximation of charge transfer interactions between investigated compounds. In optimised geometries, TDDFT computations were implemented for the determination of the electronic transitions. UV-visible absorption spectra of the studied molecules were elucidated by performing TDDFT computations with the CAM-B3LYP/6-311G(d,p) basis set combination.\textsuperscript{43} To determine the solvent (DMSO) effect, a conductor-like polarizable continuum model (CPCM) was used.\textsuperscript{44} The Gaussian output file gave ten hyperpolarizability tensors ($\beta_{xxn}$, $\beta_{yyn}$, $\beta_{zzn}$, $\beta_{xyy}$, $\beta_{xzy}$, $\beta_{xyz}$, $\beta_{yzz}$, $\beta_{xzz}$, $\beta_{yzx}$, $\beta_{yzy}$) and six linear polarizability tensors ($\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$, $\alpha_{xy}$, $\alpha_{xz}$, $\alpha_{yz}$) along the $x$, $y$ and $z$ directions, respectively. Eqn (1) and (2) are used to calculate the volume of first hyperpolarizability ($\beta_{\text{tot}}$) and average polarizability ($\alpha$).\textsuperscript{44}

\begin{equation}
\alpha = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})
\end{equation}

\begin{equation}
\beta_{\text{tot}} = [(\beta_{xxn} + \beta_{yyn} + \beta_{zzn})^2 + (\beta_{xyy} + \beta_{xzy} + \beta_{xyz})^2 + (\beta_{yzz} + \beta_{xzz} + \beta_{yzx} + \beta_{yzy})]^2/12
\end{equation}

\section*{Results and discussion}

\subsection*{Design of A–D–π–A and D–A–D–π–A molecular models}

DFT calculations in this work were performed on molecules designed from the Q1 and Q2 parent structures to have good NLO properties. Compound Q1 is of the D–A type and Q2 is of D–A–D type. In these structures, the highly electron-rich carbazole moiety acts as an electron donor and the quinolone

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig_1.pdf}
\caption{A sketch map of two families of compounds. The first is designed from Q1 (donor–acceptor) and the second is designed from Q2 (donor–acceptor–donor) configurations.}
\label{fig:1}
\end{figure}
moiety as an electron acceptor. In all the designed molecules, these parent structures were modified by connection of a further acceptor moiety via a π spacer. This design strategy is set out in Fig. 1. In all cases, this π spacer was 2-(thiophen-2-yl) thiophene. Three different terminal acceptor moieties, shown in Fig. 2, were introduced to produce three designed compounds based on each of the two parent compounds Q1 and Q2.

Hence, the three compounds with A-D-π-A architecture designed from Q1 are Q1D1 (2-((5’-(2-(4-bromoquinolin-2-yl)-9H-carbazol-9-y1)-(2,2’-bithiophen)-5-yl)methylene)malonic acid); Q1D2 (2-((5’-(2-(4-bromoquinolin-2-yl)-9H-carbazol-9-yl)-(2,2’-bithiophen)-5-yl)methylene)malononitrile); Q1D3 (Z)-3-((5’-2-(4-bromoquinolin-2-yl)-9H-carbazol-9-yl)-(2,2’-bithiophen)-5-yl)-2-cyanoacrylic acid).

Similarly, three compounds with D-A-D-π-A architecture were designed from Q2: Q2D1 (2-((5’-(2-(9H-carbazol-2-yl)quinolin-4-yl)-9H-carbazol-9-yl)-(2,2’-bithiophen)-5-yl)methylene)malonic acid); Q2D2 (2-((5’-(2-(9H-carbazol-2-yl)quinolin-4-yl)-9H-carbazol-9-yl)-(2,2’-bithiophen)-5-yl)methylene)malononitrile); Q2D3 ((E)-3-((5’-(2-(9H-carbazol-2-yl)quinolin-4-yl)-9H-carbazol-9-yl)-(2,2’-bithiophen)-5-yl)-2-cyanoacrylic acid).

With the exception of the terminal acceptor shown in Fig. 2 and which is modulated in all compounds designed from Q1 and Q2, the D-A part is preserved throughout the designs. The structures of the investigated compounds (Q1, Q1D1-Q1D3, Q2, Q2D1-Q2D3) are portrayed in Fig. 3. DFT and TDDFT calculations were performed to investigate how π-conjugated spacers and various acceptors established with quinoline and carbazole units influence the NLO properties: (i) hyperpolarizability (β), (ii) polarizability (α) and (iii) absorption wavelength.

Electronic structure

FMO analysis is an excellent model to explain the chemical stability and the electronic and optical properties of molecules. In conjugated systems, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) determine numerous interactions between molecules, types of reaction, the UV-visible spectrum and fluorescence. The HOMO energy ($E_{\text{HOMO}}$), LUMO energy ($E_{\text{LUMO}}$) and HOMO–LUMO energy gap ($E_{\text{LUMO}} - E_{\text{HOMO}}$) are significant factors in understanding the chemical softness, hardness, dynamic stability and chemical reactivity of the compounds under investigation. Materials with a large HOMO–LUMO energy gap ($E_{\text{gap}}$) are considered to be hard molecules with high kinetic strength and low chemical reactivity. Conversely, compounds with a lower HOMO–LUMO energy gap are smooth molecules with lower stability and higher reactivity. These compounds are highly polarizable and show excellent NLO properties. Calculations of the energies of $E_{\text{HOMO}}$, $E_{\text{LUMO}}$ and their energy gap for the parent (Q1 and Q2) and designed (Q1D1-Q1D3 and Q2D1–Q2D3) molecules have been carried out using TDDFT computations and the results are shown in Table 1.

The data in Table 1 show that of the parent molecules, Q1 has the lower HOMO–LUMO energy gap (6.160 eV). Furthermore, the band gap is observed to be smaller in the designed molecules. For the Q1 family, Q1 has the highest $E_{\text{gap}}$ value (6.160 eV) and the HOMO–LUMO energy gap decreases in the order Q1 > Q1D1 > Q1D3 > Q1D2 to 5.047 eV. A similar effect on

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$E_{\text{HOMO}}$</th>
<th>$E_{\text{LUMO}}$</th>
<th>Band gap</th>
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<tr>
<td>Q1</td>
<td>-7.232</td>
<td>-1.072</td>
<td>6.160</td>
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<tr>
<td>Q1D1</td>
<td>-7.226</td>
<td>-1.793</td>
<td>5.433</td>
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<td>Q1D2</td>
<td>-7.189</td>
<td>-2.142</td>
<td>5.047</td>
</tr>
<tr>
<td>Q1D3</td>
<td>-7.362</td>
<td>-2.030</td>
<td>5.332</td>
</tr>
<tr>
<td>Q2</td>
<td>-7.196</td>
<td>-0.969</td>
<td>6.227</td>
</tr>
<tr>
<td>Q2D1</td>
<td>-7.171</td>
<td>-1.699</td>
<td>5.472</td>
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<td>Q2D2</td>
<td>-7.203</td>
<td>-2.151</td>
<td>5.052</td>
</tr>
<tr>
<td>Q2D3</td>
<td>-7.137</td>
<td>-1.934</td>
<td>5.203</td>
</tr>
</tbody>
</table>
$E_{\text{gap}}$ is seen in the Q2 family, with the energy gap being highest in Q2 (6.227 eV) and falling in the order Q2 > Q2D1 > Q2D3 > Q2D2 to 5.052 eV. Overall, the value of the $E_{\text{gap}}$ of all the investigated molecules increases in the order: Q1D2 < Q2D2 < Q2D3 < Q1D3 < Q1D1 < Q2D1 < Q1 < Q2. Thus, the introduction of a planar spacer linker to join different suitable acceptor units is an effective way to lower $E_{\text{gap}}$ and thus to enhance and influence the NLO properties. Of the terminal acceptors studied, 2-ethylidenemalononitrile (EMN) exhibits the greatest increase in the ordering relative to the compounds. Overall, the band gap is found to be low in Q2 family, with the energy gap being highest in the Q2 family. Thus, the introduction of different suitable acceptor units to the two donor carbazole units, while the LUMO density is concentrated on the acceptor quinoline part. The HOMO in Q2 is on the donor carbazole segment and the LUMO is on the acceptor quinoline part. The HOMO charge density is positioned partially on the bridge unit and largely on the terminal acceptor parts. Thus, significant charge transfer in the studied compounds was directed from the donor HOMO to an acceptor via by the π-spacers. This facilitation of charge transfer indicates that all the designed compounds should be excellent NLO materials.

Global reactivity parameters

The energy values of FMOs ($E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$) are useful for discovering global reactivity information, including global hardness ($\eta$), global softness ($\sigma$), global electrophilicity index ($\omega$), electron affinity (EA), ionization potential (IP), electronegativity ($\chi$) and the chemical potential ($\mu$)\textsuperscript{51-54} and calculated by utilizing eqn (3) and (4):

$$IP = -E_{\text{HOMO}}$$

$$EA = -E_{\text{LUMO}}$$

where EA is electron affinity (a.u.) and IP is the ionization potential (a.u.).

The chemical hardness ($\eta$), chemical potential ($\mu$) and electronegativity ($\chi$) have been calculated by utilizing Koopmans’s theorem and the following eqn (5)–(7):\textsuperscript{55,56}

$$X = \frac{(IP + EA)}{2} = -\frac{(E_{\text{LUMO}} + E_{\text{HOMO}})}{2}$$

$$\eta = \frac{(IP - EA)}{2} = -\frac{(E_{\text{LUMO}} - E_{\text{HOMO}})}{2}$$

$$\mu = \frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2}$$

The global softness ($\sigma$) is described by eqn (8):

$$\sigma = \frac{1}{2\eta}$$

An electrophilicity index ($\omega$) was introduced by Parr et al., as in eqn (9):

$$\omega = \frac{\mu^2}{2\eta}$$

Fig. 4 HOMOs and LUMOs of quinoline–carbazole based Q1 (A–D–π–A) and Q2 (D–A–D–π–A) families of molecules.
The results obtained from eqn (3)–(9) are collected in Table 2.

The global reactivity parameters relate to the reactivity of the molecules studied. For example, ionization potential relates to electrophilic nature, electron-donating ability and electronegativity relates to the ability of a compound to attract electrons. The negative values of these parameters in Table 2 correlate, therefore, with electron-donating ability and electronegativity, and diagonal and off-diagonal NBO Fock matrix elements, respectively. The results of NBO analysis for the two families of molecules are given in Table 3.

Four types of electronic transitions were commonly observed; $\sigma \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $\text{LP} \rightarrow \sigma^*$ and $\text{LP} \rightarrow \pi^*$. Among these $\pi \rightarrow \pi^*$ were most prominent while $\sigma \rightarrow \sigma^*$ were least dominant and $\text{LP} \rightarrow \sigma^*$ and $\text{LP} \rightarrow \pi^*$ were slightly dominant transitions. The presence of conjugation and charge transfer in these compounds can be examined by studying the $\pi \rightarrow \pi^*$ transitions. The most significant $\pi \rightarrow \pi^*$ electronic interactions are $\pi^*(C_{27}-C_{32}) \rightarrow \pi^*(C_{28}-C_{33})$, $\pi^*(C_{27}-C_{32}) \rightarrow \pi^*(C_{29}-C_{33})$, $\pi^*(C_{47}-C_{52}) \rightarrow \pi^*(C_{48}-C_{53})$ and $\pi^*(C_{47}-C_{52}) \rightarrow \pi^*(C_{48}-C_{53})$ with stabilization energies of 372.21, 34.05, 34.36 and 32.17 kcal mol$^{-1}$ found in Q1, Q1D1, Q1D2 and Q1D3, respectively. These excitations are the highest such transitions in the Q1 family.

Similarly the most feasible $\pi \rightarrow \pi^*$ interactions among the Q2 family of molecules were $\pi^*(C_{45}-C_{50}) \rightarrow \pi^*(C_{48}-C_{53})$, $\pi^*(C_{47}-C_{52}) \rightarrow \pi^*(C_{51}-C_{56})$, $\pi^*(C_{47}-C_{52}) \rightarrow \pi^*(C_{51}-C_{56})$ and $\pi^*(C_{47}-C_{52}) \rightarrow \pi^*(C_{48}-C_{53})$ with stabilization energies of 391.20, 34.85, 34.49 and 34.54 kcal mol$^{-1}$ in Q2, Q2D1, Q2D2 and Q2D3, respectively.

Significant resonance interactions were observed. In the Q1 family these are LP1(N$_{26}$) $\rightarrow \pi^*(C_{27}-C_{32})$, LP2(C3) $\rightarrow \pi^*(C_{9}-C_{14})$, LP1(N$_{36}$) $\rightarrow \pi^*(C_{27}-C_{32})$, and LP1(C$_{32}$) $\rightarrow \pi^*(C_{16}-C_{18})$ with stabilization energies of 46.95, 72.78, 40.09, and 78.49 kcal mol$^{-1}$ in Q1, Q1D1, Q1D2, and Q1D3, respectively. For the Q2 family the significant transitions from lone pair orbitals are LP1(N$_{53}$) $\rightarrow \pi^*(C_{25}-C_{30})$, LP2(O$_{78}$) $\rightarrow \pi^*(C_{74}-O_{79})$, LP1(N$_{28}$) $\rightarrow \pi^*(C_{25}-C_{30})$, and LP2(O$_{78}$) $\rightarrow \pi^*(C_{74}-O_{79})$ with stabilization energies of 47.19, 58.35, 46.86 and 57.92 kcal mol$^{-1}$ in Q2, Q2D1, Q2D2, and Q2D3, respectively.

Hence NBO investigation of these molecules indicates that the extended hyper conjugation and strong intramolecular transfer of charge plays a significant role in stabilizing these systems and provides evidence of charge transfer characteristics that are crucial for potential NLO properties.

**Nonlinear optical (NLO) properties**

NLO compounds are extensively used in signal processing, optical switches, communication technology and optical memory devices. The electronic characteristics of the entire compound are responsible for the optical response, which in turn is related to the nonlinear response (hyperpolarizabilities, $\beta$ and $\gamma$) and linear responses (polarizability, $\alpha$, etc.).

The linear and nonlinear responses of NLO materials arise from the electrical characteristics of the entire molecule. The NLO response properties of the Q1 and Q2 families of compounds have been estimated and the results for values of $\langle \alpha \rangle$ and $\beta$ are presented in Tables 4 and 5, respectively.

Table 4 shows that the values of average polarizability for parent compounds Q1 and Q2 are 393.065 and 576.195 a.u., respectively. The most prominent transitions in all analysed molecules are along the $x$-axis ($\alpha_{xx}$) and modification with different acceptor moieties affects the polarization values. In both Q1 and Q2 families, the parent molecule has the lowest average polarizability and the presence of the strong acceptor unit EMN gives rise to the highest value of average polarizability. That is, the family maximum average polarizability is shown by Q1D2 and Q2D2, with the latter having the largest value for the molecules studied. Average polarizability decreases across the studied molecules in the order Q2D2 $>$ Q2D1 $>$ Q2D3 $>$ Q1D3 $>$ Q1D1 $>$ Q2 $>$ Q1.

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**Table 2** Calculated global reactivity parameters using energies of HOMO and LUMO orbitals

<table>
<thead>
<tr>
<th>Comp</th>
<th>IP</th>
<th>EA</th>
<th>$X$</th>
<th>$\eta$</th>
<th>$\mu$</th>
<th>$\omega$</th>
<th>$\sigma$</th>
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</thead>
<tbody>
<tr>
<td>Q1</td>
<td>7.23</td>
<td>1.07</td>
<td>4.15</td>
<td>3.080</td>
<td>-4.152</td>
<td>2.798</td>
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<tr>
<td>Q1D1</td>
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<td>2.716</td>
<td>-4.509</td>
<td>3.742</td>
<td>0.18</td>
</tr>
<tr>
<td>Q1D2</td>
<td>7.18</td>
<td>2.14</td>
<td>4.66</td>
<td>2.523</td>
<td>-4.665</td>
<td>4.312</td>
<td>0.19</td>
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<tr>
<td>Q1D3</td>
<td>7.36</td>
<td>2.03</td>
<td>4.70</td>
<td>2.666</td>
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<tr>
<td>Q2</td>
<td>7.19</td>
<td>0.96</td>
<td>4.08</td>
<td>3.113</td>
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<tr>
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<tr>
<td>Q2D2</td>
<td>7.20</td>
<td>2.15</td>
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<td>4.329</td>
<td>0.19</td>
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<tr>
<td>Q2D3</td>
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<td>1.93</td>
<td>4.15</td>
<td>2.601</td>
<td>-4.035</td>
<td>3.953</td>
<td>0.19</td>
</tr>
</tbody>
</table>

$^a$ IP = ionization potential, EA = electron affinity, $X$ = electronegativity, $\mu$ = chemical potential, $\eta$ = global hardness, $\sigma$ = global softness and $\omega$ = global electrophilicity. Units are eV.
Dipole polarizability values (along the $x$-axis) are computed using eqn (11):

$$
\alpha \propto \frac{M_{gm}^2}{E_{gm}}
$$

(11)

In this equation $M_{gm}^2$ indicates the ground and $m^{th}$ excited state transition moment and $E_{gm}$ is the transition energy. In general, a molecule with large value of $M_{gm}^2$ and a smaller value of $E_{gm}$ will exhibit a high hyperpolarizability value. Hence, dipole polarizability is a quantitative measure of the NLO response properties of compounds. Second-order polarizability – first hyperpolarizability ($\beta_{oa}$) – values for the Q1 and Q2 families of compounds are shown in Table 5.

Table 5 shows that for the parent molecules the hyperpolarizability value of Q1 (5568.09 a.u.) is 1.2 times greater than...
molecules are significantly greater than for urea ($\beta_{tot}(\text{urea}) = 43$ a.u.), a standard molecule for the analysis of NLO response.\textsuperscript{29} Hyperpolarizability values of Q1, Q1D1–Q1D3, Q2, Q2D1–Q2D3 are determined to be 129 times, 335 times, 381 times, 106 times, 174 times, 389 times and 243 times higher than the second-order polarizability value of urea, respectively.

To examine the electronic excitations in the optimized geometries, TDDFT calculations were performed. TDDFT generally overestimates the excitation energies in case of charge transfer transitions and extended conjugated systems. It was therefore necessary to adopt a robust and high level of theory to model the UV-visible absorption spectrum of the studied compounds. For this purpose, TDDFT calculations were conducted using the CAM-B3LYP level with the 6-311G(d,p) basis set in DMSO solvent. In performing TDDFT calculations, the six most reduced singlet–singlet transitions were examined in Q1, Q2 and their derivatives. The results for the calculated absorption wavelength ($\lambda_{\text{max}}$), transition energy, nature of transitions ($E_{\text{ge}}$) and oscillator strength ($f_{\text{on}}$) are listed in Tables S17–S23 (ESI)\textsuperscript{†} while some important values of these compounds are shown in Table 6.

**UV-vis spectra analysis**

All the molecules show absorbance in the visible region. The calculated $\lambda_{\text{max}}$ values for Q1 and Q2 of 321 and 319 nm, respectively, are in good agreement with the experimentally reported values of 326 and 323 nm, respectively.\textsuperscript{36} Of the

<table>
<thead>
<tr>
<th>System</th>
<th>$\alpha_{xx}$/C0</th>
<th>$\alpha_{yy}$/C0</th>
<th>$\alpha_{zz}$/C0</th>
<th>$\alpha_{tot}$/C0</th>
</tr>
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<tbody>
<tr>
<td>Q1</td>
<td>644.744</td>
<td>396.922</td>
<td>137.529</td>
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<tr>
<td>Q1D1</td>
<td>955.102</td>
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<td>681.095</td>
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<th>System</th>
<th>$\beta_{xxx}$/C0</th>
<th>$\beta_{xxy}$/C0</th>
<th>$\beta_{xyy}$/C0</th>
<th>$\beta_{yxy}$/C0</th>
<th>$\beta_{xyz}$/C0</th>
<th>$\beta_{zxy}$/C0</th>
<th>$\beta_{zyz}$/C0</th>
<th>$\beta_{zzz}$/C0</th>
<th>$\beta_{total}$/C0</th>
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<tbody>
<tr>
<td>Q1</td>
<td>5702.17</td>
<td>884.16</td>
<td>−229.03</td>
<td>183.80</td>
<td>−10.97</td>
<td>11.08</td>
<td>−2.17</td>
<td>5568.09</td>
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<tr>
<td>Q1D1</td>
<td>9834.81</td>
<td>−6526.60</td>
<td>397.07</td>
<td>−3776.22</td>
<td>−16.26</td>
<td>128.33</td>
<td>55.11</td>
<td>14420.20</td>
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<tr>
<td>Q1D2</td>
<td>−12728.50</td>
<td>−11190.89</td>
<td>−4179.96</td>
<td>−5623.95</td>
<td>19.92</td>
<td>70.96</td>
<td>−65.46</td>
<td>23885.90</td>
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<tr>
<td>Q1D3</td>
<td>−11016.63</td>
<td>−7465.43</td>
<td>−806.15</td>
<td>−3600.90</td>
<td>−193.28</td>
<td>46.25</td>
<td>92.98</td>
<td>16392.40</td>
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<tr>
<td>Q2</td>
<td>−1653.41</td>
<td>2627.86</td>
<td>−673.04</td>
<td>1288.99</td>
<td>27.04</td>
<td>22.09</td>
<td>32.91</td>
<td>4570.66</td>
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<td>Q2D1</td>
<td>−6660.35</td>
<td>473.68</td>
<td>−493.84</td>
<td>2352.61</td>
<td>193.75</td>
<td>−65.34</td>
<td>−31.74</td>
<td>7498.18</td>
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<tr>
<td>Q2D2</td>
<td>−3633.41</td>
<td>5694.79</td>
<td>−7459.25</td>
<td>4279.34</td>
<td>−573.46</td>
<td>−298.39</td>
<td>510.96</td>
<td>16748.70</td>
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<td>Q2D3</td>
<td>−10000.88</td>
<td>−405.63</td>
<td>−498.86</td>
<td>2153.84</td>
<td>186.47</td>
<td>−79.76</td>
<td>−1.95</td>
<td>10452.70</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$E_{\text{ge}}$ (eV)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$f_{\text{on}}$</th>
<th>LHE</th>
<th>$M_{\text{LHE}}$ (a.u.)</th>
<th>MO transition\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>3.860</td>
<td>321 [326]\textsuperscript{b}</td>
<td>1.447</td>
<td>0.964</td>
<td>1.989</td>
<td>H – 1 → L (83%)</td>
</tr>
<tr>
<td>Q1D1</td>
<td>3.878</td>
<td>320</td>
<td>1.438</td>
<td>0.964</td>
<td>2.101</td>
<td>H – 1 → L + 1 (85%)</td>
</tr>
<tr>
<td>Q1D2</td>
<td>2.844</td>
<td>436</td>
<td>1.450</td>
<td>0.965</td>
<td>3.366</td>
<td>H – 1 → L (65%)</td>
</tr>
<tr>
<td>Q1D3</td>
<td>2.993</td>
<td>414</td>
<td>1.502</td>
<td>0.969</td>
<td>2.533</td>
<td>H – 1 → L (60%)</td>
</tr>
<tr>
<td>Q2</td>
<td>3.885</td>
<td>319 [323]\textsuperscript{b}</td>
<td>1.459</td>
<td>0.965</td>
<td>0.830</td>
<td>H – 1 → L (44%), H → L (32%)</td>
</tr>
<tr>
<td>Q2D1</td>
<td>3.912</td>
<td>317</td>
<td>1.283</td>
<td>0.948</td>
<td>0.140</td>
<td>H – 1 → L + 1 (69%)</td>
</tr>
<tr>
<td>Q2D2</td>
<td>3.874</td>
<td>320</td>
<td>1.455</td>
<td>0.965</td>
<td>2.442</td>
<td>H – 1 → L + 1 (55%)</td>
</tr>
<tr>
<td>Q2D3</td>
<td>3.954</td>
<td>314</td>
<td>1.184</td>
<td>0.934</td>
<td>2.046</td>
<td>H – 1 → L + 1 (46%)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}H = HOMO, L = LUMO, H – 1 = HOMO – 1, L + 1 = LUMO + 1 etc. \textsuperscript{b} Experimental values in parentheses are from ref. 36.
designed molecules, Q1D2 and Q2D3 show the highest $\lambda_{\text{max}}$ values. The calculated absorption spectra are shown in Fig. 5. Among all the studied compounds, the maximum absorption wavelength and minimum transition energy are observed in Q1D2.

Structural tailoring of compounds Q1 and Q2 modifies the contribution of different orbitals to the electronic transitions. In Q1, Q1D1–Q1D3, Q2, Q2D1–Q2D3, the crucial excited states are produced due to the promotion of electrons mainly from HOMO and HOMO – 1 to LUMO and LUMO + 1. This sort of charge transfer is required for NLO active compounds and forms the basis for the NLO responses of the compounds investigated here.

A crucial factor that determines the optical productivity of the molecules studied here is the light harvesting efficiency (LHE), which is determined using the $f_{\text{os}}$ values given by the TDDFT calculations. It is commonly observed that molecules with a large value of LHE exhibit high photocurrent properties. The value of LHE of the analyzed compounds is calculated using eqn (12) and the results are shown in Table 6.

$$\text{LHE} = 1 - 10^{-\gamma}$$ (12)

The LHE values of all studied compounds are similar to each other. Structure–property relationships help us to gain an understanding of the reason for an improved NLO in response to changing the nature of the acceptor units. Oudar and Chemla formulated a two-state model, eqn (13), which is frequently used in the literature for NLO estimation.

$$\beta_{\text{CT}} = \frac{\Delta \mu_{\text{gs}} f_{\text{gs}}}{E_{\text{gs}}^3}$$ (13)

In this model the product of oscillation strength ($f_{\text{gs}}$) and transition moment ($\Delta \mu_{\text{gs}}$) is directly proportional and the transition energy cube $E_{\text{gs}}^3$ is inversely proportional to $\beta$. Thus, compounds exhibiting a large $f_{\text{gs}}$ and $\Delta \mu_{\text{gs}} $ and small $E_{\text{gs}}^3$ exhibit good NLO response properties. These parameters were estimated and their values are shown in Table 5. The relationship between $\beta_{\text{tot}}$ values and the corresponding two-level model ($\Delta \mu_{\text{gs}} f_{\text{gs}}/E_{\text{gs}}^3$) values for the studied molecules are displayed in Fig. 6, in which the $\beta_{\text{tot}}$ and two-level model values can be seen to be in very good agreement with each other.

Conclusions

The purpose of the work was to explore A–D–π–A and D–A–D–π–A configured novel quinoline–carbazole based highly efficient nonlinear optical compounds with promising NLO properties. All designed compounds Q1D1–Q1D3 and Q2D1–Q2D3 show absorbance wavelength in the visible region with low transition energy and oscillating strength. The largest reduction in band gap was shown by Q1D2 and Q2D2. As the NLO properties of the studied molecules were shown to correlate well with the band gap energy, this demonstrated that, of the three terminal groups investigated, EMN has the greatest impact on NLO properties. NBO results showed that electrons are effectively moved by means of the π-conjugated linker from D to A, facilitating the development of a charge transfer state. The FMOs analysis demonstrates that $E_{\text{gap}}$ in the designed compounds is found to be narrow relative to the parent compounds. Furthermore, the LUMO is arranged over the acceptor moiety and partially on the π linker while the HOMO is delocalized over the donor group and the π-conjugated linker, which represents the intramolecular charge transfer from donor to acceptor moieties mediated through π-bridge linkers. Global reactivity results showed that the decreasing order of softness is: Q1D2 > Q2D2 > Q2D3 > Q1D3 > Q1D1 > Q2D1 > Q1 > Q2, which is exactly the same as the order of decreasing $E_{\text{gap}}$ and the reverse of the order of global hardness values. In general, all the designed compounds in this study have demonstrated large theoretical $\beta_{\text{tot}}$ values in the range of 4570.66 to 23 885.90 (a.u.). Among the studied compounds, Q2D2 has shown the highest $\langle \alpha \rangle$ value of 888.63 (a.u.) while the highest $\beta_{\text{tot}}$ was shown to be 23 885.90 (a.u.) in Q1D2. Moreover, $\beta_{\text{tot}}$ values of the studied molecules were demonstrated to be in broad agreement with the two-level model ($\Delta \mu_{\text{gs}} f_{\text{gs}}/E_{\text{gs}}^3$) values. The design of NLO materials is currently an active domain of research and this theoretical study provides valuable insight with which experimentalists can structure superior NLO materials for electronics and optics.

Fig. 6 Relationship between the $\beta_{\text{tot}}$ (red star) values and the corresponding $\Delta \mu_{\text{gs}} f_{\text{gs}}/E_{\text{gs}}^3$ (blue triangles) values for the investigated compounds.
Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References


