Correlated Study of Linear Optical Absorption in Lower Symmetry Coronene Derivatives

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Abstract

The electronic and optical properties of four different coronene derivatives with lower symmetry, namely, benzo[a] coronene (C_{28}H_{14}), naphtho[2,3a] coronene (C_{32}H_{16}), anthra[2,3a] coronene (C_{36}H_{18}) and naphtho[8,1,2abc] coronene (C_{30}H_{14}) were investigated. For the purpose, we performed electron-correlated calculations using screened and standard parameters in the π-electron Pariser-Parr-Pople (PPP) Hamiltonian, and the correlation effects were included, both for ground and excited states, using MRSDCI methodology. The PPP model Hamiltonian includes long range Coulomb interactions which increases the accuracy of our calculations. The results of our calculations predict that with the increasing sizes of the coronene derivatives, optical spectra are red shifted as well as the optical gaps decrease. In each spectrum, the first peak represents the optical gap which is moderately intense, while the more intense peaks appear at higher energies. Our computed spectra are in good agreement with the available experimental data.

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I. INTRODUCTION

Now-a-days, π-conjugated molecules are used for manufacturing immensely effective as well as low-cost electronic devices such as organic thin-film (or field-effect) transistors (OTFTs or OFETs)[1–4], solar cells,[5, 6] and light-emitting diodes (LEDs).[7–10] Polycyclic aromatic hydrocarbons (PAHs) are a class of π-conjugated molecules consisting of multiple aromatic rings, found to exist almost everywhere in the universe. A huge percentage of carbon in universe is present in the form of PAHs. From a technical point of view, this species of hydrocarbons is advantageous to society in several ways, but they are also carcinogenic to humans as well as other living beings. PAH molecules and their isomers exhibit very unique properties and have high optical sensitivity. Therefore, to utilize this class of molecules in technological applications, a thorough investigation of their electronic structure and related properties is needed.

In an earlier work involving our group,[11] electronic structure and optical properties of coronene and related molecules with relatively high D_{6h} point group symmetry were studied. In this work our aim is to study coronene derivatives with lower symmetry (C_{2v} or lower), so as to understand the role which symmetry plays in determining the electronic and optical properties of PAHs. For the purpose we employ a Pariser-Parr-Pople (PPP) model[12, 13] based correlated electron methodology, established in several of our earlier works.[14–21] In particular, we study the optical properties of benzo[a]coronene (C_{28}H_{14}), naphtho[2,3a]coronene (C_{32}H_{16}), anthra[2,3a]coronene (C_{36}H_{18}), and naphtho[8,1,2-abc]coronene (C_{30}H_{14}). So far several groups have studied these coronene derivatives experimentally. Khan measured the photo-absorption spectra of several cations of coronene and its derivatives, including benzo[a]coronene and naphtho[2,3a]coronene.[22] Bagley et al. reported the optical absorption spectra of six- to nine-ring PAHs including benzo[a]coronene, and naphtho[8,1,2-abc]coronene.[23] The ultra-violet spectra of many large PAHs, including benzo[a]coronene were studied by Fetzer et al.[24] Fluorescence emission spectra of all the molecules considered in this work were experimentally studied by Acree et al.[25] Given the fact that no previous calculations of optical properties of these molecules exist, our work is timely. These molecules are also interesting from another point of view; they can be seen as finite graphene fragments with hydrogen-passivated edges.

The remainder of this paper is organized as follows. In the next section, we discuss
the theoretical methodology adopted in this work. In section III, we present and discuss
the calculated optical absorption spectra of these molecules, and compare our results to
experiments, wherever possible. Finally, in section IV, we present our conclusions.

II. THEORETICAL APPROACH AND COMPUTATIONAL DETAILS

A. Geometry

The molecules considered in this work are shown in Fig. 1. It is assumed that all the
molecules lie in the \(xy\)-plane, with uniform bond lengths and bond angles of 1.4 Å, and 120°,
respectively. All the molecules belongs to the \(C_{2v}\) point group, along with a closed-shell \(^1A_1\)
Electronic ground state, except naphtho[8,1,2-abc]coronene, which has \(C_s\) point group, and
\(A'\) ground state. According to the dipole selection rule, the one photon excited states have
\(^1A_1\) (x-polarized) and \(^1B_2\) (y-polarized) symmetries for the \(C_{2v}\) molecules, while for the \(C_s\)
molecule they have \(^1A'\) (xy-polarized) symmetry. In this work, we only consider the excited
states corresponding to photons polarized in the plane of the molecule.

B. Pariser-Parr-Pople (PPP) model Hamiltonian

Calculations on the \(\pi\)-conjugated molecules considered in this work were performed
using a semi-empirical approach, based upon PPP model Hamiltonian,[12, 13] which can be
written as

\[
H_{PPP} = -\sum_{i,j,\sigma} t_{ij} (c^\dagger_{i\sigma} c_{j\sigma} + c^\dagger_{j\sigma} c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{i<j} V_{ij} (n_i - 1)(n_j - 1).
\]

In the above equation, \(c^\dagger_{i\sigma}\) (\(c_{i\sigma}\)) is the creation (annihilation) operator, \(i.e.,\) it creates
(annihilates) a \(\pi\)-electron with spin \(\sigma\), localized on \(i^{th}\) carbon atom. \(n_{i\sigma} = c^\dagger_{i\sigma} c_{i\sigma}\) indicates
the total number of \(\pi\)-electrons with spin \(\sigma\), whereas \(n_i = \sum_\sigma n_{i\sigma} = \sum_\sigma c^\dagger_{i\sigma} c_{i\sigma}\) denotes the
total number of \(\pi\)-electrons on \(i^{th}\) carbon atom. In the second and the third terms of Eq.
(1), \(U\) and \(V_{ij}\) represents the on-site and long-range Coulomb interactions, respectively. \(t_{ij}\)
denotes the one-electron hopping matrix element, which in this work, has been restricted
to nearest neighbors only, with the value \(t_0 = 2.4\) eV, in agreement with our previous
works on \(\pi\)-conjugated systems, such as conjugated polymers,[15, 16] polycyclic aromatic
Figure 1: Schematic diagram of coronene derivatives considered in this work. All the molecules are assumed to be in the in $xy$-plane. The yellow dots represent the carbon atoms, and the C-C bond lengths and bond angles are assumed to be 1.4 Å and 120°, respectively.

hydrocarbons,[14, 17–19] and graphene quantum dots.[20, 21]

To parameterize the Coulomb interactions, we used the Ohno relationship,[26]

$$V_{i,j} = \frac{U}{\kappa_{i,j}}(1 + 0.6117R_{i,j}^2)^{1/2},$$

where $U$ denotes on-site electron-electron repulsion term as discussed above, $\kappa_{i,j}$ indicates the dielectric constant of the system, using which we can include the screening effects, and $R_{i,j}$ is the distance between the $i^{th}$ and $j^{th}$ carbon atoms. In this paper, we computed the optical spectra using two types of Coulomb parameters: (a) screened parameters[27] [$U = 8.0$ eV, $\kappa_{i,j} = 2.0$ (i $\neq$ j) and $\kappa_{i,i} = 1.0$], and (b) standard parameters[26] [$U = 11.13$ eV, and $\kappa_{i,j} = 1.0$]. We have observed that our earlier calculations performed using the screened parameters were in better agreement with the experimental results, as compared to the standard parameter based ones.[16, 17]
C. Optical absorption spectrum

For computing the optical absorption spectrum of an electronic system, we need to obtain a good representation of its ground and excited state wave functions. To that end, we performed the calculations using the multi-reference singles-doubles configuration-interaction (MRSDCI) methodology, as implemented in the computer program MELD.[28] For the purpose, first we transformed the Hamiltonian from the site representation to the molecular orbital (MO) representation, which was achieved by performing mean field restricted Hartree-Fock (RHF) calculations using a code based on PPP model, developed in our group.[29] Then, a singles-doubles CI (SDCI) calculation was performed both for ground state, and excited states, by employing the transformed Hamiltonian, and choosing a correct single reference wave function. The computed excited state wave functions were used to calculate the optical absorption spectrum at SDCI level of theory. Next, the excited state wave functions contributing to the various peaks of optical spectra obtained using SDCI calculation were used as reference states for the MRSDCI calculations. Again the many-body wave functions of the excited states contributing to the various peaks of optical spectra obtained using MRSDCI calculation, were analyzed, and used as reference for the next level of MRSDCI calculation with lower cutoff of the contributing coefficients of the wave functions. This process is iterative, and was continued until the computed optical spectra was converged with the previous one within an acceptable tolerance. In our group, The MRSDCI approach has been used extensively.[14–18, 20, 21, 30–32]

The wave functions of the ground and the excited states thus obtained are used to compute the electric dipole matrix elements, as well as the optical absorption spectra $\sigma(\omega)$, by employing the following formula

$$\sigma(\omega) = 4 \pi \alpha \sum_i \frac{\omega_{i0} |\langle i | \hat{\mathbf{e}} \cdot \mathbf{r} | 0 \rangle|^2 \gamma^2}{(\omega_{i0} - \omega)^2 + \gamma^2},$$  \hspace{1cm} (3)

where $|0\rangle$ denotes the ground state wave function, $|i\rangle$ is the wave function of the $i$-th excited state, $\omega$, $\hat{\mathbf{e}}$, $\mathbf{r}$, $\alpha$, respectively, represent the frequency of the incident light, polarization direction of the incident light, the position operator, and the fine structure constant. Furthermore, $\omega_{i0}$ is the energy difference (in frequency units) between the ground state ($|0\rangle$), and the $i$-th excited state ($|i\rangle$), while $\gamma$ is the uniform lined width associated with each excited state energy level.
In Eq. 3, the summation over $i$ indicates a sum over infinite number of excited states, which, we restrict for practical reasons to excited states with excitation energies up to 10 eV.

### III. RESULTS AND DISCUSSION

In this section, we present and analyze the computed linear optical absorption spectra obtained using MRSDCI approach for the four different coronene derivative molecules considered in this work. To be familiar with the large scale nature of the MRSDCI calculations, we present the total number of spin-adapted configurations ($N_{\text{total}}$) i.e., the dimension of the CI matrix in Table I for all the symmetries of each molecule. The large numbers of spin-adapted configurations considered in these calculations indicate that the electron-correlation effects have been included adequately.
Table I: $N_{\text{total}}$ represents the total number of spin-adapted configurations included in the MRSDCI calculations for each symmetry of four different coronene derivatives. The superscripts 'a' and 'b' indicate the value of $N_{\text{total}}$ obtained using the screened and the standard parameters, respectively.

| Molecule                        | Point group | Symmetry | $N_{\text{total}}^a$ | $N_{\text{total}}^b$ |
|---------------------------------|-------------|----------|----------------------|----------------------|
| Benzo[a]coronene                | $C_{2v}$    | $A_1$    | 1107236              | 1359626              |
| (C$_{28}$H$_{14}$)              |             | $B_2$    | 688351               | 1598428              |
| Naphtho[2,3a]coronene           | $C_{2v}$    | $A_1$    | 1252070              | 2611234              |
| (C$_{32}$H$_{16}$)              |             | $B_2$    | 2018406              | 2622562              |
| Anthra[2,3a]coronene            | $C_{2v}$    | $A_1$    | 3541980              | 4778775              |
| (C$_{36}$H$_{18}$)              |             | $B_2$    | 4034925              | 6002917              |
| Naphtho[8,1,2-abc]coronene      | $C_1$       | $A$      | 2054952              | 4200367              |
| (C$_{30}$H$_{14}$)              |             |          |                      |                      |

A. Optical gap

In order to understand the influence of electron-correlation effects in a quantitative manner, in Table II we present the results on the HOMO-LUMO gap of these molecules using the independent-electron approaches, namely, the tight-binding (TB) model and the restricted Hartree-Fock (RHF) approach. Note that when we set $U=0$ (i.e. no electron-electron in-
teractions) in the PPP Hamiltonian (see Eqs. 1 and 2), we obtain the tight-binding model. The same table also contains the results on optical gaps of these molecules obtained using the PPP model and MRSDCI approach. Optical gaps obtained from electron-correlated calculations are counterparts of the HOMO-LUMO gaps of one-electron theory.

Table II: HOMO-LUMO band gap for four different coronene derivatives calculated using TB model as well as PPP model. In case of PPP model, the gap is computed considering screened (scr) and standard (std) parameter, separately, using both RHF and MRSDCI level of theory. At the MRSDCI level of theory, optical gap is the counterpart of the HOMO-LUMO (H-L) gap. In the last column, experimental values of the optical gaps (where available), are presented.

| Coronene Derivatives | TB model H-L gap (in eV) | PPP (RHF) H-L gap (in eV) | PPP (MRSDCI) Optical gap (in eV) | Optical gap (in eV) experiment |
|----------------------|--------------------------|-----------------------------|----------------------------------|-------------------------------|
| Benzo[a](C_{28}H_{14}) | 2.25 | 3.95 | 7.13 | 3.42 | 3.44 | 3.38 |
| Naphtho[2,3a](C_{32}H_{16}) | 1.89 | 3.57 | 6.71 | 2.93 | 3.32 | - |
| Anthra[2,3a](C_{36}H_{18}) | 1.49 | 3.14 | 6.23 | 2.70 | 3.10 | - |
| Naphtho[8,1,2-abc](C_{30}H_{14}) | 1.83 | 3.43 | 6.48 | 2.95 | 3.23 | 3.02 |

A careful observation of Table II provides the following important information: (a) for C_{2v} symmetry coronene derivatives, the gaps decrease with the increasing size, independently of the models and the methods used in this work, (b) in case of TB model, the computed
gaps are smaller than the results obtained using PPP model, (c) the gaps obtained using PPP-RHF level of theory with the standard parameters are much larger as compared to the other computed results, (d) the optical gaps, calculated by employing PPP-MRSDCI level of theory, are significantly red-shifted as compared to the gaps obtained from PPP-RHF level of theory, specially with the standard parameter calculations. For screened parameter calculations, the correlation-induced shifts are small, (e) the results of screened and standard parameters, obtained using PPP-MRSDCI level of theory are in good quantitative agreement with each for the smallest molecule, but differ somewhat for the larger ones.

1. Comparison with coronene ($C_{24}H_{12}$)

In a work involving our group, experimental measurements of the linear and non-linear optical absorption of coronene molecule ($D_{6h}$ symmetry) was performed, supported theoretically by calculations based on PPP-CI methodology. Measurements of linear absorption found optical gap near 3.55 eV, characterized by weak intensity, while the most intense peak was found to be at 4.1 eV.[11] The supporting theory correctly predicted the most intense peak, but was unable to predict the optical gap because the excited states near its location were found to be dipole forbidden because of electron-hole symmetry.[11] In case of coronene derivative molecules studied here, again the optical gap is characterized by weak intensity, however, theory is able to correctly predict it owing to the lower symmetries of these molecules. As far as quantitative comparison is concerned, for all the molecules studied here, the optical gap is lower than 3.55 eV measured for coronene.[11]

B. Linear optical absorption spectrum

In this section we present and discuss the calculated optical absorption spectra of the four coronene derivatives in detail. The calculations were performed using the MRSDCI approach, and the spectra are plotted in Figs. 2-5. Detailed information related to the excited states contributing to the spectra is presented in tables S1-S8 of the Supporting Information.

A careful examination of the spectra illustrates the following important points: (a) spectra obtained from screened parameter are always red-shifted as compared to the absorption
spectra computed using standard parameters, consistent with the similar shift observed for the HOMO-LUMO gap mentioned above, (b) with the increasing size, the absorption spectrum are red-shifted for the $C_{2v}$ symmetric coronene derivatives, and the first peak of the optical spectra appears due to the absorption of a photon, polarized along y-direction because of a transition from their ground state ($^1B_2$) to the $^1A_1$ excited state characterized by singly excited configuration $|H \rightarrow L\rangle$, which is the optical gap. For the $C_1$ symmetry structure, the first peak representing the optical gap is due to the absorption of a photon with mixed x-y polarization, to a state dominated again by $|H \rightarrow L\rangle$ configuration, (c) the first peak obtained from the screened parameter calculations, is moderately intense, whereas the standard parameter calculations predict the first peak to be of very low intensity for each molecule, (d) the position of the first peak and higher energy peaks have significant dependency on the Coulomb parameters employed in the calculations.

The experimental data for the optical gap is available only for benzo[a]coronene and naphtho[8,1,2-abc]coronene molecules, presented in the last column of the Table II. It is obvious from the table that the MRSDCI-PPP approach predicts the optical gaps much more accurately as compared to the TB model, and PPP-RHF approach. Therefore, we only compare the MRSDCI-PPP results with the experimental data. The first peak (3.38 eV) of the experimentally obtained spectra of benzo[a]coronene is in good agreement with the screened parameter value (3.42 eV), as well as the standard parameter one (3.44 eV). For naphtho[8,1,2-abc]coronene also, the experimental value of the optical gap (3.02 eV) is in good agreement with the screened parameter value (2.95 eV), but standard parameter value (3.23 eV) is significantly higher. This suggests that our screened parameter MRSDCI-PPP values of the optical gaps of the two other molecules, for which no experimental results are available, are likely to be close to the true values. Next, we discuss our MRSDCI results for the higher energy regions of the absorption spectra of individual molecules.

1. Benzo[a]coronene ($C_{28}H_{14}$)

The geometry of benzo[a]coronene is presented in Fig. 1(a). We computed the linear optical spectra of benzo[a]coronene, plotted in the Fig. 2, using both the Coulomb parameters, screened and standard. The dominant configurations contributing to the wave functions of the excited states of the corresponding peaks are provided in tables S1-S2 of the Supporting
Figure 2: The linear optical absorption spectrum of benzo[a]coronene (C\textsubscript{28}H\textsubscript{14}) computed by employing our PPP-MRSDCI methodology. Both the Coulomb parameters, screened and standard were separately used to compute the spectra. Uniform line-width of 0.1 eV was adopted to plot the absorption spectra. Subscripts of peak labels indicate the polarization direction of the photon absorbed in the transition.

From Fig. 2 it is obvious that, irrespective of the Coulomb parameters, there are two major peaks in the spectra, in addition to a number of less intense peaks. A solution phase experimental study of optical absorption in this molecule was performed by Bagley et al.\cite{23}. Our screened parameter peak positions are compared to the measured ones in Table III, and it is obvious that the two sets of values are in generally very good agreement with each other. On the other hand, for these peaks, the agreement between the experimental values and the standard parameter results was poor. From Table III it is obvious that, except for two peaks located at 3.47 and 4.09 eV, the quantitative agreement between our calculations and the experiments is excellent. Our screened parameter calculations predict an intense peak (peak VI) near 5.8 eV, however, there is no experimental data beyond 5.39 eV. We hope in future experiments this higher energy region of the spectrum will be probed, so as to verify whether or not the predictions of our computed spectrum in that region hold.

Next we analyze the wave functions of the excited states contributing to the two most intense peaks in the computed spectra. Peak II of both the spectra located at 3.67 eV...
(screened) and 4.38 eV (standard) are dominated by the singly excited configurations $|H \rightarrow L + 1\rangle$, and $|H - 1 \rightarrow L\rangle$, while the second intense features near 5.8 eV (peak VI, screened parameters) and 6.5 eV (peak V of standard parameters) are due to states whose wave functions are largely composed of the single excitations $|H - 3 \rightarrow L+2\rangle$, and $|H - 2 \rightarrow L+3\rangle$. For the weaker peaks of the absorption spectra also the contribution to the wave functions of excited states are derived mainly from the singly excited configurations.

Table III: Comparison of experimental peak locations with those calculated using the screened parameters, in the absorption spectrum of benzo[a]coronene.

| Molecule       | symmetry | Peak position (eV) | Peak position (eV) |
|----------------|----------|--------------------|--------------------|
|                |          | Expt. work[23]     | This work (Theory) |
| Benzo[a]coronene | -        | 3.47               | -                  |
| (C$_{28}$H$_{14}$) | $^1$A$_1$ | 3.61               | 3.67               |
|                | $^1$B$_2$ | 3.95               | 3.95               |
|                | -        | 4.09               | -                  |
|                | $^1$B$_2$ | 4.51               | 4.58               |
|                | $^1$A$_1$ | 4.65               | 4.66               |

2. Naphtho[2,3a]coronene ($C_{32}H_{16}$)

The geometry of the molecule is presented in the Fig. 1(b), whereas the Fig. 3 represents the linear optical photoabsorption spectra of naphtho[2,3a]coronene computed using PPP-CI approach with screened and standard parameters, separately. The configurations with significant contribution to the peaks of the optical spectra are presented in tables S3 and S4 of the Supporting Information with quantitative description of some other parameters.

The spectra obtained using both sets of Coulomb parameters starts with a very similar trend, and the second peaks of the absorption spectra, which are the most intense peaks, are followed by several weaker peaks. For this molecule, no experimental data is available for comparison with our computed photoabsorption spectra.

Next we discuss the wave functions of the excited states contributing to intense peaks of the computed spectra. The most intense peak (peak-II) of both the spectra near 3.48
4.19 eV (standard) appear due to the states whose wave functions are characterized by the two equally contributing singly-excited configurations $|H \to L + 1\rangle$ and $|H - 1 \to L\rangle$. Peak III near 3.88 eV (screened) and 4.50 eV (standard) is due to transition to states whose wave functions are dominated by the single excitation $|H - 1 \to L + 1\rangle$ with the photon polarized along the $y$-direction. In the screened parameter spectrum, peaks VII (6.00 eV) and VIII (6.30 eV) are the last two closely spaced intense peaks. For peak VII the excited state wave function is dominated by single excitation $|H - 3 \to L + 3\rangle$ and double excitations $|H - 2 \to L; H - 1 \to L\rangle$ and $|H \to L + 2; H \to L + 1\rangle$. The excited state corresponding to peak VIII, on the other hand, is strictly composed of the single excitations $|H - 4 \to L + 5\rangle$ and $|H - 5 \to L + 4\rangle$. The last peak (peak X, standard parameters) near 7.4 eV is due to a state whose wave functions are mainly derived from the singly excited configurations $|H - 3 \to L + 6\rangle$, $|H - 6 \to L + 3\rangle$, $|H - 9 \to L + 1\rangle$ and $|H - 1 \to L + 9\rangle$.

Figure 3: The linear optical absorption spectrum of naphtho[2,3a]coronene ($C_{32}H_{16}$) computed by employing our PPP-MRSDCI methodology. Both the Coulomb parameters, screened and standard were separately used to compute the spectra. Uniform line-width of 0.1 eV was adopted to plot the absorption spectra. Subscripts of peak labels indicate the polarization direction of the photon absorbed in the transition.
3. Anthra[2,3a]coronene (C\textsubscript{36}H\textsubscript{18})

The Fig. 4 presents the optical spectra of anthra[2,3a]coronene molecule calculated using PPP-CI methodology with both, screened and standard parameters. The dominant configurations contributing to the wave functions of the excited states of the corresponding peaks are provided in tables S5 and S6 of the Supporting Information.

The spectra computed using the two sets of Coulomb parameters have similar qualitative features in that both start with a small peak, followed by the maximum intensity peak. The higher energy regions of the two spectra contain a series of low to moderate intensity peaks. For this molecule also no experimental data on its optical absorption is available.

The many-body wave functions of the excited states corresponding to the second peak of both the spectra, which are the most intense ones, are dominated by the equally contributing single excitations |H → L + 2⟩, and |H → L + 2⟩, with the polarization along x-direction. Peaks III of both the spectra appear near 4.1 eV (screened) and 4.7 eV (standard) due to the excited states whose many-body wave functions are composed of equally contributing singly-excited configurations |H → L + 4⟩, and |H → L + 4⟩. Moderately intense peak IX at 7.3 eV (standard) is dominated by the singly excited configurations |H → L + 3⟩ and |H → L + 3⟩, whereas peak VIII at 6.5 eV (screened) exhibits strong mixing of single and double excitations |H → L + 6⟩, |H → L + 6⟩, |H → L + 1; H → L + 3⟩, and |H → L; H → L + 3⟩.
Figure 4: The linear optical absorption spectrum of anthra[2,3a]coronene (C_{36}H_{18}) computed by employing our PPP-MRSDCI methodology. Both the Coulomb parameters, screened and standard were separately used to compute the spectra. Uniform line-width of 0.1 eV was adopted to plot the absorption spectra. Subscripts of peak labels indicate the polarization direction of the photon absorbed in the transition.

4. Naphtho[8,1,2-abc]coronene (C_{30}H_{14})

The linear optical spectra of naphtho[8,1,2-abc]coronene is presented in Fig. 5 computed using both, screened, and standard parameters within the framework of PPP-CI methodology. The quantitative descriptions of the configurations of the wave functions contributing to the peaks of the optical spectrum are presented in tables S7 and S8 of the Supporting Information. The results of calculations performed using the screened parameters are compared with the experimental data in Table IV.
Figure 5: The linear optical absorption spectrum of naphtho[8,1,2-abc]coronene (C₃₀H₁₄) computed by employing our PPP-MRSDCI methodology. Both the Coulomb parameters, screened and standard were separately used to compute the spectra. Uniform line-width of 0.1 eV was adopted to plot the absorption spectra. Subscripts of peak labels indicate the polarization direction of the photon absorbed in the transition.

Table IV: Comparison of experimental peak locations with those calculated using the screened parameters, in the absorption spectrum of naphtho[8,1,2-abc]coronene.

| Molecule symmetry | Peak position (eV) | Peak position (eV) |
|-------------------|-------------------|-------------------|
|                   | Expt. work[23]    | This work (Theory)|
| Naphtho[8,1,2-abc]coronene | - | 3.19 | - |
| (C₃₀H₁₄)          | ¹A                | 3.34             | 3.43 |
|                   | -                 | 3.62             | -   |
|                   | -                 | 3.78             | -   |
|                   | ¹A                | 3.95             | 3.89 |
|                   | ¹A                | 4.75 - 4.83      | 4.56 - 4.72 |

From Fig. 5 it is obvious that, independent of Coulomb parameters employed, both the spectra contain two intense peaks, in addition to a number of weaker peaks. Bagley and Wornat carried out an experimental study of optical absorption of this molecule in
the solution phase.[23] In Table IV we have compared only the screened parameter based results with the measured peaks,[23] because we obtain much better agreement with those, as compared to standard parameter ones. For the second peak of the experimental spectrum at 3.19 eV, we find no candidate in our results. The location of third experimental peak (3.34 eV) is in decent agreement with the second peak (3.43 eV) of our computed spectra. Then, two more experimental peaks (3.62 eV and 3.78 eV) are also absent in our calculations, but peak III of our calculations at 3.89 eV is near the experimentally obtained peak near 3.95 eV. The calculated set of peaks in the range 4.56 - 4.72 eV slightly underestimate the experimental peaks in the 4.75 - 4.83 eV energy range.[23] Our calculated spectrum contains several peaks in the higher energy region as well. However, the experimental data terminates at 4.9 eV.[23] Therefore, we hope that the future experiments will extend to energies higher than this.

Now we discuss the wave functions of the excited states contributing to the peaks of the absorption spectra. The most intense peaks near 3.4 eV (screened) and 4.2 eV (standard) of both the absorption spectra are dominated by the singly excited configurations $|H - 1 \rightarrow L\rangle$ and $|H \rightarrow L + 1\rangle$, but the intense peaks obtained from the standard parameters are comparatively broader. The second intense peaks of both the optical spectra near 5.9 eV (screened) and 6.6 eV (standard) are broader, and appear due to the states whose wave functions consist mainly of single excitations $|H - 3 \rightarrow L + 4\rangle$, $|H - 4 \rightarrow L + 3\rangle$, and $|H - 2 \rightarrow L + 6\rangle$, $|H - 6 \rightarrow L + 2\rangle$, respectively.

IV. CONCLUSIONS

We calculated the optical properties of four different PAH molecules, namely, benzo[a]coronene ($C_{28}H_{14}$), naphtho[2,3a]coronene ($C_{32}H_{16}$), anthra[2,3a]coronene ($C_{36}H_{18}$), and naphtho[8,1,2-abc]coronene ($C_{30}H_{14}$) by employing the large scale electron-correlated PPP-CI methodology. Our computed spectra of benzo[a]coronene and naphtho[8,1,2-abc]coronene are in good agreement with available experimental data. We hope future experimental efforts to measure the higher energy region of optical spectra of these two molecules, and photoabsorption spectra of the other two molecules i.e., naphtho[2,3a]coronene, anthra[2,3a]coronene, against which our results could be benchmarked. A few important conclusions, which can be drawn from our calculations, are:
1. Our screened parameter results predict moderately intense absorption at the optical gap, while standard parameter predicts much smaller intensity.

2. For C$_{2v}$ symmetry coronene derivatives, the computed optical spectra is red shifted with the increasing size of the molecules, and the distance between the first two peak locations are also gradually increasing.

3. The computed optical spectra obtained using the screened parameters are in good agreement with the experimental data as compared to the standard parameter results.

4. As compared to coronene molecule, the optical gaps of all the four coronene derivatives studied here are smaller.

As far as future directions are concerned, it will be interesting to probe photoinduced excited state absorptions from the optical gap of these molecules. Given the fact that none of these molecules have inversion symmetry, it will be interesting to investigate whether or not they exhibit second order optical nonlinearities. Additionally, electroabsorption spectra of these molecules may provide further useful information about the nature of its low-lying excited states. Triplet excited states of these molecules may shed some light on the influence of electron correlation effects. At present, calculations along these directions are underway in our group, and the results will be reported in future works.

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Notes

The authors declare no competing financial interests.
ACKNOWLEDGEMENTS

Work of P.B. was supported by a Senior Research Fellowship offered by University Grants Commission, India.

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Supporting Information
Correlated Study of Linear Optical Absorption in Lower Symmetry Coronene Derivatives

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Table S1. Many particle wave functions of the excited states contributing to the peaks in the linear optical absorption spectra of benzo[a]coronene (C$_{24}$v) [Fig. 1a, main article] computed using the screened parameters in the PPP semi-empirical method and MRSDCI methodology. In the 'Peak' column, x, y and x&y subscripts indicate the polarization directions of absorbed photons. The excited state symmetries of the corresponding peaks are also presented below. $f = \frac{2\alpha^2}{3\pi \hbar^2} (E) \sum_j |\langle e | O_j | R \rangle|^2$ indicate the oscillator strength for a particular transition where $E$, $|e\rangle$, $|R\rangle$ and $O_j$ representing the peak energy, excited states of the corresponding peak, reference state and electric dipole operator for different Cartesian components, respectively. In the last column, the fractional numbers inside the first bracket represent the contributing coefficients to the CI wave-functions for each corresponding configuration.

| Peak  | Symmetry | E (eV) | $f$          | Wave function                      |
|-------|----------|--------|--------------|------------------------------------|
| I$_y$ | $^1$B$_2$| 3.42   | 2.898        | $|H \rightarrow L\rangle(0.8658)$ |
|       |          |        |              | $|H - 1 \rightarrow L + 1\rangle(0.1582)$ |
| II$_x$| $^1$A$_1$| 3.67   | 13.010       | $|H \rightarrow L + 1\rangle(0.6075)$ |
|       |          |        |              | $|H - 1 \rightarrow L\rangle(0.6075)$ |
| III$_y$| $^1$B$_2$| 3.95   | 6.345        | $|H - 1 \rightarrow L + 1\rangle(0.8540)$ |
|       |          |        |              | $|H \rightarrow L\rangle(0.1473)$ |
| IV$_{x&y}$| $^1$B$_2$| 4.58   | 0.608        | $|H \rightarrow L + 2\rangle(0.5913)$ |
|       | $^1$A$_1$| 4.66   | 0.362        | $|H - 2 \rightarrow L\rangle(0.5913)$ |
|       |          |        |              | $|H - 3 \rightarrow L\rangle(0.5379)$ |
|       |          |        |              | $|H \rightarrow L + 3\rangle(0.5379)$ |
| V$_x$ | $^1$A$_1$| 4.93   | 0.385        | $|H - 1 \rightarrow L + 2\rangle(0.4674)$ |
|       |          |        |              | $|H - 2 \rightarrow L + 1\rangle(0.4674)$ |
| VI$_{x&y}$| $^1$A$_1$| 5.78   | 6.957        | $|H - 3 \rightarrow L + 2\rangle(0.4952)$ |
|       | $^1$B$_2$| 5.83   | 2.919        | $|H - 2 \rightarrow L + 3\rangle(0.4952)$ |
|       | $^1$B$_2$| 6.08   | 2.726        | $|H - 4 \rightarrow L + 2\rangle(0.5333)$ |
|       |          |        |              | $|H - 2 \rightarrow L + 4\rangle(0.5333)$ |
|       |          |        |              | $|H - 3 \rightarrow L + 3\rangle(0.4925)$ |
|       |          |        |              | $|H - 1 \rightarrow L + 7\rangle(0.3147)$ |
| VII$_{x&y}$| $^1$B$_2$| 6.37   | 2.983        | $|H - 1 \rightarrow L + 7\rangle(0.4461)$ |
|       | $^1$A$_1$| 6.45   | 1.825        | $|H - 7 \rightarrow L + 1\rangle(0.4461)$ |
|       |          |        |              | $|H - 8 \rightarrow L\rangle(0.3886)$ |
|       |          |        |              | $|H \rightarrow L + 8\rangle(0.3886)$ |
| VIII$_{x&y}$| $^1$A$_1$| 6.71   | 0.727        | $|H - 3 \rightarrow L + 6\rangle(0.5157)$ |
|       | $^1$B$_2$| 6.83   | 2.254        | $|H - 6 \rightarrow L + 3\rangle(0.5157)$ |
|       |          |        |              | $|H - 2 \rightarrow L + 6\rangle(0.3769)$ |
|       |          |        |              | $|H - 6 \rightarrow L + 2\rangle(0.3769)$ |
Table S2. Many particle wave functions of the excited states contributing to the peaks in the linear optical absorption spectra of benzo[a]coronene (C$_{2v}$) [Fig. 1a, main article] computed using the standard parameters in the PPP semi-empirical method and MRSDCI methodology. In the 'Peak' column, x, y and x&y subscripts indicate the polarization directions of absorbed photons. The excited state symmetries of the corresponding peaks are also presented below. $f = \frac{2}{\pi\hbar^2} (\omega) \sum |\langle \psi | O_j | \phi \rangle|^2$ indicate the oscillator strength for a particular transition where $\omega$, $|\psi\rangle$, $|\phi\rangle$ and $O_j$ representing the peak energy, excited states of the corresponding peak, reference state and electric dipole operator for different Cartesian components, respectively. In the last column, the fractional numbers inside the first bracket represent the contributing coefficients to the CI wave-functions for each corresponding configuration.

| Peak | Symmetry | E (eV) | $f$ | Wave function |
|------|----------|------|-----|---------------|
| I$_y$ | $^1$B$_2$ | 3.44 | 0.649 | $|H \rightarrow L\rangle$(0.7528) $|H - 1 \rightarrow L + 1\rangle$(0.4314) |
| II$_{x&y}$ | $^1$A$_1$ | 4.38 | 12.181 | $|H \rightarrow L + 1\rangle$(0.5829) $|H - 1 \rightarrow L\rangle$(0.5829) |
| | $^1$B$_2$ | 4.45 | 6.315 | $|H - 1 \rightarrow L + 1\rangle$(0.6870) $|H \rightarrow L\rangle$(0.3860) |
| III$_x$ | $^1$A$_1$ | 5.37 | 0.508 | $|H - 3 \rightarrow L\rangle$(0.3829) $|H \rightarrow L + 3\rangle$(0.3829) |
| IV$_x$ | $^1$A$_1$ | 5.67 | 0.442 | $|H - 1 \rightarrow L + 2\rangle$(0.4246) $|H - 2 \rightarrow L + 1\rangle$(0.4246) |
| V$_{x&y}$ | $^1$A$_1$ | 6.54 | 11.628 | $|H - 2 \rightarrow L + 3\rangle$(0.3241) $|H - 3 \rightarrow L + 2\rangle$(0.3241) |
| | $^1$B$_2$ | 6.64 | 7.875 | $|H - 4 \rightarrow L + 2\rangle$(0.3611) $|H - 2 \rightarrow L + 4\rangle$(0.3611) |
| VI$_{x&y}$ | $^1$A$_1$ | 7.03 | 2.237 | $|H - 3 \rightarrow L + 4\rangle$(0.2981) $|H - 4 \rightarrow L + 3\rangle$(0.2981) |
| | $^1$B$_2$ | 7.17 | 5.022 | $|H - 5 \rightarrow L + 5\rangle$(0.3502) $|H - 3 \rightarrow L + 3\rangle$(0.2922) |
| | $^1$B$_2$ | 7.39 | 1.165 | $|H - 4 \rightarrow L + 6\rangle$(0.2894) $|H - 6 \rightarrow L + 4\rangle$(0.2894) |
Table S3. Many particle wave functions of the excited states contributing to the peaks in the linear optical absorption spectra of Naphtho[2,3a]coronene (C\(_{22}\)) [Fig. 1b, main article] computed using the screened parameters in the PPP semi-empirical method and MRSDCI methodology. In the 'Peak' column, x, y and x&y subscripts indicate the polarization directions of absorbed photons. The excited state symmetries of the corresponding peaks are also presented below. \( f = \frac{2\pi m_e E}{\hbar^2} \sum_j |\langle e|O_j|R \rangle|^2 \) indicate the oscillator strength for a particular transition where \( E, |e\rangle, |R\rangle \) and \( O_j \) representing the peak energy, excited states of the corresponding peak, reference state and electric dipole operator for different Cartesian components, respectively. In the last column, the fractional numbers inside the first bracket represent the contributing coefficients to the CI wave-functions for each corresponding configuration.

| Peak | Symmetry | E (eV) | \( f \) | Wave function |
|------|----------|--------|-----|--------------|
| I\(_x\) | \(^1\)B\(_2\) | 2.93 | 2.651 | \(|H \rightarrow L\rangle(0.8638)
| |  |  |  | \(|H - 1 \rightarrow L + 1\rangle(0.0667)\) |
| I\(_y\) | \(^1\)A\(_1\) | 3.48 | 17.442 | \(|H \rightarrow L + 1\rangle(0.6118)
| |  |  |  | \(|H - 1 \rightarrow L\rangle(0.6118)\) |
| III\(_x\) | \(^1\)B\(_2\) | 3.88 | 5.994 | \(|H - 1 \rightarrow L + 1\rangle(0.7912)
| |  |  |  | \(|H - 2 \rightarrow L\rangle(0.2232)\) |
| III\(_y\) | \(^1\)A\(_1\) | 4.33 | 1.119 | \(|H - 1 \rightarrow L + 2\rangle(0.5879)
| |  |  |  | \(|H - 2 \rightarrow L + 1\rangle(0.5879)\) |
| IV\(_x\&y\) | \(^1\)B\(_2\) | 4.45 | 3.117 | \(|H - 2 \rightarrow L + 2\rangle(0.8243)
| |  |  |  | \(|H \rightarrow L + 6\rangle(0.1066)\) |
| | \(^1\)A\(_1\) | 4.48 | 1.543 | \(|H \rightarrow L + 3\rangle(0.5364)
| |  |  |  | \(|H - 3 \rightarrow L\rangle(0.5364)\) |
| V\(_x\&y\) | \(^1\)B\(_2\) | 5.16 | 1.624 | \(|H - 2 \rightarrow L + 4\rangle(0.5825)
| |  |  |  | \(|H - 4 \rightarrow L + 2\rangle(0.5825)\) |
| | \(^1\)A\(_1\) | 5.21 | 3.558 | \(|H - 2 \rightarrow L + 3\rangle(0.5182)\)
| |  |  |  | \(|H - 3 \rightarrow L + 2\rangle(0.5182)\) |
| | \(^1\)A\(_1\) | 5.38 | 0.918 | \(|H \rightarrow L + 7\rangle(0.4545)\)
| |  |  |  | \(|H - 7 \rightarrow L\rangle(0.4545)\) |
| VI\(_x\) | \(^1\)A\(_1\) | 5.62 | 2.090 | \(|H - 1 \rightarrow L + 6\rangle(0.4026)\)
| |  |  |  | \(|H - 6 \rightarrow L + 1\rangle(0.4026)\) |
| VII\(_x\&y\) | \(^1\)A\(_1\) | 5.88 | 1.722 | \(|H \rightarrow L + 9\rangle(0.4545)\)
| |  |  |  | \(|H - 9 \rightarrow L\rangle(0.4545)\) |
| | \(^1\)B\(_2\) | 6.07 | 3.035 | \(|H \rightarrow L + 9\rangle(0.4929)\)
| |  |  |  | \(|H - 2 \rightarrow L + 3\rangle(0.4929)\) |
| |  |  |  | \(|H - 2 \rightarrow L; H - 1 \rightarrow L\rangle(0.2906)\) |
| VIII\(_x\&y\) | \(^1\)A\(_1\) | 6.28 | 2.475 | \(|H - 4 \rightarrow L + 5\rangle(0.2986)\)
| |  |  |  | \(|H - 5 \rightarrow L + 4\rangle(0.2986)\) |
| | \(^1\)B\(_2\) | 6.33 | 0.730 | \(|H - 2 \rightarrow L + 8\rangle(0.4299)\)
| |  |  |  | \(|H - 8 \rightarrow L + 2\rangle(0.4299)\) |
| IX\(_x\&y\) | \(^1\)B\(_2\) | 6.84 | 0.302 | \(|H - 6 \rightarrow L + 6\rangle(0.7206)\)
| |  |  |  | \(|H - 11 \rightarrow L + 1\rangle(0.1724)\) |
| | \(^1\)A\(_1\) | 7.03 | 0.662 | \(|H - 8 \rightarrow L + 3\rangle(0.5536)\)
| |  |  |  | \(|H - 3 \rightarrow L + 8\rangle(0.5536)\) |
Table S4. Many particle wave functions of the excited states contributing to the peaks in the linear optical absorption spectra of Naphtho[2,3a]coronene (C_{2v}) [Fig. 1b, main article] computed using the standard parameters in the PPP semi-empirical method and MRSDCI methodology. In the 'Peak' column, x, y and x&y subscripts indicate the polarization directions of absorbed photons. The excited state symmetries of the corresponding peaks are also presented below. \( f = \frac{2\mu_{\text{max}}}{\hbar^2}(E)\sum_j |\langle e|O_j|R\rangle|^2 \) indicate the oscillator strength for a particular transition where \( E \), \( |e\rangle \), \( |R\rangle \) and \( O_j \) representing the peak energy, excited states of the corresponding peak, reference state and electric dipole operator for different Cartesian components, respectively. In the last column, the fractional numbers inside the first bracket represent the contributing coefficients to the CI wave-functions for each corresponding configuration.

| Peak | Symmetry | E (eV) | \( f \) Wave function |
|------|----------|-------|------------------------|
| \( I_x \) | \(^1B_2\) | 3.32  | 1.187 \( |H \rightarrow L\rangle(0.7861) \) \( |H - 1 \rightarrow L + 1\rangle(0.3266) \) |
| \( I_y \) | \(^1B_2\) | 4.19  | 15.692 \( |H - 1 \rightarrow L\rangle(0.5783) \) \( |H \rightarrow L + 1\rangle(0.5783) \) |
| \( III_x \) | \(^1A_1\) | 4.50  | 3.826 \( |H - 1 \rightarrow L\rangle(0.6668) \) \( |H - 2 \rightarrow L\rangle(0.2850) \) |
| \( IV_{x&y} \) | \(^1B_2\) | 5.22  | 3.403 \( |H - 2 \rightarrow L + 2\rangle(0.5454) \) \( |H - 1 \rightarrow L + 3\rangle(0.2414) \) \( |H - 2 \rightarrow L + 1\rangle(0.4793) \) \( |H - 1 \rightarrow L + 2\rangle(0.4793) \) \( |H \rightarrow L + 3\rangle(0.4040) \) \( |H - 3 \rightarrow L\rangle(0.4040) \) |
| \( V_x \) | \(^1A_1\) | 5.96  | 1.833 \( |H - 1 \rightarrow L\rangle(0.4476) \) \( |H - 4 \rightarrow L + 1\rangle(0.4476) \) |
| \( VI_{x&y} \) | \(^1A_1\) | 6.24  | 3.457 \( |H - 2 \rightarrow L + 3\rangle(0.3554) \) \( |H - 2 \rightarrow L + 4\rangle(0.3554) \) |
| \( VII_x \) | \(^1A_1\) | 6.59  | 2.025 \( |H - 2 \rightarrow L\rangle(0.4343) \) \( |H - 4 \rightarrow L + 2\rangle(0.4343) \) |
| \( VIII_{x&y} \) | \(^1A_1\) | 6.85  | 0.772 \( |H - 9 \rightarrow L\rangle(0.2840) \) \( |H \rightarrow L + 9\rangle(0.2840) \) \( |H - 4 \rightarrow L + 4\rangle(0.4994) \) \( |H - 5 \rightarrow L + 5\rangle(0.2536) \) |
| \( IX_{x&y} \) | \(^1B_2\) | 7.04  | 1.970 \( |H - 3 \rightarrow L + 3\rangle(0.4102) \) \( |H - 7 \rightarrow L + 1\rangle(0.2334) \) \( |H - 3 \rightarrow L + 4\rangle(0.3228) \) \( |H - 4 \rightarrow L + 3\rangle(0.3228) \) |
| \( X_{x&y} \) | \(^1A_1\) | 7.34  | 3.468 \( |H - 3 \rightarrow L + 6\rangle(0.3729) \) \( |H - 6 \rightarrow L + 3\rangle(0.3729) \) \( |H - 9 \rightarrow L + 1\rangle(0.3128) \) \( |H - 1 \rightarrow L + 9\rangle(0.3128) \) |
Table S5. Many particle wave functions of the excited states contributing to the peaks in the linear optical absorption spectra of Anthra[2,3a]coronene (C_{22v}) [Fig. 1c, main article] computed using the screened parameters in the PPP semi-empirical method and MRSDCI methodology. In the 'Peak' column, x, y and x&y subscripts indicate the polarization directions of absorbed photons. The excited state symmetries of the corresponding peaks are also presented below. The oscillator strengths for a particular transition where $E$, $|e\rangle$, $|R\rangle$ and $O_j$ representing the peak energy, excited states and MRSDCI methodology. In the 'Peak' column, x, y and x&y subscripts indicate the polarization directions of absorbed photons. The excited state symmetries of the corresponding peaks are also presented below. $f = \frac{2}{\pi \alpha^2} \langle E \rangle \sum_j |\langle e|O_j|R\rangle|^2$ indicate the oscillator strength for a particular transition where $E$, $|e\rangle$, $|R\rangle$ and $O_j$ representing the peak energy, excited states of the corresponding peak, reference state and electric dipole operator for different Cartesian components, respectively. In the last column, the fractional numbers inside the first bracket represent the contributing coefficients to the CI wave-functions for each corresponding configuration.

| Peak   | Symmetry | E (eV) | $f$                      | Wave function                                      |
|--------|----------|--------|--------------------------|-----------------------------------------------------|
| I_y    | $^1B_2$  | 2.70   | 1.964                    | $|H \rightarrow L\rangle(0.8495)$                  |
|        |          |        |                          | $|H \rightarrow L+1\rangle(0.0707)$                |
| II_x&y | $^1B_2$  | 3.32   | 0.232                    | $|H \rightarrow L+1\rangle(0.5981)$                |
|        |          |        |                          | $|H \rightarrow L+1\rangle(0.5981)$                |
|        | $^1A_1$  | 3.41   | 17.298                   | $|H \rightarrow L+2\rangle(0.6023)$                |
|        |          |        |                          | $|H \rightarrow L+2\rangle(0.6023)$                |
| III_x&y| $^1B_2$  | 4.04   | 8.611                    | $|H \rightarrow 2\rightarrow L+2\rangle(0.6536)$  |
|        |          |        |                          | $|H \rightarrow 1\rightarrow L+1\rangle(0.4869)$  |
|        | $^1A_1$  | 4.16   | 4.877                    | $|H \rightarrow 2\rightarrow L+1\rangle(0.5713)$  |
|        |          |        |                          | $|H \rightarrow 1\rightarrow L+2\rangle(0.5713)$  |
| IV_x&y | $^1B_2$  | 4.30   | 1.698                    | $|H \rightarrow 5\rightarrow L\rangle(0.5545)$    |
|        |          |        |                          | $|H \rightarrow 5\rightarrow L\rangle(0.5545)$    |
|        | $^1A_1$  | 4.40   | 3.663                    | $|H \rightarrow 4\rightarrow L\rangle(0.5701)$    |
|        |          |        |                          | $|H \rightarrow 4\rightarrow L\rangle(0.5701)$    |
| V_x&y  | $^1A_1$  | 4.98   | 0.877                    | $|H \rightarrow 4\rightarrow L+1\rangle(0.3220)$  |
|        |          |        |                          | $|H \rightarrow 1\rightarrow L+4\rangle(0.3220)$  |
|        | $^1B_2$  | 5.10   | 0.342                    | $|H \rightarrow 7\rightarrow L\rangle(0.4830)$    |
|        |          |        |                          | $|H \rightarrow 7\rightarrow L\rangle(0.4830)$    |
|        | $^1A_1$  | 5.12   | 0.851                    | $|H \rightarrow 8\rightarrow L\rangle(0.3172)$    |
|        |          |        |                          | $|H \rightarrow 8\rightarrow L\rangle(0.3172)$    |
| VI_x   | $^1A_1$  | 5.33   | 1.948                    | $|H \rightarrow 8\rightarrow L\rangle(0.4022)$    |
|        |          |        |                          | $|H \rightarrow 8\rightarrow L\rangle(0.4022)$    |
| VII_x&y| $^1A_1$  | 5.90   | 2.248                    | $|H \rightarrow 10\rightarrow L\rangle(0.4076)$   |
|        |          |        |                          | $|H \rightarrow 10\rightarrow L\rangle(0.4076)$   |
|        | $^1B_2$  | 6.08   | 2.730                    | $|H \rightarrow 3\rightarrow L+3\rangle(0.4667)$  |
|        |          |        |                          | $|H \rightarrow 5\rightarrow L+5\rangle(0.2173)$  |
| VIII_x&y| $^1A_1$ | 6.50   | 1.508                    | $|H \rightarrow L+1; H \rightarrow L+3\rangle(0.3760)$ |
|        |          |        |                          | $|H \rightarrow 1\rightarrow L; H \rightarrow 3\rightarrow L\rangle(0.3760)$ |
|        | $^1B_2$  | 6.50   | 1.338                    | $|H \rightarrow 6\rightarrow L+6\rangle(0.4974)$  |
|        |          |        |                          | $|H \rightarrow 5\rightarrow L+5\rangle(0.4342)$  |
| IX_x&y | $^1B_2$  | 6.78   | 3.160                    | $|H \rightarrow 7\rightarrow L+5\rangle(0.5244)$  |
|        |          |        |                          | $|H \rightarrow 5\rightarrow L+7\rangle(0.5244)$  |
Table S6. Many particle wave functions of the excited states contributing to the peaks in the linear optical absorption spectra of Anthra[2,3a]coronene (C\textsubscript{21}H\textsubscript{16}) [Fig. 1c, main article] computed using the standard parameters in the PPP semi-empirical method and MRSDCI methodology. In the 'Peak' column, x, y and x\&y subscripts indicate the polarization directions of absorbed photons. The excited state symmetries of the corresponding peaks are also presented below.  

\[ f = \frac{2e^2 \mu_{eR}}{\hbar c} \sum |\langle e | O_j | R \rangle|^2 \]

indicate the oscillator strength for a particular transition where \(E\), \(|e\rangle\), \(|R\rangle\) and \(O_j\) representing the peak energy, excited states of the corresponding peak, reference state and electric dipole operator for different Cartesian components, respectively. In the last column, the fractional numbers inside the first bracket represent the contributing coefficients to the CI wave-functions for each corresponding configuration.

| Peak | Symmetry | E (eV) | \(f\) | Wave function |
|------|----------|--------|------|-------------|
| I\textsubscript{y} | \(1\)B\textsubscript{2} | 3.10 | 1.561 | \(|H \rightarrow L\rangle(0.8104)\) | \(|H - 2 \rightarrow L + 2\rangle(0.1950)\) |
| II\textsubscript{x} | \(1\)A\textsubscript{1} | 4.10 | 19.168 | \(|H - 2 \rightarrow L\rangle(0.5721)\) | \(|H \rightarrow L + 2\rangle(0.5721)\) |
| III\textsubscript{y} | \(1\)B\textsubscript{2} | 4.71 | 2.906 | \(|H \rightarrow L + 4\rangle(0.3390)\) | \(|H - 4 \rightarrow L\rangle(0.3390)\) |
| IV\textsubscript{x\&y} | \(1\)B\textsubscript{2} | 4.99 | 2.144 | \(|H - 1 \rightarrow L + 1\rangle(0.4079)\) | \(|H - 2 \rightarrow L + 3\rangle(0.3218)\) |
| | \(1\)A\textsubscript{1} | 5.12 | 4.876 | \(|H - 2 \rightarrow L + 1\rangle(0.4783)\) | \(|H - 1 \rightarrow L + 2\rangle(0.4783)\) |
| | \(1\)B\textsubscript{2} | 5.15 | 1.693 | \(|H - 1 \rightarrow L + 1\rangle(0.3198)\) | \(|H - 1 \rightarrow L + 4\rangle(0.2917)\) |
| V\textsubscript{x\&y} | \(1\)A\textsubscript{1} | 5.90 | 2.332 | \(|H - 6 \rightarrow L\rangle(0.3121)\) | \(|H \rightarrow L + 6\rangle(0.3121)\) |
| | \(1\)B\textsubscript{2} | 5.94 | 0.740 | \(|H - 5 \rightarrow L + 1\rangle(0.3600)\) | \(|H - 1 \rightarrow L + 5\rangle(0.3600)\) |
| VI\textsubscript{x} | \(1\)A\textsubscript{1} | 6.24 | 1.454 | \(|H - 8 \rightarrow L\rangle(0.3152)\) | \(|H \rightarrow L + 8\rangle(0.3152)\) |
| VII\textsubscript{x\&y} | \(1\)A\textsubscript{1} | 6.90 | 1.418 | \(|H - 7 \rightarrow L + 2\rangle(0.2677)\) | \(|H - 2 \rightarrow L + 7\rangle(0.2677)\) |
| | \(1\)B\textsubscript{2} | 6.93 | 2.132 | \(|H - 5 \rightarrow L + 5\rangle(0.2927)\) | \(|H - 6 \rightarrow L + 6\rangle(0.2493)\) |
| VIII\textsubscript{x\&y} | \(1\)B\textsubscript{2} | 7.06 | 1.157 | \(|H - 6 \rightarrow L + 6\rangle(0.2126)\) | \(|H - 4 \rightarrow L + 4\rangle(0.2085)\) |
| | \(1\)A\textsubscript{1} | 7.10 | 2.757 | \(|H - 8 \rightarrow L + 1\rangle(0.3200)\) | \(|H - 1 \rightarrow L + 8\rangle(0.3200)\) |
| IX\textsubscript{x\&y} | \(1\)A\textsubscript{1} | 7.29 | 1.751 | \(|H - 5 \rightarrow L + 3\rangle(0.4112)\) | \(|H - 3 \rightarrow L + 5\rangle(0.4112)\) |
| | \(1\)B\textsubscript{2} | 7.30 | 4.616 | \(|H - 3 \rightarrow L + 3\rangle(0.3333)\) | \(|H - 4 \rightarrow L + 4\rangle(0.3218)\) |
Table S7. Many particle wave functions of the excited states contributing to the peaks in the linear optical absorption spectra of naphtho[8,1,2-abc]coronene (C₁) [Fig. 1d, main article] computed using the screened parameters in the PPP semi-empirical method and MRSDCI methodology. In the ‘Peak’ column, x, y and x&y subscripts indicate the polarization directions of absorbed photons. The excited state symmetries of the corresponding peaks are also presented below. \( f (= \frac{2 \times \text{Im}^2 (E) \sum_j |\langle e|O_j|R \rangle|^2) \) indicate the oscillator strength for a particular transition where \( E \), \( |e \rangle \), \( |R \rangle \) and \( O_j \) representing the peak energy, excited states of the corresponding peak, reference state and electric dipole operator for different Cartesian components, respectively. In the last column, the fractional numbers inside the first bracket represent the contributing coefficients to the CI wave-functions for each corresponding configuration.

| Peak     | Symmetry | E (eV) | \( f \)   | Wave function                                                                 |
|----------|----------|--------|-----------|--------------------------------------------------------------------------------|
| IX_x&y   | \(^1\text{A}\)  | 2.95   | 4.123     | \( |H \rightarrow L\rangle(0.8665)\) \( |H - 1 \rightarrow L + 1\rangle(0.0766)\) |
| II_x&y   | \(^1\text{A}\)  | 3.43   | 12.024    | \( |H - 1 \rightarrow L\rangle(0.6096)\) \( |H \rightarrow L + 1\rangle(0.6096)\) |
| III_x&y  | \(^1\text{A}\)  | 3.89   | 3.940     | \( |H - 1 \rightarrow L + 1\rangle(0.6975)\) \( |H - 2 \rightarrow L\rangle(0.3205)\) |
| IV_x&y   | \(^1\text{A}\)  | 4.56   | 1.023     | \( |H - 2 \rightarrow L + 1\rangle(0.4278)\) \( |H - 1 \rightarrow L + 2\rangle(0.4278)\) |
|          |          |        | 4.72      | \( |H - 3 \rightarrow L + 1\rangle(0.5139)\) \( |H - 1 \rightarrow L + 3\rangle(0.5139)\) |
|          |          |        | 0.841     |                                                |
| V_x&y    | \(^1\text{A}\)  | 5.03   | 1.974     | \( |H - 4 \rightarrow L + 1\rangle(0.6446)\) \( |H - 1 \rightarrow L + 4\rangle(0.2761)\) |
| VI_x&y   | \(^1\text{A}\)  | 5.54   | 1.877     | \( |H - 6 \rightarrow L + 1\rangle(0.4299)\) \( |H - 1 \rightarrow L + 6\rangle(0.4299)\) |
| VII_x&y  | \(^1\text{A}\)  | 5.72   | 2.535     | \( |H - 8 \rightarrow L\rangle(0.4521)\) \( |H \rightarrow L + 8\rangle(0.4521)\) |
| VIII_x&y | \(^1\text{A}\)  | 5.91   | 4.752     | \( |H - 3 \rightarrow L + 4\rangle(0.3762)\) \( |H - 4 \rightarrow L + 3\rangle(0.3762)\) |
| IX_x&y   | \(^1\text{A}\)  | 6.39   | 2.840     | \( |H - 1 \rightarrow L + 8\rangle(0.2899)\) \( |H - 8 \rightarrow L + 1\rangle(0.2899)\) |
Table S8. Many particle wave functions of the excited states contributing to the peaks in the linear optical absorption spectra of naphtho[8,1,2-abc]coronene (C$_{224}$) [Fig. 1d, main article] computed using the standard parameters in the PPP semi-empirical method and MRSDCI methodology. In the 'Peak' column, x, y and x&y subscripts indicate the polarization directions of absorbed photons. The excited state symmetries of the corresponding peaks are also presented below. $f (= 2 \times 3 \times \hbar^2 \sum_j |\langle e | O_j | R \rangle|^2$) indicate the oscillator strength for a particular transition where $E$, $|e\rangle$, $|R\rangle$ and $O_j$ representing the peak energy, excited states of the corresponding peak, reference state and electric dipole operator for different Cartesian components, respectively. In the last column, the fractional numbers inside the first bracket represent the contributing coefficients to the CI wave-functions for each corresponding configuration.

| Peak  | Symmetry | E (eV) | $f$ | Wave function |
|-------|----------|--------|-----|---------------|
| I$_{x&y}$ | $^1A$ | 3.23 | 1.810 | $|H \rightarrow L\rangle(0.7986)$ $|H - 1 \rightarrow L + 1\rangle(0.3175)$ |
| II$_{x&y}$ | $^1A$ | 3.98 | 4.083 | $|H - 2 \rightarrow L\rangle(0.4359)$ $|H \rightarrow L + 2\rangle(0.4359)$ |
| III$_{x&y}$ | $^1A$ | 4.21 | 6.136 | $|H - 1 \rightarrow L\rangle(0.4236)$ $|H \rightarrow L + 1\rangle(0.4236)$ |
| IV$_{x&y}$ | $^1A$ | 4.37 | 4.586 | $|H - 1 \rightarrow L + 1\rangle(0.6742)$ $|H \rightarrow L\rangle(0.2422)$ |
| V$_{x&y}$ | $^1A$ | 5.04 | 0.741 | $|H - 6 \rightarrow L\rangle(0.3924)$ $|H \rightarrow L + 6\rangle(0.3924)$ |
| VI$_{x&y}$ | $^1A$ | 5.41 | 1.648 | $|H - 1 \rightarrow L + 2\rangle(0.3027)$ $|H - 2 \rightarrow L + 1\rangle(0.3027)$ |
| VII$_{x&y}$ | $^1A$ | 5.75 | 1.905 | $|H - 2 \rightarrow L + 2\rangle(0.3136)$ $|H \rightarrow L; H - 1 \rightarrow L\rangle(0.2754)$ |
| VIII$_{x&y}$ | $^1A$ | 6.59 | 3.736 | $|H - 2 \rightarrow L + 6\rangle(0.2730)$ $|H - 6 \rightarrow L + 2\rangle(0.2730)$ |
| IX$_{x&y}$ | $^1A$ | 7.11 | 3.910 | $|H - 5 \rightarrow L + 5\rangle(0.2417)$ $|H - 1 \rightarrow L; H - 1 \rightarrow L + 1\rangle(0.2375)$ |