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Radiation Effects from First Principles: The Role of Excitons in Electronic- Excited Processes

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Radiation Effects from First Principles: The Role of Excitons in Electronic-Excited Processes

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Abstract

Electron-hole pairs, or excitons, are created within materials upon optical excitation or irradiation with X-rays/charged particles. The ability to control and predict the role of excitons in these energetically-induced processes would have a tremendous impact on understanding the effects of radiation on materials. In this report, the excitonic effects in large cycloparaphenylene carbon structures are investigated using various first-principles methods. These structures are particularly interesting since they allow a study of size-scaling properties of excitons in a prototypical semi-conducting material. In order to understand these properties, electron-hole transition density matrices and exciton binding energies were analyzed as a function of size. The transition density matrices allow a global view of electronic coherence during an electronic excitation, and the exciton binding energies give a quantitative measure of electron-hole interaction energies in these structures. Based on overall trends in exciton binding energies and their spatial delocalization, we find that excitonic effects play a vital role in understanding the unique photoinduced dynamics in these systems.

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Introduction

Electron-hole pairs, or excitons, can be created within materials via optical excitation and by irradiation with X-rays or charged particles. Within a semi-classical view, an exciton is an excited electronic state of the material with an energy-level structure that is similar to a hydrogen atom (Figure 1). In an extended solid, this localized electron-hole pair can migrate through the material and create defects by interacting with the surrounding atoms. Depending on the type of excitation, excitons can have energies ranging from high-energy K-shell excitations or low-energy excitations close to the band gap.

Figure 1. Schematic of an exciton in an insulating crystal. Upon electronic excitation, an electron-hole pair is produced which can migrate through the crystal lattice.

An ability to predict and understand the behavior of excitons in materials is necessary for our fundamental understanding of electronic excitations and for designing new functional materials and devices. In this report, we explore the applicability of first-principles methods to predict excitonic properties as a function of size, shape, and composition. We focus on cycloparaphenylene carbon nanostructures (Figure 2) since they allow a study of size-scaling properties of excitons in a prototypical semi-conducting material. In particular, since cycloparaphenylene nanostructures are composed of aromatic subunits with radially-oriented *p* orbitals, these materials can support mobile charge carriers on the delocalized valence and conduction orbitals along the backbone chain.¹⁻³ As a result, cycloparaphenylenes and other well-ordered macrocycles may find applications as conducting materials in molecular electronics, organic field-effect transistors (OFETs), and nonlinear optics (NLOs) due to their unique optoelectronic properties.⁴⁻⁹

Figure 2. [N]-cycloparaphenylenes with $N = 9, 12$, and 18.

Each cycloparaphenylene is composed solely of phenyl rings sequentially connected in the *para* position to form a single nanoring.

A peculiar feature of these cycloparaphenylenes is their unusual excited-state properties as a function of molecular size. Specifically, as the carbon nanoring size is increased, the lowest computed absorption energy becomes larger. This result is surprising and counterintuitive to our usual expectations. For example, our chemical intuition from organic chemistry tells us that as the number of repeat units in a macromolecule increases, the distance between molecular energy levels diminishes, effectively decreasing the optical absorption gap. This trend (which actually arises from quantum confinement effects^{10a}) qualitatively describes the variation of absorbance properties in π -conjugated systems as the number of monomer units increase in a polymer. However, in the case of cyclic nanorings, the excitation energies as a function of size seem to contradict this quantum-confinement-effect argument.^{10b} To rationalize these trends, with a view of understanding the nature of electronic excitations in these nanorings, we have carried out *ab initio* calculations on both cyclic and linear paraphenylenes (Figure 3) comprised of 5 to 18

phenyl repeat units each. Results obtained from time-dependent density functional theory (TDDFT) give electronic band gaps, optical absorption energies, and oscillator strengths which can be used to estimate exciton binding energies as a function of paraphenylene size. The TDDFT calculations also allow us to perform a two-dimensional real-space analysis of transition densities which represent coherent electronic transitions between ground- and electronically-excited states.¹¹⁻¹⁹ These transition densities provide a panoramic view of electron-hole coherence and exciton delocalization in each of the paraphenylene systems. Based on overall trends in exciton binding energies and their spatial delocalization, we find that excitonic effects play a significant role in understanding the unique photoinduced dynamics of these cycloparaphenylene nanoring systems.

Figure 3. Molecular structures and atom labels for (a) cyclic paraphenylenes and (b) linear paraphenylenes. The specific atom numbers depicted in these figures define an ordered basis for generating the density matrices discussed in the Theory and Methodology section.

Theory and Methodology

The cyclic and linear paraphenylenes ($N = 5 - 18$) analyzed in this work are shown in Figure 3. All quantum chemical calculations were carried out with the parameter-free PBE0 hybrid density functional which incorporates a fixed combination of 25% Hartree-Fock exchange and Perdew's GGA corrections in the correlation contribution.²⁰ Previous investigations by Tretiak et al. have shown that the use of pure local and gradient-corrected functionals (i.e., LDA and PBE) results in unphysical unbound exciton states, while hybrid functionals partially overcome this problem by mixing in a fraction of nonlocal Hartree-Fock exchange.^{15,16} Based on their studies, we have chosen the PBE0 functional for this work since the PBE0 kernel provides a balanced description of neutral excitons (both singlets and triplets) in conjugated polymers and carbon nanotubes.^{15,16,21-24}

Ground-state geometries of all cyclic and linear paraphenylenes were optimized at the PBE0/6-31G(d,p) level of theory. Geometry optimizations were calculated without symmetry constraints, and root-mean-squared forces converged to within 0.00003 a.u. At the optimized ground-state geometries, we performed TDDFT calculations with a larger, diffuse 6-31+G(d,p) basis set to obtain the lowest singlet vertical excitations. For both the ground-state and TDDFT calculations, we used a high-accuracy Lebedev grid consisting of 96 radial and 302 angular points. All *ab initio* calculations were performed with a locally modified version of GAMESS.²⁵

Within the TDDFT approach, one obtains the excited-state electron density,

$$\rho(\mathbf{r}) \equiv |\psi(\mathbf{r})|^2 = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 \quad (1)$$

composed of N -occupied molecular orbitals $\phi_i(\mathbf{r})$ as solutions from the time-dependent Kohn-Sham equations. In the same way that one can calculate transition density matrices from time-dependent Hartree-Fock orbitals, one can use orbitals from the noninteracting Kohn-Sham system to form transition densities which include many-body correlation effects from the TDDFT formalism. Following the two-dimensional real-space analysis approach of Tretiak et al.¹¹⁻¹⁵, we can construct coordinate $\mathbf{Q}_v$ and momentum $\mathbf{P}_v$ matrices with elements given by

$$(Q_v)_{mn} = \langle \psi_v | c_m^\dagger c_n | \psi_g \rangle + \langle \psi_g | c_m^\dagger c_n | \psi_v \rangle \quad (2)$$

$$(P_v)_{mn} = \langle \psi_v | c_m^\dagger c_n | \psi_g \rangle - \langle \psi_g | c_m^\dagger c_n | \psi_v \rangle \quad (3)$$

where ψ_g and ψ_v are ground and excited states, respectively. The Fermi operators $c_i^\dagger$ and c_i represent the creation and annihilation of an electron in the i th basis set orbital in ψ . For the cyclic and linear paraphenylenes analyzed in this work, the $\mathbf{Q}_v$ and $\mathbf{P}_v$ matrices each form a two-dimensional xy -grid running over all the carbon sites along the x - and y -axes. The specific ordering of the carbon sites used in this work is shown in Figure 2. The $(P_v)_{mn}$ momentum matrix represents the probability amplitude of an electron-hole pair oscillation between carbon sites m and n , and the $(Q_v)_{mn}$ coordinate matrix gives a measure of exciton delocalization between sites m and n , respectively. Each of these matrices provides a global view of electron-hole coherence and exciton delocalization for optical transitions within the paraphenylene systems.

Results and Discussion

Geometries and excitation energies

In the ground-state optimizations for the linear paraphenylenes, the dihedral angle between adjacent benzene rings was calculated to be 37° . This is close to the dihedral angle in isolated biphenyl, and was consistent in all of the linear paraphenylenes regardless of length. In contrast,

for the smallest and highly-strained $N = 5$ cyclic paraphenylene, the benzene rings adopt a wide variety of smaller dihedral angles between 9° and 27° . As the size of the cyclic paraphenylene increases, the strain energy becomes smaller, and the dihedral angles between benzene rings increase to 36° .

To investigate excited-state trends as a function of size and shape, optical absorption energies, E_{opt} , were computed for all the cyclic and linear ground-state geometries. Figure 4 displays E_{opt} as a function of size, and Table 1 compares the lowest excitation energies and oscillator strengths between the cyclic and linear paraphenylenes. The other higher-lying singlet excitations (up to S_4) can be found in the Appendix. As the number of benzene rings increases, the lowest excitation energies for both the cyclic and linear paraphenylenes asymptotically approach a value of 3.48 eV. However, as Figure 4 illustrates, the manner in which they approach this asymptotic value is considerably different: E_{opt} for the cyclic systems increases with size, while E_{opt} for the acyclic systems decreases.

Figure 4. Optical excitation energies (E_{opt}) for the cyclic and acyclic paraphenylenes as a function of the number of benzene rings. E_{opt} for the cyclic systems increases with size, while E_{opt} for the acyclic systems decreases. All excitation energies were obtained from PBE0/6-31+G(d,p) TDDFT calculations at PBE0/6-31G(d,p)-optimized geometries.

Number of benzene rings	Cyclic Paraphenylenes		Linear Paraphenylenes	
	E_{opt} (eV)	Oscillator Strength	E_{opt} (eV)	Oscillator Strength
5	2.08	0.0022	3.91	1.8284
6	2.29	0.0000	3.78	2.2543
7	2.50	0.0016	3.71	2.6725
8	2.96	0.0000	3.66	3.0790
9	3.00	0.0170	3.61	3.5264
10	2.98	0.0000	3.58	3.9501
11	3.16	0.0267	3.55	4.4078
12	3.24	0.0000	3.54	4.8332
13	3.20	0.0012	3.52	5.2735
14	3.30	0.0000	3.51	5.7073
15	3.29	0.0416	3.50	6.1508
16	3.30	0.0476	3.49	6.6022
17	3.30	0.0002	3.48	7.0560
18	3.35	0.0000	3.48	7.5174

Table 1. $S_1 \leftarrow S_0$ excitation energies and oscillator strengths for the cyclic and linear paraphenylenes. All properties were computed from PBE0/6-31+G(d,p) TDDFT calculations at PBE0/6-31G(d,p)-optimized geometries.

Another significant difference between the two systems is the variation of oscillator strengths as a function of size. For the linear paraphenylenes, the oscillator strengths increase linearly as a function of chain length, while the oscillator strengths for most of the even-membered cyclic systems are zero (due to symmetry). Although the DFT geometry optimizations were performed without symmetry constraints, most of the calculations for the smaller ($N \leq 12$) even-membered nanorings converged to a C_{2v} -like symmetric structure. For nanorings containing an odd number of benzenes, the optimized structures have a reduced symmetry, and the oscillator strengths are nonzero. However, as the number of benzene rings increases, the strain energy becomes smaller, and several conformers with different dihedral angles can exist with similar energies. We found

that these different conformers have various oscillator strengths (due to reduced symmetry) but nearly identical energies. A complete analysis of the conformational landscape available to the nanorings is beyond the scope of this work and would have a negligible effect on the excitation energies in the larger systems. The small $S_1 \leftarrow S_0$ oscillator strengths obtained for the nanorings also have a close analogy with the very recent study by Kilina et al. which calculated optoelectronic properties of finite-length carbon nanotubes.²⁶ In their study, it was found that hybrid functionals determine the lowest singlet-excited state to be an optically inactive (“dark”) state with the optically active (“bright”) state lying higher in energy. For the larger nanorings with $N \geq 9$, the second singlet excitation is a bright state with a strongly allowed transition. The trend in oscillator strengths for the nanorings can also be explained qualitatively in terms of a simple exciton model where one transition dipole moment is assigned to each benzene ring (Figure 5). For the lowest $S_1 \leftarrow S_0$ excitation, the transition moments in both the linear and cyclic paraphenylenes are aligned in a head-to-tail arrangement. However, because of their circular geometries, the transition moments in the cyclic paraphenylenes effectively cancel, while the total transition moment increases as a function of length in the linear systems (for the larger, more flexible nanorings, some of the transition dipole moments have a small component perpendicular to the ring, and the vectorial sum is slightly nonzero). As a result, the structural difference between cyclic and linear geometries imposes symmetry constraints which determine the oscillator strengths in these conjugated systems.

Figure 5. Arrangements of individual transition dipole moments for (a) cyclic and (b) linear paraphenylenes during the $S_1 \leftarrow S_0$ excitation. The transition moments in the cyclic geometry effectively cancel, but the total transition moment increases proportionally with length in the linear systems.

Transition density matrix analysis

To provide further insight into these optoelectronic trends, we carried out a two-dimensional real-space analysis of density matrices for both the cyclic and linear systems. Figure 6 displays the absolute values of the coordinate density matrix elements, $|(Q_1)_{mn}|$, for the lowest excitation energy ($S_1 \leftarrow S_0$) in the $N = 5, 9, 14$, and 18 paraphenylenes. Figure 7 displays the corresponding momentum density matrix elements, $|(P_1)_{mn}|$, for the same systems. Density matrices for the other paraphenylene systems can be found in the Appendix. In both figures, the x - and y -axes represent the benzene repeat units in the molecule, and the individual matrix elements are depicted by the various colors.

Figure 6. Contour plots of coordinate density matrices (Q_1) for the lowest excitation energy ($S_1 \leftarrow S_0$) in the cyclic and linear paraphenylenes. The x - and y -axis labels represent the number of benzene repeat units in the molecule. The elements of the coordinate matrix, Q_{mn} , give a measure of exciton delocalization between sites m (x -axis) and n (y -axis). The color scale is given at the bottom.

Figure 7. Contourplots of momentum density matrices (P_1) for the lowest excitation energy ($S_1 \leftarrow S_0$) in the cyclic and linear paraphenylenes. The x- and y-axis labels represent the number of benzene repeat units in the molecule. The elements of the momentum matrix, P_{mn} , represent the probability amplitude of an electron-hole pair oscillation between sites m (x-axis) and n (y-axis). The color scale is given at the bottom.

Although the cyclic and linear paraphenylenes are composed of similar benzene repeat units, the density-matrix delocalization patterns in each system are considerably different. For the linear systems, the electron-hole pair created upon optical excitation becomes primarily localized in the middle of the molecule and away from the edges. In contrast, the density matrices for the cyclic systems have significant off-diagonal elements which persist even for the largest $N = 18$ nanoring. The magnitude of the off-diagonal elements represents electronic coherence between different atoms, and Figures 6 and 7 show that the electron-hole states are delocalized over the entire circumference in the cyclic systems. The coherence size, which characterizes the distance

between an electron and a hole, is given by the width of the momentum density matrix along the coordinate axes in Figure 7. (In this work, we define the coherence width as the distance where the momentum decreases to 10% of its maximum value). These figures show that, for a given number of benzene rings, the coherence size in the linear paraphenylenes is slightly larger than their cyclic counterparts. For the smaller paraphenylenes ($N < 9$), the coherence size in the linear systems is larger by approximately one repeat unit in comparison to the cyclic systems. As the number of benzene units increases to 18, the coherence size for both the cyclic and linear systems approach the same value of 9 repeat units. Both $|(Q_1)_{mn}|$ and $|(P_1)_{mn}|$ also show that the linear systems only have strong optical coherences induced at their center, while the optical coherences in the cyclic geometries are nearly equally distributed throughout the entire molecule. These different density-matrix delocalization patterns and coherence sizes result in distinct exciton properties in the cyclic and linear systems, an effect which we quantify in the next section.

Exciton effects

In order to understand electron-hole interactions on a more quantitative level, we calculated exciton binding energies for the cyclic and linear paraphenylenes as a function of size. As illustrated in Figure 8, the exciton binding energy, E_{exc} , is given by the difference between the quasiparticle energy gap [ionization potential (IP) – electron affinity (EA)] and the optical absorption gap (E_{opt}). Both the IP and EA were obtained from PBE0/6-31+G(d,p) electronic energy calculations on the $N - 1$, N , and $N + 1$ electron systems at the neutral PBE0/6-31G(d,p) optimized geometry. In this work, the vertical IP is defined by

$$\text{IP} = E_{N-1} - E_N, \quad (4)$$

and the magnitude of the vertical EA is given by

$$\text{EA} = E_N - E_{N+1}. \quad (5)$$

With these definitions, the magnitude of the exciton binding energy is then

$$E_{\text{exc}} = \text{IP} - \text{EA} - E_{\text{opt}}. \quad (6)$$

Figure 8. Schematic representation of energy levels defining the exciton binding energy (E_{exc}), optical absorption gap (E_{opt}), ionization potential (IP), and electron affinity (EA). The exciton binding energy is given by $E_{\text{exc}} = \text{IP} - \text{EA} - E_{\text{opt}}$.

Table 2 gives ionization potentials, electron affinities, and exciton binding energies for the cyclic and linear paraphenylenes. Figure 9 shows the quasiparticle energy gap ($IP - EA$), and Figure 10 displays E_{exc} as a function of size.

Number of benzene rings	Cyclic Paraphenylenes			Linear Paraphenylenes		
	IP (eV)	EA (eV)	E_{exc} (eV)	IP (eV)	EA (eV)	E_{exc} (eV)
5	6.34	1.17	3.09	7.05	0.51	2.62
6	6.34	1.22	2.82	6.90	0.66	2.46
7	6.35	1.25	2.60	6.80	0.76	2.32
8	6.50	1.10	2.44	6.71	0.84	2.21
9	6.45	1.16	2.29	6.64	0.92	2.10
10	6.39	1.25	2.16	6.58	0.98	2.02
11	6.43	1.20	2.07	6.52	1.04	1.93
12	6.43	1.20	1.99	6.48	1.08	1.87
13	6.37	1.27	1.90	6.45	1.12	1.81
14	6.39	1.25	1.85	6.41	1.16	1.75
15	6.36	1.28	1.79	6.38	1.19	1.70
16	6.34	1.31	1.73	6.35	1.22	1.65
17	6.31	1.33	1.68	6.33	1.24	1.61
18	6.32	1.33	1.65	6.31	1.26	1.57

Table 2. Ionization potentials (IP), electron affinities (EA), and exciton binding energies (E_{exc}) for the cyclic and linear paraphenylenes. All properties were computed from PBE0/6-31+G(d,p) electronic energy calculations on the $N - 1$, N , and $N + 1$ electron systems at the neutral PBE0/6-31G(d,p)-optimized geometries.

Figure 9. Quasiparticle energy gaps (IP – EA) for the cyclic and acyclic paraphenylenes as a function of the number of benzene rings. The quasiparticle energy gap for the acyclic paraphenylenes decreases much more rapidly than the energy gap for the corresponding cyclic systems.

Figure 10. Exciton binding energies (IP – EA – E_{opt}) for the cyclic and acyclic paraphenylenes as a function of the number of benzene rings. For a given number of benzene rings, the exciton binding energies in the cyclic paraphenylenes are larger than their acyclic counterparts.

As Figure 9 shows, with the exception of some small fluctuations, the quasiparticle energy gap in both systems decreases with size, in agreement with quantum-confinement effects. Furthermore, the quasiparticle energy gap for the linear paraphenylenes decreases much more rapidly than the energy gap for the corresponding cyclic systems. Figure 10 displays the exciton binding energies of both systems calculated from eq 6. In contrast to Figures 4 and 9, the exciton binding energies in both systems show a smooth monotonic variation as a function of size. Interestingly, for a given number of benzene rings, the exciton binding energies in the cyclic paraphenylenes are always larger (and decrease at a faster rate) than their acyclic counterparts. This trend is in agreement with the coherence sizes obtained from the momentum density matrices in the

previous section. Compared to the linear paraphenylenes, the average electron-hole distance in the cyclic systems is smaller, leading to an increase in the binding energy. However, as the number of benzene units increases, the coherence sizes in both systems become nearly equal, and the binding energies asymptotically approach the same value. These results, in combination with the quasiparticle energy gaps and electron-hole delocalization patterns, explain the anomalous absorption energy trends in the cyclic paraphenylenes. In the linear systems, the quasiparticle energy gap ($IP - EA$) decreases much more rapidly than the exciton binding energy, E_{exc} . As a result, the behavior of the $IP - EA$ term dominates the right-hand-side of eq 6, and the optical absorption gap ($E_{opt} = IP - EA - E_{exc}$) in the linear paraphenylenes decreases as a function of size. In contrast, $IP - EA$ in the cyclic systems decreases at a significantly slower rate than E_{exc} (cf. Figures 9 and 10). Consequently, E_{opt} in the cyclic paraphenylenes will be largely determined by the behavior of E_{exc} . Since E_{exc} decreases faster than $IP - EA$ in the carbon nanorings, the resulting optical absorption gap in the expression $E_{opt} = IP - EA - E_{exc}$ *increases* as a function of size, in agreement with the TDDFT calculations.

Conclusion

In this study, we have investigated the excitonic properties in a series of cycloparaphenylenes which form the molecular structure of carbon nanorings. In order to understand their unusual electronic properties as a function of molecular size, we have analyzed TDDFT excited-state energies, examined electron-hole transition density matrices, and calculated quasiparticle and exciton binding energies for both the cyclic and linear paraphenylenes systems. Our TDDFT calculations and transition density analyses show that the cyclic and linear paraphenylenes exhibit dramatically different size-dependent effects which can be understood in the framework of a simple exciton theory. Specifically, the main differences between the absorption spectra of the cyclic and linear paraphenylenes are caused by their unique electron-hole interaction energies. In the linear systems, the exciton binding energy decreases slower than the quasiparticle energy gap, and the resulting optical absorption gap decreases with molecular size, as expected. In contrast, the effective Coulomb attraction between an electron-hole pair is larger in the cyclic geometry and decreases at a faster rate than the quasiparticle band gap. As a result, the overall optical absorption gap in the cyclic paraphenylenes increases as a function of size.

In conclusion, we have shown that the different exciton effects in the cyclic and linear paraphenylenes play a vital role in determining their distinct photophysical properties. The unique spatial distributions of electron-hole states, as depicted by their transition density delocalization patterns, result in different electron-hole interaction energies which ultimately control the electronic excitations in these systems. Looking forward, it would be very interesting to see if the unusual optical trends resulting from the lowest, weakly-allowed transition in these nanorings can be observed spectroscopically. The most “direct” way to observe these lowest transitions would be via low-temperature spectroscopic studies with an applied magnetic field to brighten the dark excitons. A magnetic flux through the open center of the nanorings would distort the circular symmetry of the electronic wavefunction and produce bright excitons due to

the Aharonov-Bohm effect.^{27,28} It is also possible that one can already observe these lowest transitions spectroscopically without the use of an applied magnetic field. Since these nanorings are significantly more flexible than carbon nanotubes, the lowest dark exciton may be strongly allowed through symmetry breaking. Vibronic coupling, which allows a borrowing of intensity from the bright state, may also play a significant role in observing these weakly-allowed transitions.^{29,30} From a theoretical point of view, it would also be interesting to extend the current ab initio methods to radiation processes which are above threshold (i.e. energies higher than ionization). Calculations of this type would require the use of R-matrix approaches to calculate bound and unbound electronic states which are currently underway in our group.³¹

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Appendix

Number of benzene rings	S ₁ State		S ₂ State		S ₃ State		S ₄ State	
	E_{opt} (eV)	Oscillator Strength	E_{opt} (eV)	Oscillator Strength	E_{opt} (eV)	Oscillator Strength	E_{opt} (eV)	Oscillator Strength
5	2.08	0.0022	3.50	0.0168	3.53	0.0109	3.56	0.0004
6	2.29	0.0000	3.43	0.0056	3.57	0.0001	3.63	0.5459
7	2.50	0.0016	3.48	0.0002	3.53	0.0010	3.60	1.2204
8	2.96	0.0000	3.71	1.1785	3.71	1.1808	3.74	0.1596
9	3.00	0.0170	3.61	1.6001	3.66	1.4770	3.68	0.0133
10	2.98	0.0000	3.46	1.9694	3.58	0.0002	3.60	1.6925
11	3.16	0.0266	3.57	2.0466	3.61	1.9538	3.75	0.0042
12	3.24	0.0000	3.60	2.2387	3.60	2.2389	3.82	0.0044
13	3.20	0.0012	3.52	2.5531	3.53	2.4691	3.75	0.0018
14	3.30	0.0000	3.57	2.7355	3.57	2.7334	3.84	0.0023
15	3.29	0.0416	3.53	3.0027	3.56	2.9460	3.82	0.0017
16	3.30	0.0476	3.52	3.2317	3.53	3.2360	3.82	0.0010
17	3.30	0.0001	3.49	3.5386	3.51	3.5344	3.82	0.0015
18	3.35	0.0000	3.54	3.8007	3.54	3.8010	3.88	0.0010

Table A-1. $S_n \leftarrow S_0$ excitation energies and oscillator strengths up to S_4 for the cyclic paraphenylenes. All properties were computed from PBE0/6-31+G(d,p) TDDFT calculations at PBE0/6-31G(d,p)-optimized geometries.

Number of benzene rings	S ₁ State		S ₂ State		S ₃ State		S ₄ State	
	E_{opt} (eV)	Oscillator Strength	E_{opt} (eV)	Oscillator Strength	E_{opt} (eV)	Oscillator Strength	E_{opt} (eV)	Oscillator Strength
5	3.91	1.8285	4.59	0.0000	4.61	0.0000	4.62	0.0000
6	3.78	2.2541	4.37	0.0000	4.41	0.0000	4.57	0.0000
7	3.71	2.6725	4.20	0.0000	4.30	0.0000	4.64	0.4837
8	3.66	3.0789	4.08	0.0000	4.22	0.0000	4.48	0.5345
9	3.61	3.5264	3.97	0.0000	4.15	0.0000	4.32	0.5587
10	3.58	3.9501	3.89	0.0000	4.11	0.0000	4.21	0.5730
11	3.54	4.4077	3.82	0.0000	4.06	0.0000	4.11	0.5800
12	3.54	4.8329	3.78	0.0000	4.04	0.5959	4.05	0.0000
13	3.52	5.2740	3.74	0.0000	3.98	0.6066	4.03	0.0000
14	3.51	5.7074	3.70	0.0000	3.92	0.6424	4.01	0.0000
15	3.50	6.1498	3.67	0.0030	3.88	0.6591	4.00	0.0000
16	3.49	6.6009	3.65	0.0057	3.83	0.6811	3.98	0.0000
17	3.48	7.0545	3.62	0.0036	3.80	0.7112	3.97	0.0000
18	3.48	7.5154	3.61	0.0072	3.77	0.7229	3.94	0.0006

Table A-2. $S_n \leftarrow S_0$ excitation energies and oscillator strengths up to S_4 for the linear paraphenylenes. All properties were computed from PBE0/6-31+G(d,p) TDDFT calculations at PBE0/6-31G(d,p)-optimized geometries.

Figure A-1. Contour plots of coordinate density matrices (Q_1) for the lowest excitation energy ($S_1 \leftarrow S_0$) in the cyclic and linear paraphenylenes. The x- and y-axis labels represent the number of benzene repeat units in the molecule. The elements of the coordinate matrix, Q_{mn} , give a measure of exciton delocalization between sites m (x-axis) and n (y-axis). The color scale is given at the bottom.

Figure A-1 (continued). Contour plots of coordinate density matrices (Q_1) for the lowest excitation energy ($S_1 \leftarrow S_0$) in the cyclic and linear paraphenylenes. The x - and y -axis labels represent the number of benzene repeat units in the molecule. The elements of the coordinate matrix, Q_{mn} , give a measure of exciton delocalization between sites m (x -axis) and n (y -axis). The color scale is given at the bottom.

Figure A-1 (continued). Contour plots of coordinate density matrices (Q_1) for the lowest excitation energy ($S_1 \leftarrow S_0$) in the cyclic and linear paraphenylenes. The x - and y -axis labels represent the number of benzene repeat units in the molecule. The elements of the coordinate matrix, Q_{mn} , give a measure of exciton delocalization between sites m (x -axis) and n (y -axis). The color scale is given at the bottom.

Figure A-1 (continued). Contour plots of coordinate density matrices (Q_1) for the lowest excitation energy ($S_1 \leftarrow S_0$) in the cyclic and linear paraphenylenes. The x - and y -axis labels represent the number of benzene repeat units in the molecule. The elements of the coordinate matrix, Q_{mn} , give a measure of exciton delocalization between sites m (x -axis) and n (y -axis). The color scale is given at the bottom.

Figure A-1 (continued). Contour plots of coordinate density matrices (Q_1) for the lowest excitation energy ($S_1 \leftarrow S_0$) in the cyclic and linear paraphenylenes. The x - and y -axis labels represent the number of benzene repeat units in the molecule. The elements of the coordinate matrix, Q_{mn} , give a measure of exciton delocalization between sites m (x -axis) and n (y -axis). The color scale is given at the bottom.

Figure A-2. Contour plots of coordinate density matrices (P_1) for the lowest excitation energy ($S_1 \leftarrow S_0$) in the cyclic and linear paraphenylenes. The x- and y-axis labels represent the number of benzene repeat units in the molecule. The elements of the momentum matrix, P_{mn} , represent the probability amplitude of an electron-hole pair oscillation between sites m (x-axis) and n (y-axis). The color scale is given at the bottom.

Figure A-2 (continued). Contour plots of coordinate density matrices (P_1) for the lowest excitation energy ($S_1 \leftarrow S_0$) in the cyclic and linear paraphenylenes. The x - and y -axis labels represent the number of benzene repeat units in the molecule. The elements of the momentum matrix, P_{mn} , represent the probability amplitude of an electron-hole pair oscillation between sites m (x -axis) and n (y -axis). The color scale is given at the bottom.

Figure A-2 (continued). Contour plots of coordinate density matrices (P_1) for the lowest excitation energy ($S_1 \leftarrow S_0$) in the cyclic and linear paraphenylenes. The x - and y -axis labels represent the number of benzene repeat units in the molecule. The elements of the momentum matrix, P_{mn} , represent the probability amplitude of an electron-hole pair oscillation between sites m (x -axis) and n (y -axis). The color scale is given at the bottom.

Figure A-2 (continued). Contour plots of coordinate density matrices (P_1) for the lowest excitation energy ($S_1 \leftarrow S_0$) in the cyclic and linear paraphenylenes. The x - and y -axis labels represent the number of benzene repeat units in the molecule. The elements of the momentum matrix, P_{mn} , represent the probability amplitude of an electron-hole pair oscillation between sites m (x -axis) and n (y -axis). The color scale is given at the bottom.

Figure A-2 (continued). Contour plots of coordinate density matrices (P_1) for the lowest excitation energy ($S_1 \leftarrow S_0$) in the cyclic and linear paraphenylenes. The x - and y -axis labels represent the number of benzene repeat units in the molecule. The elements of the momentum matrix, P_{mn} , represent the probability amplitude of an electron-hole pair oscillation between sites m (x -axis) and n (y -axis). The color scale is given at the bottom.

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