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W. J. D. Beenken[1], M. Sun[2], G. Zhao[3], and T. Pullerits[4]

[1] Theoretical Physics I, Technische Universität Ilmenau, Weimarer Str. 25, 98693 Ilmenau, Germany
[2] Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603-146, Beijing 100080, P.R. China
[3] State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Dalian 116023, P.R. China
[4] Department of Chemical Physics, Lund University, P.O. Box 124, 22100 Lund, Sweden

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Stimulated by the recent experimental report of optical properties of charged oligofluorenes [S. Fratiloiu et al., J. Phys. Chem. B **110**, 5984–5993 (2006)], we have used time-dependent density functional theory (TD-DFT) to study the electronic structure of neutral and charged ter-fluorene with and without keto-defect. We have characterized the excited states by site- and space-based representations of the density matrix. For the defectless neutral species we found typical excitons, while the first excited states of the corresponding charged species represent long-range oscillations of the electron or hole along the whole oligomer. For the neutral ketonized ter-fluorene we found trapping of the excited electron. Similarly, the unpaired electron of the anion ground state is trapped. The excited state properties of the cation, however, are insensitive to the keto-defect.

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[*] Corresponding author: e-mail wichard.beenken@tu-ilmenau.de

Stimulated by the recent experimental report of optical properties of charged oligofluorenes [S. Fratiloiu et al., J. Phys. Chem. B **110**, 5984–5993 (2006)], we have used time-dependent density functional theory (TD-DFT) to study the electronic structure of neutral and charged ter-fluorene with and without keto-defect. We have characterized the excited states by site- and space-based representations of the density matrix. For the defectless neutral species we found typical excitons, while the first excited states of the corresponding charged species represent long-range oscillations of the electron or hole along the whole oligomer. For the neutral ketonized ter-fluorene we found trapping of the excited electron. Similarly, the unpaired electron of the anion ground state is trapped. The excited state properties of the cation, however, are insensitive to the keto-defect.

1 Introduction Optical absorption of radical cations and anions of oligo-fluorenes were recently reported [1]. Oligomers are good model-systems for better understanding of optical properties and charge carriers of the corresponding polymeric systems. For example they can help to clarify the effects caused by chemical defects – here keto-groups as product of oxidation of polyfluorene. It is known that the presence of keto-defects reduce the electrical conductivity [2] and turn the desired blue emission into undesired blue-green emission [3, 4]. Both effects may be caused by keto-defects acting as deep trap for one of the charge carrier – most probably the electron. In this context quantum-chemical calculations are a very useful tool to investigate the relation between the chemical structure and not only the optical but also the electrical properties of π–conjugated materials, as needed for quantum-chemistry-aided rational design of OLEDs [5]. Neutral ter-fluorenes, ter-fluoren-9′-one (see Fig. 1) and other oligo-fluorenes have already been studied intensively, especially by semiempirical quantum-chemical methods like ZINDO [3].

Here we apply time-dependent density functional theory (TD-DFT) [6] on ter-fluorene and ter-fluoren-9′-one. The calculations are carried out for both neutral and charged species. The TD-DFT has been shown to provide accurate optical absorption and fluorescence spectra for neutral short conjugated oligomers [7, 8].

2 Computational methods The geometry optimization of the electronic ground state was performed by density functional theory (DFT) [9]. For charged conjugated oligomers, which represent open-shell systems, DFT is less accurate than for neutral species but still better than many other quantum-chemical methods [7, 10]. A particular advantaged of using DFT and TD-DFT is that we can use analogous methods to optimize the structure in the ground and excited state [11]. In both methods we use the hybrid

Figure 1 (online colour at: www.pss-b.com) Chemical structure of ter-fluorene. Carbon atoms are indexed (differently from IUPAC standard) for site-representation in the *Q*- and *P*-plots (cf. Fig. 3).

functional B3-LYP and SV(P) basis set as implemented in the TURBOMOLE suite [12].

In order to illustrate the effects caused by the keto-defect we apply space- as well as site-based representations of the transition density matrix yielded by the TD-DFT calculations [10, 13]. The former characterization method provides three-dimensional isosurfaces of the transition density (TD), which reveals the orientation and strength of the transition dipole [14], and the charge difference density (CDD), which features the charge transfer [15]. The second, site-based, approach is related to the collective electron oscillator (CEO) model [13] and provides two plots for the quantities

$$|Q_{\mathrm{AB}}|^2 = \left|\sum_{\substack{\mu\in\mathrm{A}\\ \nu\in\mathrm{B}}} (C_{\nu\mu} + C_{\mu\nu})\right|^2 \quad \text{and} \quad |P_{\mathrm{AB}}|^2 = \left|\sum_{\substack{\mu\in\mathrm{A}\\ \nu\in\mathrm{B}}} (C_{\nu\mu} - C_{\mu\nu})\right|^2, \tag{1}$$

where Q represents the generalized CEO-coordinate and P the corresponding generalized CEO-momentum. $C_{\nu\mu}$ is the excitation vector determined by TD-DFT, which describes moving of an electron from the atomic orbital μ on atom A to the orbital ν on atom B upon excitation.

Note that the main diagonal (left bottom to right top) in the *Q*-plot represents the transition-density projected to the respective atom. The off-diagonal elements characterize the electron–hole distance in units of the atomic sites. While the *Q*-plot shows where electron and hole reside in the excited state, the *P*-plot shows their dynamics. Trivially the values at the diagonal of the *P*-plot vanish. The off-diagonal elements indicate the sites where the excited electron and oppositely the hole move to and fro.

3 Results and discussion The calculated transition energies and oscillator strengths of neutral ter-fluorene are in agreement with experimental data and previous calculations [1, 16]. The 1st vertically excited singlet state of the ter-fluorene we found at 3.52 eV (the experimental value [16] is 3.24 eV) with oscillator strength $f = 2.2$. Characterized by TD and CDD (see Fig. 2) we found this to be the $\pi \rightarrow \pi^*$ transition typical for conjugated oligomers [14, 15]. The CDD shows clearly that the electronic structure changes from benzoid to quinoid character, i.e. shifting the electron by one bond. Thereby the connecting single-bonds between the phenyl rings get more double-bond character. The extension of the TD reflects the delocalization of the exciton over nearly the whole oligomer.

Looking to the details of the *Q*- and *P*-plot (see Fig. 3), we see the molecular structure of the monomers, which produce a pattern very specific for $\pi \rightarrow \pi^*$ transitions in conjugated systems. In ter-fluorene matrix elements of neighboring sites (except the sites 7, 20, and 33, since they represent non-conjugated carbon atoms) show an alteration of high and low values. This reflects the movement of the excited electron from the benzoid to the quinoid positions of the double-bonds, which we have already seen in the CDD.

For neutral ter-fluoren-9′-one, like for ter-fluorene, the calculated transition energies and oscillator strengths are in good agreement with experimental data [1, 3, 16]. In particular we found the reported red-shifted absorption bands at 2.33 eV and 3.22 eV. However, as we will show below, we may interpret these bands as additional charge-transfer states rather than as chemical shifted $\pi \rightarrow \pi^*$ transitions. Differently from ter-fluorene, the CDD of the 1st vertically excited state for neutral ter-fluoren-9′-one gives a clear hint about an electron transfer onto the keto-group, where the excited electron is trapped. Notably the remaining hole is completely delocalized. This means that we have the rare case of a localizing excitation. Note that the 1st and 4th excited states of ter-fluoren-9′-one have lower oscillator strengths (0.2 and 0.3) than the corresponding transitions of the ter-fluorene.

Also in the *Q*- and *P*-plots the qualitative difference between the 1st excited singlet states of ter-fluorene and ter-fluoren-9′-one is more than apparent (cf. Figs. 3 and 4). While in the *Q*- and *P*-plot of ter-fluorene the non-vanishing values of $|Q_{\mathrm{AB}}|^2$ as well as $|P_{\mathrm{AB}}|^2$ are more or less equally distributed over all site pairs – only smoothly decreasing towards the boarders of the oligomer – for ter-fluoren-9′-one we found a cross-shaped pattern. The latter

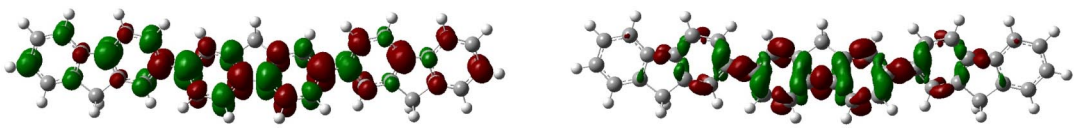

Figure 2 (online colour at: www.pss-b.com) Isosurfaces for the transition density (TD; left) and charge difference density (CDD; right) of the 1st vertically excited singlet state of ter-fluorene. In the CDD an increase of electron density is indicated by red, of hole density by green colour.

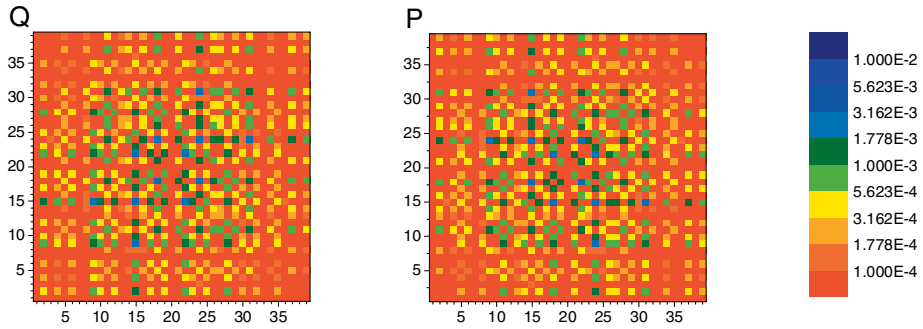

Figure 3 (online colour at: www.pss-b.com) *Q*- and *P*-plot of the 1st vertically excited singlet state of neutral ter-fluorene. Colour-code shows values of the matrix elements $|Q_{AB}|^2$ and $|P_{AB}|^2$ as given by Eq. (1) and (2), respectively. Sites numbered as in Fig. 1.

is the clear indication of the trapping of an initially delocalized electron by the central fluoren-9-one monomer (sites 15–27). Note that a charge transfer only from the end-standing fluorenyl monomers produces a different pattern where the center of the cross would be less occupied.

Notably, the 5th singlet transition of ter-fluoren-9′-one and the 1st of ter-fluorene have the same energy (3.52 eV) and both high oscillator strength (1.2 and 2.2, respectively). Thus, we may assume that it is the 5th excited singlet state that represents the $\pi \rightarrow \pi^*$ transition of neutral ter-fluoren-9′-one, whereas the four transitions lower in energy are of charge-transfer character. This hypothesis is strongly supported by the fact that the *Q*-plot for the 5th excited singlet state of neutral ter-fluoren-9′-one resembles more or less the same pattern as that found for the 1st of neutral ter-fluorene (cf. Figs. 3 and 4), though the corresponding TDs and CDDs are slightly different (cf. Fig. 2). For the 5th excited singlet state of ter-fluoren-9′-one we see a little concentration of the excited electron density around the keto-group like found for the four lower excited singlet states. This we assigned to a partial charge transfer. Notably, for all excited states of ter-fluoren-9′-one, the *Q*-plots show an alternation pattern indicating a weak benzoid to quinoid rearrangement of the electronically excited structure. Thus there is always a mixing between CT and π^* character in the excited singlet states of neutral ter-fluoren-9′-one.

For charged species, anion and cation of ter-fluorene and ter-fluoren-9′-one, the CDDs of the 1st vertically excited state look quite similar – all reveal localization of one charge carrier on the central monomer. However, analysis of the *Q*- and *P*-plots demonstrates that the transitions have

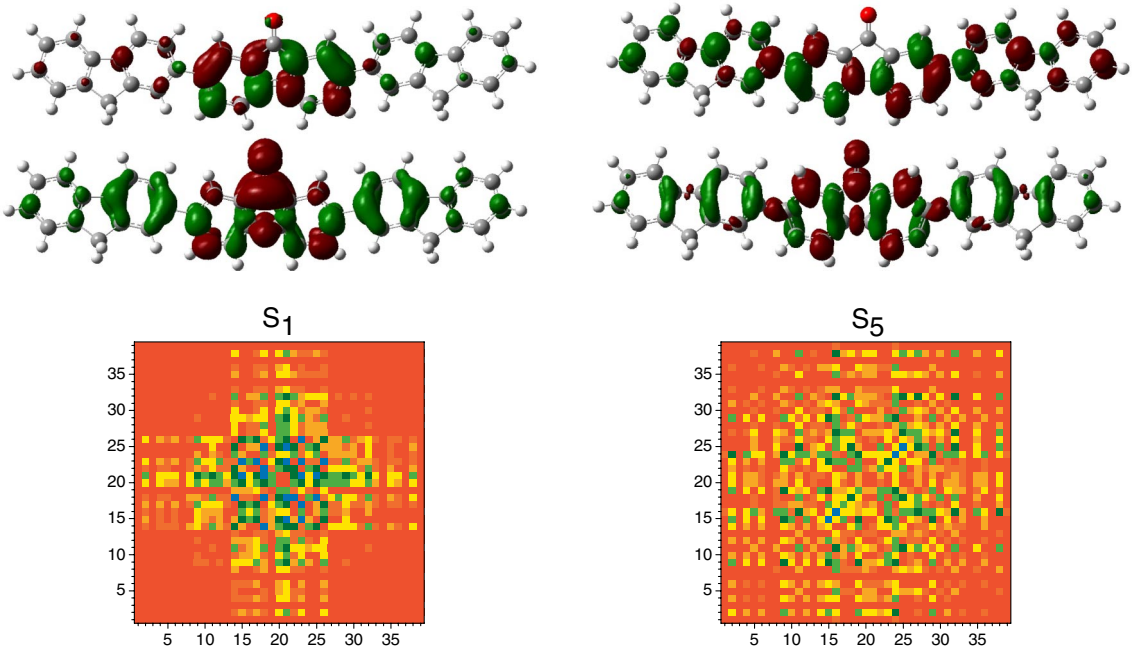

Figure 4 (online colour at: www.pss-b.com) Transition densities (TD; top), charge difference densities (CDD; middle), and *Q*-plots (bottom) for the 1st (left) and 5th (right) vertically excited singlet state of ter-fluoren-9′-one. Isosurface colouring as in Fig. 2; *Q*-plot colouring as in Fig. 3. For site indices see Fig. 1. Note that the keto-group is on site 20 and 21.

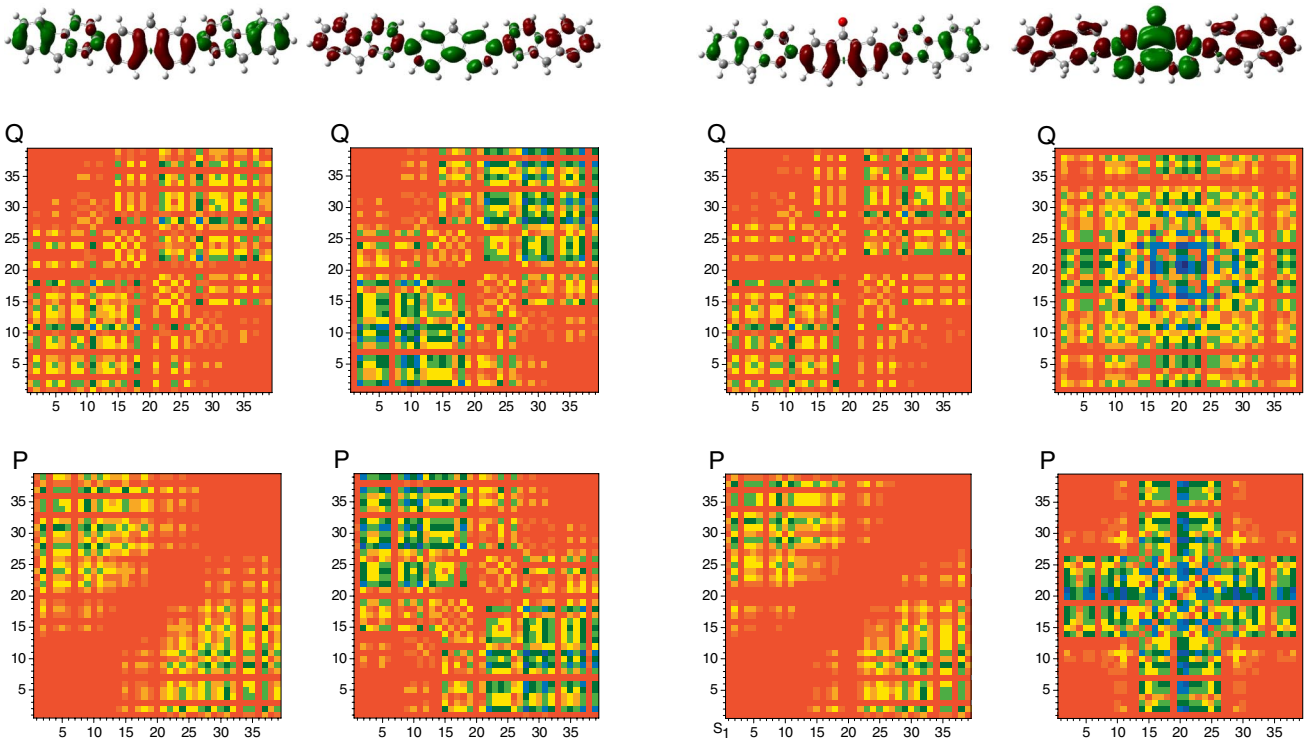

Figure 5 (online colour at: www.pss-b.com) Charge difference densities (top), *Q*-plots (middle), and *P*-plots (bottom) for the 1st excited singlet states of the charged species of ter-fluorene and ter-fluoren-9′-one. Isosurface colouring as in Fig. 2; *Q*- and *P*-plot colouring as in Fig. 3. For the site numbering see Fig. 1.

very different character. For this purpose we reinvestigate the particle-in-a-box model for the envelope of the *Q*- and *P*-matrix occupation. For anion (cation) we have to assume, that the half-sine shaped ground-state in the box is occupied by the additional electron (hole). Exciting this charge carrier will consequently transfer it to the next higher (lower), full-sine-shaped state with a node in the center. This is exactly what we found by inspection of the *Q*-plots as well as the TD of the 1st excited singlet state of the ter-fluorene anion and cation, respectively.

From a closer look of the CDD of the anion one can see that the electron really uses for its motion only the quinoid double bond positions, which in the neutral species were the destinations of the excited electron. In the same way for the cation it is the hole which moves on bond positions which were left by the excited electron in the excited neutral ter-fluorene. For both charged species the *P*-plots show non-zero matrix elements in the off-diagonal corners. This illustrates wide-spanning motions of the charge carriers from one end of the oligomer to the other and is in full accordance with the quantum-mechanical expectation from the particle-in-a-box model. The model also predicts that in the *Q*-plot the non-zero matrix elements should appear only in main diagonal corners. Figure 5 demonstrates that this is indeed the case.

The particle-in-a-box picture, which we have seen is a good approximation for the anion and cation of ter-fluorene, holds likewise for the cation of ter-fluoren-9′-one. This means that holes alone are little affected by the keto-defect. For the ter-fluoren-9′-one anion, however, the model fails. In the respective *Q*- and *P*-plots we find the same cross-shaped patterns as for the 1st excited singlet state of neutral ter-fluoren-9′-one. This is easily explained by the assumption that in the ground state the additional electron of the anion – like the excited one in the neutral species – is trapped by the keto-defect. By optical excitation this trapped electron is then “freed”, i.e. transferred into a delocalized higher excited state. The corresponding CDD of the 1st excited state of the anion confirms this picture by showing that the electron density moves from the central fluoren-9-one monomer towards the end-standing fluorenyl monomers thereby equalizing the initial charge concentration around the keto-group. We point out that similar conclusions about trapping of the electron by the keto-defect have been drawn based on analyses of the molecular orbitals calculated by semiempirical methods [3].

Finally we have to note, that differences of the ground-state geometries between neutral and charged ter-fluorenes as well as ter-fluoren-9’-one, all obtained from DFT calculations, are negligible. This indicates that a small-polaron formation is insignificant for the abovementioned electron trapping.

4 Conclusion We found that in ter-fluorene a keto-defect at the 9′ position traps electrons, whereas holes are only affected by the Coulomb interaction with such trapped electrons. Thereby polaron-formation is of only

minor importance. It is the electron affinity of the keto-group which causes the trapping and reduction of conductivity. The red-shift of the transition energy by oxidation of poly-fluorenes is not a chemical shift of the $\pi \rightarrow \pi^*$ transition but the appearance of additional charge-transfer states at lower excitation energies.

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