Communication: Tailoring the optical gap in light-harvesting molecules

A. Karolewski, T. Stein, R. Baer, and S. Kümmel

Citation: The Journal of Chemical Physics **134**, 151101 (2011); doi: 10.1063/1.3581788
View online: http://dx.doi.org/10.1063/1.3581788
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/134/15?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Tuned range separated hybrid functionals for solvated low bandgap oligomers
J. Chem. Phys. **143**, 034101 (2015); 10.1063/1.4926468

Charge-transfer excitations in low-gap systems under the influence of solvation and conformational disorder: Exploring range-separation tuning
J. Chem. Phys. **141**, 084303 (2014); 10.1063/1.4892937

The effect of structural changes on charge transfer states in a light-harvesting carotenoid-diaryl-porphyrin-C60 molecular triad
J. Chem. Phys. **140**, 204309 (2014); 10.1063/1.4876075

Unusual size dependence of the optical emission gap in small hydrogenated silicon nanoparticles
Appl. Phys. Lett. **90**, 123116 (2007); 10.1063/1.2715101

Screened-exchange determination of the optical properties of large gap insulators: CaF 2
Appl. Phys. Lett. **84**, 3579 (2004); 10.1063/1.1737073

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 132.64.30.166 On: Sat, 29 Aug 2015 15:55:55

Communication: Tailoring the optical gap in light-harvesting molecules

A. Karolewski,[1] T. Stein,[2] R. Baer,[2] and S. Kümmel[1,a)]
[1]*Theoretical Physics IV, University of Bayreuth, D-95440 Bayreuth, Germany*
[2]*Fritz Haber Center for Molecular Dynamics, Hebrew University, Jerusalem 91904, Israel*

(Received 31 January 2011; accepted 1 April 2011; published online 21 April 2011)

Systematically varying the optical gap that is associated with charge-transfer excitations is an important step in the design of light-harvesting molecules. So far the guidance that time-dependent density functional theory could give in this process was limited by the traditional functionals' inability to describe charge-transfer excitations. We show that a nonempirical range-separated hybrid approach allows to reliably predict charge-transfer excitations for molecules of practically relevant complexity. Calculated absorption energies agree with measured ones. We predict from theory that by varying the number of thiophenes in donor-acceptor-donor molecules, the energy of the lowest optical absorption can be tuned to the lower end of the visible spectrum. Saturation sets in at about five thiophene rings.
© *2011 American Institute of Physics*. [doi:10.1063/1.3581788]

Harvesting solar energy in organic electronic devices is an attractive option for satisfying future energy needs. An important aspect of such devices is to capture as large a part of the solar spectrum as possible and use the corresponding energy for charge separation. Therefore, systems in which the energy of optically active excitations with considerable charge-transfer (CT) character can be tuned in a well controlled way are of great interest. Synthesizing such systems can be a challenge, therefore *a priori* guidance from theory is highly desirable. Density functional theory (DFT) and time-dependent density functional theory (TDDFT) are generally very popular for computational studies of electronic systems due to their favorable ratio of accuracy to computational load.[1] However, in the past TDDFT has become (in)famous for its inability to accurately predict CT excitations.[2,3] Theoretically, the reason for this deficiency is well understood.[4,5] Commonly used functionals lack the steplike structures in the exchange-correlation (xc) potential that reflect particle-number discontinuities. The latter are a property of the exact time-dependent xc potential,[6] but are not reproduced by standard functionals.

Orbital functionals incorporate particle number discontinuities by construction[7] and, therefore, offer the potential to describe CT excitations with TDDFT. However, achieving the subtle balancing of self-interaction errors that is necessary for a quantitatively correct description of the above-mentioned steplike structures is a difficult task.[8] Based on the range-separated hybrid functional idea that has proved a quite successful development in general,[9–14] a functional has recently been devised[15] based on two fundamental ideas. First, the range separation parameter must be system dependent and second, this system dependence can be determined in a nonempirical way by ensuring that the functional consistently agrees as close as possible with Mulliken's rule.[16,17]

In previous studies, the new approach (there and in the following termed γBNL functional) was applied to model systems with an emphasis on excitations of long-range CT character. However, from a light-harvesting perspective one is interested in excitations that can be excited optically. In this paper we show that the γBNL functional works reliably in the practically most important case of excitations between closely connected molecular subunits and excitations of mixed valence and CT character that carry appreciable oscillator strength.

We calculated the photoresponse of a series of donor–acceptor systems carrying thiophenes as donor and naphthalene diimide (NDI) as acceptor. For some of the molecules we could compare the theoretical results to recently measured experimental data.[18] Close agreement between theory and experiment is obtained. We demonstrate that the absorption energy can indeed be changed in an appreciable energy range by extending the donor parts of the molecules, and we theoretically predict the limit of how much the absorption energy can be modified in this way. With five thiophenes the lower end of the visible range is reached.

We study the molecules N,N-diisopropyl-2,6-di(x) naphthalene-1,4,5,8-tetracarboxylic acid diimide (x stands for 1: thiophen-2-yl, 2: α-bithiophen-5-yl, etc. up to α-septithiophene) which we abbreviate as NDI-x in the following. Their structure is schematically depicted in Fig. 1. We calculated the molecular geometry by minimizing the ground-state energy using the B3LYP functional[19] and the def2-SV(P) basis set. B3LYP is known to yield reliable geometries for organic systems. However, we also checked the influence that using a different functional and basis set for the geometry optimization has on the excitation energies that are reported below. If the geometry is optimized using the PBE-GGA (Ref. 20) the B3LYP excitation energies change by 0.1 eV and if we use the def2-TZVP basis set, they change by 0.03 eV. Thus, the results are rather robust.

The NDI-x system is of practical interest because the lowest excitation energy of NDI-x is in the visible range and

a)Author to whom correspondence should be addressed. Electronic mail: stephan.kuemmel@uni-bayreuth.de.

 © 2011 American Institute of Physics

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 132.64.30.166 On: Sat, 29 Aug 2015 15:55:55

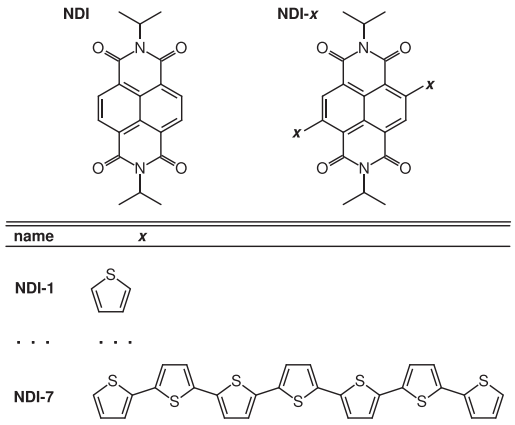

FIG. 1. Structural formula of NDI and NDI-x.

has CT character. The CT character is visible in standard linear response TDDFT by looking at the particle-hole amplitudes of the excitation of interest. For example, for NDI-3 with B3LYP the excitation is dominantly (with an amplitude of 0.997) a transition from the HOMO to the LUMO. Inspecting these orbitals, shown in Fig. 2, clearly reveals the CT character of the corresponding excitation. However, it also shows that there is an appreciable overlap between the orbitals, making this a more complicated situation than the very long-range CT excitations which are frequently discussed in TDDFT literature[7,21] and for which bare exact exchange can be sufficient. As shown in detail below, the NDI-x excitation carries appreciable oscillator strength.

Another aspect which makes the situation that we study here more complicated, but also more interesting, is the fact that NDI-x is not just a donor–acceptor system, but a donor-acceptor-donor arrangement. Combining alternating donor and acceptor units is one of the strategies for designing low band gap materials. This strategy has been successfully utilized to harvest the solar spectrum efficiently.[22–24] Polymers based on NDI and thiophene units are known compounds for the use as electron acceptor (n type) materials. Such polymers have shown high electron mobilities up to 0.8 cm^2/Vs in organic field effect transistors.[25] A decisive question is the strength of the donor unit (i.e., the number of thiophene units) which is ideal for obtaining the maximum red-shift of the absorption band in the resulting donor–acceptor polymer.

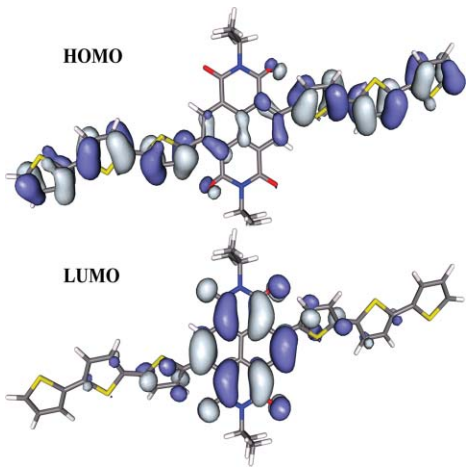

FIG. 2. Plot of HOMO and LUMO for NDI-3. The plots were obtained from DFT calculations with the γBNL functional, see text. Orbitals from the B3LYP functional look almost identical.

In our study the conjugated electronic system of the donor subunits is varied by varying the number of thiophenes. As this changes the energy of the lowest optical absorption, NDI-x molecules with varying x absorb light at different wavelengths. Combining them in a device may thus allow to absorb a broader part of the electromagnetic spectrum while still using molecules that are chemically very similar, the latter being a major advantage for processing and device building.

It is not *a priori* clear, though, how much the absorption energy can be lowered by increasing the number of thiophene rings. Intuitively one expects that there must be a saturation effect, but at which extension, i.e., number of thiophene rings, the saturation sets in is hard to predict on general grounds. However, as we demonstrate in the following, the range-separated hybrid functional that we use here allows to predict it.

For NDI without thiophene donors the spectrum shows onset of absorption with a clear peak at about 3.25 eV and vibrational structure at higher energies.[18] On going over to NDI-1 by adding thiophenes the peak structure at 3.25 eV and higher energies remains, but a new broad peak appears which is centered around 2.6 eV. Thus, the onset of optical absorption is shifted to lower energies. In NDI-2 this peak shifts further to 2.2 eV, i.e., to yet lower energies. This shows that the absorption can be tuned by increasing the donor system size. It is these low lying absorption peaks in NDI-x that are of practical interest and which will be the focus of our theoretical study.

Our calculations were carried out on NDI-x with short *N*-alkyl (isopropyl) substituents. We verified that the length of the *N*-alkyl substituents does not influence the electronic excitations. For calculating the absorption spectra of the NDI-x systems we adopt a range-separated hybrid functional.[16] The physical idea behind this approach is to split the exchange term in a long-range and a short-range part via $r^{-1} = r^{-1}\,\mathrm{erf}(\gamma r) + r^{-1}\,\mathrm{erfc}(\gamma r)$. The short-range term is treated by means of a semilocal expression and the long-range term is treated exactly. Thus, the γBNL functional does incorporate exact exchange which will contribute to cancel the spurious electronic self-interaction that is at the heart of the CT problems encountered with semilocal functionals. The range separation parameter γ defines the distance at which exact exchange becomes dominant, and the choice of γ is crucial for the quality of the theoretical results. In previous studies of the γBNL approach, the most successful strategy was to adjust γ such that the ionization energy of the neutral donor and the acceptor anion correspond as close as possible to the HOMO eigenvalue of the neutral donor and the acceptor anion, respectively. This appears as a natural condition when a clear distinction between the donor and acceptor molecules is possible.

In our present study this is not the case. In NDI-x, one cannot distinguish unambiguously between donor and accep-

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 132.64.30.166 On: Sat, 29 Aug 2015 15:55:55

tor as the constituents are covalently bound and as we are looking at a donor-acceptor-donor instead of just a donor–acceptor system. Therefore, we employ a different strategy[17] for adjusting γ which works with the molecule as a whole without the need to specify donor and acceptor. Yet, the fundamental physical principle according to which we adjust γ remains the same: The highest occupied eigenvalue of DFT should agree with the first ionization potential as calculated from total energy differences. For a given value of γ one can determine how well this condition is satisfied by evaluating the criterion

$$J2(\gamma) = \left|\epsilon^{\gamma}_{\mathrm{HOMO}}(N) + \mathrm{IP}^{\gamma}(N)\right| + \left|\epsilon^{\gamma}_{\mathrm{HOMO}}(N+1) + \mathrm{IP}^{\gamma}(N+1)\right|, \quad (1)$$

where $\epsilon^{\gamma}_{\mathrm{HOMO}}$ is the HOMO energy and IP^{γ} is the ionization potential of the N and $N+1$ electron system, respectively. The range separation parameter γ is then adjusted in an iterative procedure such that $J2$ is minimized for each system. We stress that this adjustment is a nonempirical step as no experimental or other empirical information enters and as enforcing Eq. (1) simply amounts to enforce as good as possible an exact constraint which the ultimate functional would automatically fulfill.

Following this procedure we have calculated for NDI-1 to NDI-7 the values of γ which minimize $J2$ (see Table I). These were then used in TDDFT calculations of the excitation energies and oscillator strengths. Figure 3(a) shows the first excitation energies that were obtained in this way with the $J2$-optimized γBNL functional.[26,34] For the reasons of clarity only the lowest excitation energy, which is the practically relevant one, is shown for each molecule. The experimentally measured excitation energies for NDI-1 and NDI-2 are marked as vertical lines in the plot.[18] The γBNL results for NDI-1 and NDI-2 are in good agreement with the corresponding experimental values, underestimating the experiment by about or less than 0.1 eV. A certain underestimation is plausible[27] as the experiments were conducted at room temperature and the calculations assumed 0 K. Thus, these results show that TDDFT can predict excitations of mixed CT and valence character with very reasonable accuracy.

The comparison with the lower panel of Fig. 3(b) shows that this is not a trivial result. Here, the excitations that are obtained from the popular B3LYP functional are shown. Clearly and as expected,[21] B3LYP does not describe the CT excitations properly and the deviation between B3LYP on the one hand and the γBNL results and experiment on the other is growing with increasing system size, i.e., with growing number of thiophene rings. As a further test we have also used the ωB97 and the ωB97x xc-functionals. For NDI-3, the lowest excitation is at 2.81 and 2.69 eV, respectively, i.e., at unrealistic energies.

TABLE I. First row: Range separation parameter γ for NDI-x obtained from minimizing the $J2$ criterion. γ was varied in steps of 0.005 (for NDI-6 and NDI-7 in steps of 0.001). Second row: The minimum value of $J2$ which was obtained at the end of the γ optimization. Hartree atomic units are used.

System	NDI-1	NDI-2	NDI-3	NDI-4	NDI-5	NDI-6	NDI-7
γ	0.180	0.160	0.145	0.140	0.135	0.132	0.131
$J2$	0.0040	0.0043	0.0042	0.0040	0.0034	0.0031	0.0028

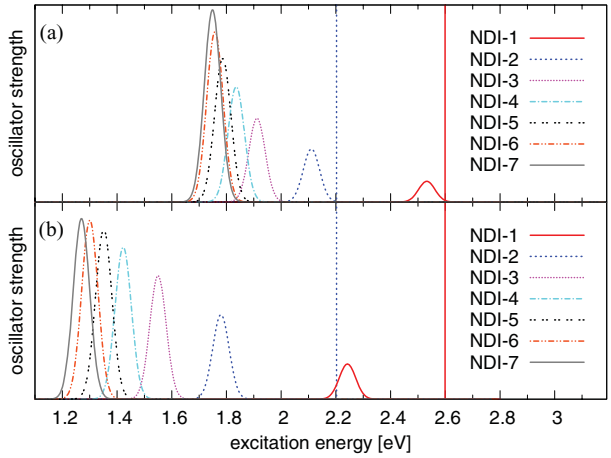

FIG. 3. First absorption peaks of the NDI-x systems calculated with linear response TDDFT. The peaks are broadened by Gaussian functions with a variance of 0.03 eV. The vertical lines indicate the maxima of the lowest experimentally observed absorption peaks (Ref. 18). **a**: γBNL. **b**: B3LYP.

For understanding why the γBNL approach is able to predict complicated excitations of mixed valence and CT character reliably one has to realize the decisive role which is played by the step in which γ is adjusted to fulfill Eq. (1). In this step the functional adapts to the system size and the character of the excitation. One may argue that the adjustment procedure makes γ a density functional—-though a very implicit and also unfortunately very nonlocal one. This is confirmed by the optimal γ-values for the NDI-x systems that we report in Table I.

From NDI-1 to NDI-7 the system size increases and γ decreases. This is understandable as γ indicates the length at which exact exchange dominates the electron–electron interaction. To conserve the same characteristic balance between semilocal exchange and exact exchange γ has to increase from NDI-7 to NDI-1 as the average distance between donor and acceptor decreases.

The second row of Table I shows the minimum value of $J2$ that was obtained for each system. All values are close to zero, which indicates that optimizing γ with respect to the ionization potential theorem is a possible and reasonable strategy. Furthermore, we note that the minimum values that we obtain are nearly identical for NDI-1 to NDI-7. Thus, one can argue that the predictive power of γBNL does not change with system size and that the calculated excitation energies of NDI-3 to NDI-7 can be expected to be of the same quality as the ones of NDI-1 and -2, which were verified by comparison with the experiments. Thus, we can use the TDDFT results to predict how much the lowest optical absorption can be shifted by adding thiophene rings to NDI.

However, before we do so we have to clarify two additional issues that are relevant for relating the TDDFT results to the experiments. First, we note that the theoretical numbers reported above were obtained for molecules in vacuum whereas the experimental excitations were

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 132.64.30.166 On: Sat, 29 Aug 2015 15:55:55

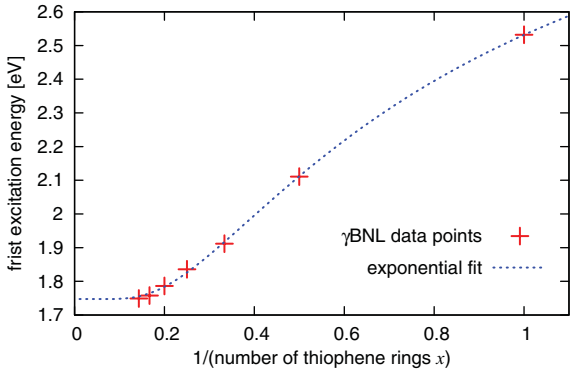

FIG. 4. Exponential fit of the calculated excitation energies to obtain the "infinite chain limit" value.

measured on molecules in a chloroform solution.[18] We checked the influence of the chloroform solvent on our calculations with TURBOMOLE (COSMO) (Ref. 28) and QCHEM (CHEMSOL).[29] This changed the excitation energies by about 0.01 eV, showing that the solvent influence on the electronic transitions can here be neglected. Second, we carefully checked the influence of the basis set. Using a smaller basis set, e.g., 6-31G(d,p) instead of 6-311G(d,p), shifts the excitation energies closer to the experimental values by up to 0.07 eV. However, it is the 6-311G(d,p) basis set which we consider as numerically sufficient and whose numbers we, therefore, report here.

Having thus clarified the reliability of our numbers we finally proceed to investigate how far the lowest absorption of NDI-x molecules can be shifted to exploit the visible spectrum. Figure 4 shows the lowest absorption energies of the NDI-x molecules as a function of the inverse number of thiophene rings x. The amount by which the absorption energy drops on adding another thiophene ring falls off dramatically from NDI-1 to NDI-7. We extrapolate to the "infinite chain limit" by fitting an exponential function to the calculated excitation energies,[30–33] and obtained a value of 1.75 eV, at the edge of the visible spectrum. Using a Kuhn or a combined Kuhn-exponential fit[27] results in a similar fit. In view of the accuracy limits of our theoretical prediction, NDI-5 with its absorption at 1.79 eV can be considered as being close to this limit.

In summary, we have investigated donor-acceptor-donor systems with NDI acting as the acceptor and thiophene rings acting as donors. Excitation energies were calculated using TDDFT with a range-separated hybrid approach that fulfills the ionization potential theorem as close as possible via nonempirical adjustment of the range separation parameter. We showed that the practically relevant excitation in the NDI-x systems is predominantly of CT character. Our results are in agreement with the experimental numbers for NDI-1 and NDI-2. We predict that the NDI-x systems with up to x=5 rings already allows to cover the absorption up to the lower end of the visible range. TDDFT emerges as a powerful tool for helping in the design of light-harvesting molecules.

We acknowledge discussions with A. Neubig, M. Thelakkat, and T. Körzdörfer, and finanical support by Deutsche Forschungsgemeinschaft(DFG) GRK1640 and the GIF.

[1]D. Rappoport and F. Furche, J. Am. Chem. Soc. **126**, 1277 (2004).
[2]A. Dreuw and M. Head-Gordon, J. Am. Chem. Soc. **126**, 4007 (2004).
[3]K. Burke, J. Werschnik, and E. K.U. Gross, J. Chem. Phys. **123**, 062206 (2005).
[4]D. Tozer, J. Chem. Phys. **119**, 12697 (2003).
[5]N. Maitra, J. Chem. Phys. **122**, 234104 (2005).
[6]M. Mundt and S. Kümmel, Phys. Rev. Lett. **95**, 203004 (2005).
[7]S. Kümmel and L. Kronik, Rev. Mod. Phys. **80**, 3 (2008).
[8]R. J. Magyar and S. Tretiak, J. Chem. Theory Comput. **3**, 976 (2007).
[9]H. Iikura *et al.*, J. Chem. Phys. **115**, 3540 (2001).
[10]J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
[11]T. Yanai *et al.*, Chem. Phys. Lett. **393**, 51 (2004).
[12]H. Sekino *et al.*, J. Chem. Phys. **126**, 014107 (2007).
[13]J.-D. Chai and M. Head-Gordon, J. Chem. Phys. **128**, 084106 (2008).
[14]M. Henderson, B. G. Janesko, and G. E. Scuseria, J. Chem. Phys. **128**, 194105 (2008).
[15]E. Livshits and R. Baer, Phys. Chem. Chem. Phys. **9**, 2932 (2007).
[16]T. Stein *et al.*, J. Am. Chem. Soc. **131**, 2818 (2009).
[17]T. Stein *et al.*, J. Chem. Phys. **131**, 244119 (2009).
[18]A. Neubig and M. Thelakkat (unpublished).
[19]P. J. Stevens *et al.*, J. Phys. Chem. **98**, 11623 (1994).
[20]J. P. Perdew *et al.*, Phys. Rev. Lett. **77**, 3865 (1996).
[21]M. J. G. Peach *et al.*, J. Chem. Phys. **128**, 044118 (2008).
[22]Z. Chen *et al.*, J. Am. Chem. Soc. **131**, 8 (2009).
[23]X. Guo *et al.*, J. Am. Chem. Soc. **131**, 7206 (2009).
[24]A. P. Zoombelt *et al.*, J. Mater. Chem. **19**, 5336 (2009).
[25]H. Yan *et al.*, Nature (London) **457**, 679 (2009).
[26]For the TDDFT calculations we used the qchem program package (Ref. 34) and the 6-311G(d,p) basis set.
[27]J. Gierschner *et al.*, Adv. Mater. **19**, 173 (2007).
[28]A. Klamt and G. Schüürmann, J. Chem. Soc. Perkin Trans. 2 **1993**, 799.
[29]J. Florián and A. Warshel, J. Phys. Chem. B **103**, 10282 (1999).
[30]H. Meier *et al.*, Acta Polym. **48**, 379 (1997).
[31]R. Martin *et al.*, Chem. -Eur. J. **6**, 3622 (2000).
[32]J. Rissler, Chem. Phys. Lett. **395**, 92 (2004).
[33]S. Tretiak *et al.*, Phys. Rev. Lett. **89**, 97402 (2002).
[34]Y. Shao *et al.*, Phys. Chem. Chem. Phys. **8**, 3172 (2006).

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 132.64.30.166 On: Sat, 29 Aug 2015 15:55:55