

Comment on “Structure–Property Relationships for Electron–Vibrational Coupling in Conjugated Organic Oligomeric Systems”

Johannes Gierschner*

Laboratory for Chemistry of Novel Materials, University of Mons-Hainaut, Belgium

Received: July 21, 2005

A recent article by O'Neill and Byrne¹ presents absorption, fluorescence, and Raman data of oligomeric π -conjugated molecules in solution in order to establish structure–property relationships. However, both the presented experimental results as well as the interpretation of the experimental data demand some comments and corrections. In detail:

1. In Figure 2a, absorption spectra of *p*-oligophenylenes in solution are depicted. The absorption characteristics of the spectra are well-known from literature, revealing no vibrational structure in the main absorption band.² But the spectra represented here differ significantly from those. Presumably, dispersed undissolved material was measured. This is probably also the reason for the long tail at the long-wavelength side of the biphenyl spectrum, which is due to strong scattering and which should not be present in molecular solutions. Further support for the presence of crystallites in the solutions is given by the fact that concentrations of ca. 10^{-5} M have been used, which is too high for the longer oligomers due to solubility problems. Moreover, the process of sonication is an arguable method for dissolving materials with a low solubility, since it tends to destroy crystallites, creating smaller ones instead of dissolving them. A treatment of only 15 min, as described in the article, is by far not enough to ensure that the material is completely dissolved. Therefore, the absorption characteristics in Figure 2a cannot serve as an argument for an increasing planarity in the molecular backbone with increasing chainlength of *p*-oligophenylenes. For the other oligomeric series, no absorption and fluorescence spectra are represented, thus the reader has no possibility to verify the spectral positions for these oligomers, given in Figures 2–4.

2. All the interpretation of the data (spectral positions, Stokes shifts, Raman intensities) is based on the “nearly-free electron model”. Here the quantities (electronic transition energies, Stokes shifts) are plotted against the reciprocal number of π -electrons. However, the conclusion that the linear behavior predicted by this model is “well established” is not correct: numerous experimental³ and theoretical⁴ studies have shown that a saturation of the electronic transition energies with longer chainlength is observed, and therefore a significant deviation from a linear behavior. This questions the applicability and significance of the approach employed here.

3. The intuitive approach to deduce a chainlength dependence of the Stokes shift (eq 3) is very limited in application and cannot be generally applied to vibronic coupling. A general procedure would be based on a Franck–Condon approach, resulting in vibronic coupling efficiencies, Huang–Rhys (HR)

factors, of *each* vibrational mode. In this context it should be mentioned that there is not only *one* single Huang–Rhys HR factor in the optical spectra of polyatomic molecules, but as many as the number of coupling vibrational modes (an exponential dependence of the HR factors on the chainlength, as stated in the article, might be applied for some of the HR factors, but not for all of them). With the whole set of HR factors and vibrational energies, reorganization energies ΔE can be obtained by a simple well-justified relation^{5,6} (for this reason ΔE , defined via the median of the spectrum,⁶ should be favored over the Stokes shift, defined via the maximum of the spectrum). With this approach, the chainlength dependence of ΔE can be indeed calculated in good agreement with experiment, see ref 6. The Franck–Condon approach also allows a quantitative investigation of the role of torsional modes on the Stokes shift either by considering thermal effects⁶ or by comparison to ladder-type materials.⁷

4. The number of $3n - 5$ normal vibrational modes in a “linear” system, as stated throughout the article, is correct only for linear arrangements of atoms (i.e., molecules with $D_{\infty h}$ or $C_{\infty v}$ symmetry), not for linear = rod-shaped oligomers where the number of vibrational modes equals $3n - 6$.

5. The relation between strong electron–phonon coupling and the efficiency of nonradiative decay processes, discussed extensively throughout the article, is in contradiction to the known photophysics in these systems. As the authors already correctly mention themselves, C–H vibrational modes can be important in the nonradiative deactivation. But these modes will not show any coupling to the electronic transition: the coupling efficiency is high if the atomic displacements of the mode coincide with the changes in the geometry upon electronic excitation.⁶ For the oligomers under study, the main change takes place in the carbon backbone.⁶ Nonradiative processes can (unfortunately) not “be monitored through relatively routine spectroscopic techniques”, as stated by the authors. However, an influence of electron–phonon coupling on the radiative decay rate k_F is expected: a larger Stokes-shift will lead to a decrease of the mean value of the emission energy. According to the Stickler–Berg equation,⁸ k_F will therefore slightly decrease. Moreover, the influence of torsional modes on k_F might be significant.⁹

References and Notes

- (1) O'Neill, L.; Byrne, H. J. *J. Phys. Chem. B* **2005**, *109*, 12685.
- (2) See for example: Nijegorodov, N. I.; Downey, W. S.; Danailov, M. B. *Spectrochim. Acta A* **2000**, *56*, 783.
- (3) See for example: (a) Meier, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2482. (b) Izumi, T.; Kobashi, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2003**, *125*, 5286.
- (4) See for example: (a) Oelkrug, D.; Egelhaaf, H.-J.; Gierschner, J.; Tompert, A.; *Synth. Met.* **1996**, *76*, 249. (b) Rissler, J. *Chem. Phys. Lett.* **2004**, *395*, 92.
- (5) Negri, F.; Zgierski, M. Z. *J. Chem. Phys.* **1994**, *100*, 2571.
- (6) Gierschner, J.; Mack, H.-G.; Luer, L.; Oelkrug, D. *J. Chem. Phys.* **2002**, *116*, 8596.
- (7) (a) Karabunarliev, S.; Bittner, E. R.; Baumgarten, M., *J. Chem. Phys.* **2001**, *114*, 5863. (b) Heimel, G.; Daghofer, M.; Gierschner, J.; List, E. J. W.; Grimsdale, A. C.; Müllen, K.; Beljonne, D.; Brédas, J.-L.; Zojler, E. *J. Chem. Phys.* **2005**, *122*, 054501.
- (8) (a) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814. (b) Vikesland, J. P.; Strickler, S. J. *J. Chem. Phys.* **1974**, *60*, 664.
- (9) Castel, N.; Fischer, E.; Bartocci, G.; Massetti, F.; Mazzucato, U. *J. Chem. Soc., Perkin Trans. 2*, **1985**, 1969.

* E-mail: johannes@averell.umh.ac.be.