

Optically induced electron transfer from conjugated organic molecules to charged metal clusters

N. Koch^{a,b,*}, A.C. Dürr^c, J. Ghijsen^d, R.L. Johnson^e, J.-J. Pireaux^d, J. Schwartz^b, F. Schreiber^{c,f,g},
H. Dosch^{c,f}, A. Kahn^a

^aDepartment of Electrical Engineering, Princeton University, Princeton, NJ 08544, USA

^bDepartment of Chemistry, Princeton University, Princeton, NJ 08544, USA

^cMax-Planck-Institut für Metallforschung, Heisenbergstrasse 3, Stuttgart D-70569, Germany

^dLaboratoire Interdisciplinaire de Spectroscopie Electronique, Facultés Universitaires Notre-Dame de la Paix, Namur B-5000 Belgium

^eII. Institut für Experimentalphysik, Universität Hamburg, Hamburg D-22761, Germany

^fInstitut für Theoretische und Angewandte Physik, Universität Stuttgart, Stuttgart, Germany

^gPhysical and Theoretical Chemistry Laboratory, Oxford University, Oxford OX1 3QZ, UK

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Abstract

The formation of small gold clusters at the initial stage of the metal growth on a thin film of the conjugated organic semiconductor diindenoperylene (DIP) leads to charging during ultraviolet photoemission spectroscopy (UPS) investigations. Additional irradiation of the sample with visible light was successfully applied to re-establish charge neutrality on the sample surface. By varying the light energy, we demonstrate that the optical formation of excitons and/or polarons results in efficient electron transfer from DIP to the positively charged Au clusters and thus the elimination of charging in UPS. This allows the collection of reliable information on the interface electronic structure.

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1. Introduction

Efficient charge injection from a metal contact is a key element of the performance of organic-based electronic and opto-electronic devices. A thorough understanding of the electronic and morphological properties of metal/organic interfaces is, therefore, essential for the development of future organic-based technologies. Device function and efficiency are commonly being evaluated assuming abrupt, homogeneous interface morphology. However, several phenomena, such as diffusion of metal species, chemical reactions and polarization of different elements in the surrounding matter, can, if occurring at the interface, lead to significantly different properties than expected [1]. Ultraviolet photoemission spectroscopy (UPS) has been shown to be an excellent tool to investigate electronic properties of metal/organic

interfaces [1]. Here we use this method to study the electronic structure and energy level alignment at interfaces formed between the organic semiconductor diindenoperylene (DIP, C₃₂H₁₆, see inset in Fig. 1) and Au under ultrahigh vacuum conditions. DIP exhibits excellent structural and hole transport properties [2–4]. The hole injection energy barrier between this material and a high work function hole-injecting metal, gold, is, therefore, of interest. Furthermore, the morphology of interfaces formed between DIP and Au has already been investigated [5], and will prove to be very helpful in the interpretation of UPS data. In particular, it has been shown that Au may form small clusters when deposited on top of the organic film at low total coverage. These isolated clusters make the photoemission study of this interface very difficult because of positive charge trapping that leads to severe sample charging. A comparable problem has already been reported for Au clusters on *p*-sexiphenyl films [6,7]. Furthermore, the importance of the electronic properties of small metal clusters embed-

*Corresponding author. Present address: Newtonstrasse 15; Berlin; Germany. Tel.: +49-30-2093-7819; fax: +49-30-2093-7632.

E-mail address: norbert.koch@physik.hu-berlin.de (N. Koch).

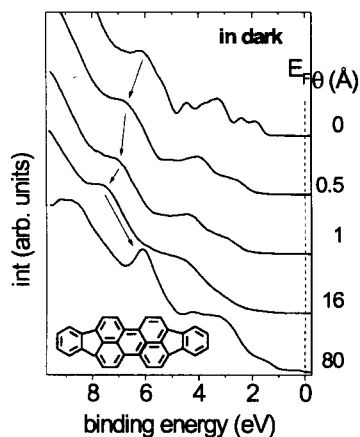


Fig. 1. UPS spectra recorded *in dark* for increasing amounts of Au (θ) on DIP.

ded in an organic matrix has been pointed out in several novel device architectures, like photovoltaic cells or bistable devices [8,9]. We present here a method to overcome the above-mentioned experimental obstacle, which involves irradiating the sample with visible light that can be absorbed by the organic molecules. Optically induced electron transfer from DIP to the clusters removes excess positive charges from the Au clusters embedded in the organic matrix, enabling the collection of meaningful UPS data.

2. Experimental details

Photoemission experiments were performed at the FLIPPER II beamline in HasyLab at DESY [10]. The evaporation of DIP and Au was performed in the preparation chambers, at pressures during evaporation lower than 5×10^{-9} mbar and 1×10^{-8} mbar, respectively. UPS was performed in the analysis chamber (base pressure 1×10^{-10} mbar) connected to the preparation chamber. DIP was purified by thermal gradient sublimation and evaporated from a resistively heated pinhole source, while Au was evaporated from a Knudsen-type cell. The mass-thickness of the DIP (bulk density: 1.35 g/cm^3) and Au (bulk density: 19.3 g/cm^3) overlayers was monitored by a quartz microbalance. The evaporation rate for both DIP and Au was approximately 2 \AA/min . Substrates were prepared by evaporating *in situ* approximately 300 \AA Au onto silicon wafers pre-coated with an adhesion layer of Cr (100 \AA) and Au (1000 \AA), which exhibit a rather smooth Au surface (roughness approx. 10 \AA). A 300 \AA thick DIP film was then grown onto the Au substrate, in order to ensure a pin-hole free organic layer. The absence of sample charging at this thickness was verified by carefully evaluating the position and width of the DIP photoemission peaks, which did not show any change as compared to thinner films. The resolution of the UPS

measurement was 0.15 eV (width of the intensity drop from 80 to 20% on the Au Fermi-edge). Au was evaporated incrementally on the DIP film, with UPS measurements at each step. The samples were negatively biased with respect to the electron spectrometer (-16 V), to allow recording of the secondary electron cutoff and the determination of binding energies with respect to the vacuum level (E_{vac}) [11]. The photon energy was set at 22 eV . Sample preparation and UPS measurements were performed at room temperature. Additional sample illumination with visible light was done with a standard halogen light source and low-pass optical filters with cut-off energies of 1.85 eV (RG 655, 2 mm) and 2.41 eV (OG 515, 1 mm) were used (both from Schott Glas, Germany).

3. Results and discussion

The UPS spectrum of the 300 \AA DIP film is shown as the uppermost curve in Fig. 1. The difference in energy between the onset of the highest occupied molecular orbital (HOMO) of DIP at the surface of the film and the Fermi-level (E_{F}) previously measured on the Au substrate is 1.45 eV . The DIP energy levels are flat when going from monolayer to multilayer coverage (except for polarization effects) as determined in a study where DIP was deposited incrementally onto Au substrates. The first ionization energy of DIP, defined as the energy difference between E_{vac} and the onset of the HOMO, is 5.80 eV .

Survey UPS spectra for increasing amounts of Au evaporated onto DIP are presented in Fig. 1. These spectra were recorded while the sample was kept in complete darkness (except for the synchrotron beam). For 0.5 \AA Au the whole spectrum appears significantly broadened, and shifted towards higher binding energy (BE) by 0.7 eV . Doubling the Au coverage leads to an increase in broadening and a shift of approximately 1 eV . The shift increases to approximately 1.3 eV for 16 \AA Au coverage, the broadening is even more pronounced and a small density of valence states (DOVS) appears in the former empty energy gap of the organic material. However, no DOVS is observed at E_{F} . After the deposition of 80 \AA Au, the whole spectrum shifts back towards lower binding energy (cf. arrows in Fig. 1). At this coverage, metallic Au is present on the sample, as shown by the finite DOVS at E_{F} that resembles the Au Fermi-edge.

These observations can readily be explained by sample charging due to the presence of small Au clusters on or near the DIP surface. A.C. Dürr et al. [5] have shown that Au evaporated onto DIP films does not always form a homogeneous metal film or an abrupt interface, especially at low total Au coverage. Most likely, Au growth does not proceed in a layer-by-layer mode. Instead, small gold clusters may be formed, which

can diffuse several nanometer into the organic film. Depending on their size, these clusters are semiconducting or metallic [12–16]. At sufficiently low Au coverage there is no direct electrical contact between individual Au clusters and no cluster percolation on the surface [17]. The removal of a photo-hole from a Au cluster through the surrounding DIP is difficult, as the hole-injection barrier from Au into DIP (or the electron-injection barrier from DIP into Au) is 1.45 eV (see above). Therefore, it is energetically favorable for holes to remain on the Au cluster instead of within the organic matrix. This results in a build-up of positive charges in the clusters, until the local electric field is high enough to allow for electron injection from DIP. Furthermore, the spatial and size distribution of clusters on the surface and the diffusion of clusters into the DIP film result in a number of differently charged sample areas. This, in turn, shifts the spectra towards higher BE and broadens them significantly (cf. Fig. 1), as already observed for Au deposition onto a thin film of *p*-sexiphenyl [6,7].

Sample charging is a major complication for the determination of electronic properties and energy level alignment at interfaces via photoemission spectroscopy. Furthermore, the common charge-compensation technique of applying an electron flood-gun is not appropriate for conjugated organic materials, which are prone to severe degradation under electron bombardment [18,19]. An alternative technique involves irradiating the sample with light of appropriate wavelength, as already reported for (thick) conjugated organic films without metal overlayers [19,20]. These previous studies have shown that an organic film that exhibits charging due to ultraviolet photoemission can be discharged via internal photoemission at the metal substrate/organic overlayer interface. Photoexcited metal electrons can be injected into the organic material if the excitation energy is larger than the electron-injection barrier at the interface. Note that light absorption in the organic material itself is not essential in this case.

In the present case, however, electrons must be injected from the organic material into the metal clusters. Direct resonant electron transfer from the organic molecule to the metal cluster, via internal photoemission, where the photon energy is equal to the electron-injection barrier (1.45 eV in the present case), is one possible mechanism. Another process likely to occur is electron transfer after optical excitation of the organic molecules, when the photon energy is equal to or larger than the optical energy gap of DIP (2.2 ± 0.1 eV [21,22]). In that case, light absorption creates excitons in DIP. The electron excited into the former lowest unoccupied molecular orbital (LUMO) of DIP lies higher in energy than the photo-hole on the Au cluster and can be transferred to the cluster and discharge it. Moreover, excitons can dissociate into positive and negative free charge carriers (polarons) [23,24], a phe-

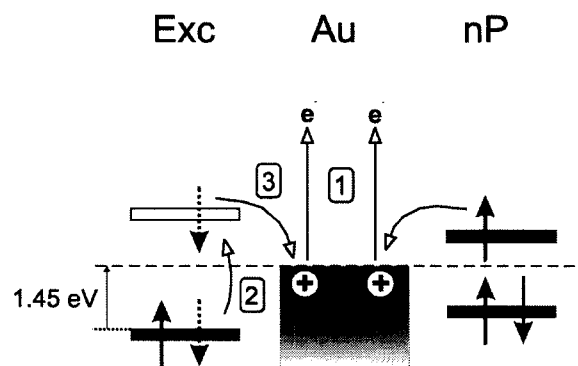


Fig. 2. Schematic energy level diagram of the DIP/Au interface, and the mechanisms leading to charge neutralization on Au clusters by additional light irradiation. Step 1 is the photoemission process, creating the positive charge on the cluster. Step 2 is the absorption of visible light by a DIP molecule, creating the transiently existing exciton (Exc); energy relaxation effects on the position of the energy levels are not taken into account. Step 3 is the electron transfer from the upper exciton level to the Au cluster. On the right hand side the direct electron transfer from a negative polaron (nP; created by dissociation of excitons) is shown. The energy levels of the nP are shown schematically, as their actual position are unknown.

nomenon which is enhanced at defects and interfaces [25–27]. If the energy of the negative polaron is larger than that of the photo-hole on the cluster, cluster neutralization can proceed. An energy level diagram of Au/DIP and the proposed charge-compensation mechanisms are depicted in Fig. 2 (for simplicity we assume here metallicity of the Au cluster).

To discriminate between these various mechanisms, we irradiated the charged Au-on-DIP sample with light from a halogen lamp while recording the photoemission spectra. The emission spectrum of the lamp extends to energies sufficient to create excitons in DIP (2.2 eV). The demonstration that this additional light can remove charging from the sample is given in Fig. 3a. The bottom curve is the UPS spectrum obtained for 1 Å Au on DIP in the dark. The top curve is obtained on the same sample after optimizing the light intensity, i.e. additional increase in light intensity did not lead to a further change of the spectrum. The middle curve corresponds to approximately half of the optimum light intensity. The spectrum clearly gains in resolution and shifts towards lower BE upon illumination. The low BE onset from the DIP HOMO is at 1.45 eV below E_F for saturated light condition, which is the same value as for the pristine DIP film (top curve in Fig. 1). Thus, it is assumed that complete discharge of the Au clusters has occurred. The situation is very similar for the 16 Å Au coverage (Fig. 3b). Without light, the UPS spectrum is broad, shifted to high BE and no DOVS is found at E_F . Under illumination, the spectrum sharpens and a DOVS appears in the energy gap of the organic material, extending almost up to E_F . Finally, the broadening and

the shift shown in Fig. 3 are entirely reversible for light on/off on the timescale of our experiments (typically 15 min per spectrum).

In the second set of experiments, optical low-pass filters are used to examine possible charge-neutralization by sub-gap absorption. The spectra shown in the right part of Fig. 3 are from a 300 Å thick DIP film (on Au) with a nominal 0.5 Å coverage of Au. Curve (c) is recorded without illumination and is thus identical to the corresponding curve in Fig. 1. Spectra (d) and (e) correspond to illumination through 1.85 eV and 2.41 eV low-pass filters, respectively. Spectrum (f) corresponds to illumination without any filter. Obviously, light with energy smaller than 1.85 eV will not be able to compensate charging, as curves (c) and (d) are virtually identical. This observation rules out the mechanism of resonant electron transfer from DIP to the Au clusters (at least at significant rate). Only illumination with higher energy light removes charging. As curves (e) and (f) are identical, we can conclude that light with energy slightly larger than the optical energy gap of DIP (2.2 eV) leads to charge transfer by the two mechanisms depicted in Fig. 2.

The evolution of valence electron spectra (obtained with illumination) of DIP upon increasing deposition of Au is shown in Fig. 4. For each coverage, the light intensity is optimized for complete elimination of charging-related shifts (see above), and the real evolution in the electronic structure of the interface can be observed. As Au is incrementally deposited, the spectral features of DIP become less prominent, and a DOVS is observed within the energy gap of the organic material. However, this DOVS does not initially extend up to E_F . For a

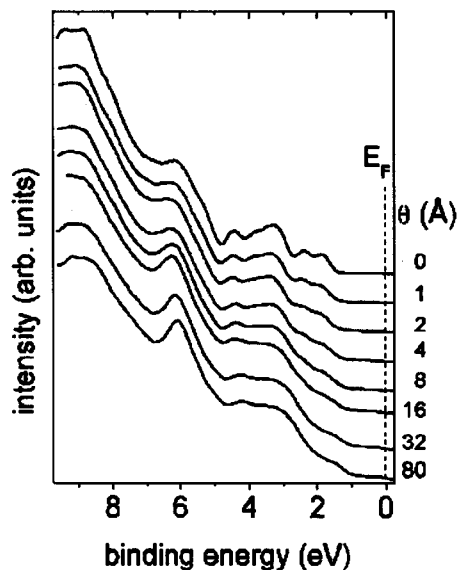


Fig. 4. UPS spectra for increasing amounts of Au (θ) on DIP. The spectra (except $\theta=0$ and 80 Å) were recorded during illumination with visible light at saturation conditions (see text).

coverage of approximately $\theta=16$ Å, a small tail-like DOVS is detected at E_F . This is attributed to the average cluster size distribution that is present at individual deposition steps. Whereas most clusters at and below $\theta=16$ Å are still too small to be metallic, an increasing number of clusters become large enough to exhibit metallic character [17]. This behavior is comparable to what was observed for other physisorptive metal/organic systems [28–31]. At $\theta=80$ Å most of the Au deposit has become metallic, a clear Fermi-edge is visible, and

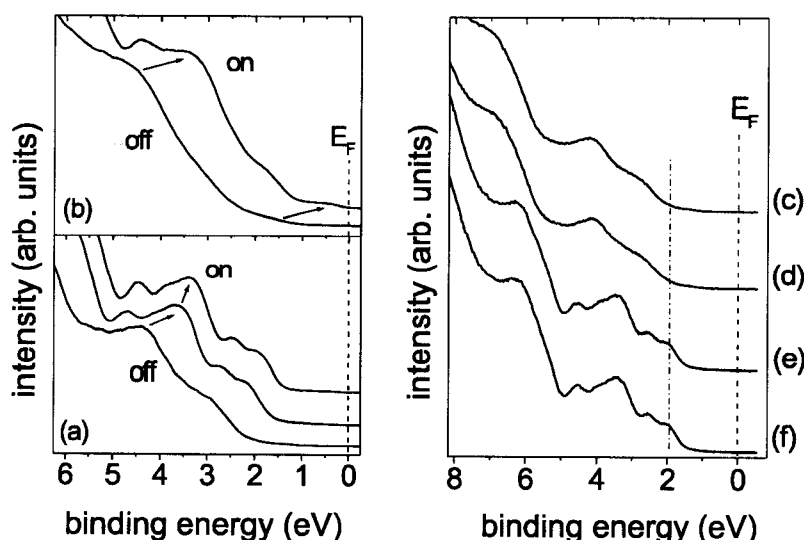


Fig. 3. UPS spectra for (a) 1 Å and (b) 16 Å Au on DIP, recorded while additional irradiation with visible light was *off* or *on* (as indicated). The arrows indicate the shift for characteristic emission features. UPS spectra for 0.5 Å Au on DIP recorded (c) in dark and with additional light irradiation, employing (d) a 1.85 eV low-pass filter, (e) a 2.41 eV low-pass filter, and (f) no filter. The dash-dotted line at approximately 2 eV is a guide to the eye for the shift.

the prominent photoemission peak at 6 eV BE is attributed to the Au 5d band. Furthermore, at this coverage there is no more shift between the spectra recorded with and without additional light irradiation. This indicates that the Au clusters, even those still too small to be metallic, have percolated and allow efficient charge transport across the surface, eliminating all effects of charging.

4. Conclusion

For Au deposition onto DIP we find evidence of the formation of Au clusters, which percolate only for Au coverages greater than 32 Å to give metallic surface conductivity. The metal clusters on the organic layer lead to significant sample charging in UPS. This charging could effectively be eliminated by additional illumination of the sample with light of sufficient energy to create excitons in DIP. The excited states of the organic material then facilitate efficient electron transfer to the charged metal clusters.

Acknowledgments

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References

- [1] W.R. Salaneck, K. Seki, A. Kahn, J.-J. Pireaux, *Conjugated Polymer and Molecular Interfaces: Science and Technology for Photonic and Optoelectronic Applications*, Marcel Dekker, New York, 2001.
- [2] N. Karl, in: R. Farchioni, G. Grosso (Eds.), *Charge Carrier Mobility in Organic Molecular Crystals*, in *Organic Electronic Materials*, Part II: Low Molecular Weight Organic Solids, Springer, Berlin, 2001.
- [3] A.C. Dürr, F. Schreiber, K.A. Ritley, V. Kruppa, J. Krug, H. Dosch, B. Struth, *Phys. Rev. Lett.* 90 (2003) 016014.
- [4] A.C. Dürr, F. Schreiber, M. Münch, N. Karl, B. Krause, V. Kruppa, H. Dosch, *Appl. Phys. Lett.* 81 (2002) 2276.
- [5] A.C. Dürr, F. Schreiber, M. Kelsch, H.D. Carstanjen, H. Dosch, *Adv. Mater.* 14 (2002) 961.
- [6] H. Oji, E. Ito, M. Furuta, H. Ishii, Y. Ouchi, K. Seki, *Synth. Met.* 121 (2001) 1721.
- [7] K. Seki, N. Hayashi, H. Oji, E. Ito, Y. Ouchi, H. Ishii, *Thin Solid Films* 393 (2001) 298.
- [8] L. Ma, S. Pyo, J. Ouyang, Q. Xu, Y. Yang, *Appl. Phys. Lett.* 82 (2003) 1419.
- [9] A. Yakimov, S.R. Forrest, *Appl. Phys. Lett.* 80 (2002) 1667.
- [10] R.L. Johnson, J. Reichardt, *Nucl. Instrum. Methods* 208 (1983) 719.
- [11] I.G. Hill, A. Rajagopal, A. Kahn, *J. Appl. Phys.* 84 (1998) 3236.
- [12] W. Eberhardt, P. Fayet, D.M. Cox, Z. Fu, A. Kaldor, R. Sherwood, D. Sondericker, *Phys. Rev. Lett.* 64 (1990) 780.
- [13] O.D. Haberlen, S.C. Chung, N. Rosch, *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.* 98 (1994) 882.
- [14] T.G. Schaaff, M.N. Shafiqullin, J.T. Khoury, I. Vezmar, R.L. Whetten, W.G. Cullen, P.N. First, C. Gutierrez-Wing, J. Ascensio, M.J. Jose-Yacamán, *J. Phys. Chem. B* 101 (1997) 7885.
- [15] M.A. Omary, M.A. Rawashdeh-Omary, C.C. Chusuei, J.P. Fackler, P.S. Bagus, *J. Chem. Phys.* 114 (2001) 10 695.
- [16] H.-G. Boyen, G. Kästle, F. Weigl, P. Ziemann, G. Schmid, M.G. Garnier, P. Oelhafen, *Phys. Rev. Lett.* 87 (2001) 27 6401.
- [17] Au clusters with a diameter smaller than ca. 20 Å have been shown to be not metallic. The onset of metallicity occurs for clusters with larger diameter. See: C.N.R. Rao, V. Vijayakrishnan, H.N. Aiyer, G.U. Kulkarni, G.N. Subbanna, *J. Phys. Chem.* 97 (1993) 11157. C. Xu, W.S. Oh, G. Liu, D.Y. Kim, D.W. Goodman, *J. Vac. Sci. Technol. A* 15(3) (1997) 1261.
- [18] P. Broms, N. Johansson, R.W. Gymer, S.C. Graham, R.H. Friend, W.R. Salaneck, *Adv. Mater.* 11 (1999) 826.
- [19] N. Koch, D. Pop, R.L. Weber, N. Böwering, B. Winter, M. Wick, G. Leising, I.V. Hertel, W. Braun, *Thin Solid Films* 391 (2001) 81.
- [20] E.-E. Koch, *Physica Scripta* T17 (1987) 120.
- [21] A. Bauer, Ph.D. Thesis, Universität Stuttgart, Stuttgart, 1991.
- [22] A.C. Dürr, Ph.D. Thesis, Universität Stuttgart, 2002.
- [23] V. Dyakonov, G. Rösler, M. Schwörer, E.L. Frankevich, *Phys. Rev. B* 56 (1997) 3852.
- [24] C. Zenz, G. Cerullo, G. Lanzani, W. Graupner, F. Meghdadi, G. Leising, S.D. Silvestri, *Phys. Rev. B* 59 (1999) 14336.
- [25] H. Antoniadis, L.J. Rothberg, F. Papadimitrakopoulos, M. Yan, M.E. Galvin, M.A. Abkowitz, *Phys. Rev. B* 50 (1994) 14911.
- [26] M. Pope, C.E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, Oxford University Press, Oxford, 1999.
- [27] W. Graupner, M. Sacher, M. Graupner, C. Zenz, G. Grampp, A. Hermetter, G. Leising, *Mater. Res. Soc. Symp. Proc.* 488 (1998) 789.
- [28] N. Koch, L.M. Yu, V. Parente, R. Lazzaroni, R.L. Johnson, G. Leising, J.J. Pireaux, J.L. Bredas, *Adv. Mater.* 10 (1998) 1038.
- [29] N. Koch, R. Pairleitner, Q.T. Le, E.W. Forsythe, Y. Gao, G. Leising, *Appl. Phys. Lett.* 76 (2000) 3738.
- [30] N. Koch, E. Zojer, A. Rajagopal, J. Ghijsen, R.L. Johnson, G. Leising, J.J. Pireaux, *Adv. Funct. Mater.* 11 (2001) 51.
- [31] N. Koch, J. Ghijsen, R.L. Johnson, J. Schwartz, J.-J. Pireaux, A. Kahn, *J. Phys. Chem. B* 106 (2002) 4192.