



# Alkyl chain effects in thin films of substituted phthalocyanines studied using infrared spectroscopy

A. Haug<sup>a</sup>, S. Harbeck<sup>a</sup>, D. Dini<sup>b</sup>, M. Hanack<sup>b</sup>, M.J. Cook<sup>c</sup>,  
H. Peisert<sup>a,\*</sup>, T. Chassé<sup>a</sup>

<sup>a</sup> *Institute of Physical and Theoretical Chemistry, University of Tübingen, Auf der Morgenstelle 8, 72076 Tübingen, Germany*

<sup>b</sup> *Institute of Organic Chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany*

<sup>c</sup> *School of Chemical Sciences & Pharmacy, University of East Anglia, Norwich NR4 7TJ, UK*

Available online 2 March 2005

## Abstract

Thin films (2–50 nm) of unsubstituted and 1,4-octa-alkyl substituted zinc phthalocyanines were investigated using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, whereas the alkyl chains are C<sub>4</sub>H<sub>7</sub>, C<sub>7</sub>H<sub>13</sub>, C<sub>10</sub>H<sub>19</sub>. The absorption bands in the whole spectral range are discussed. We observe distinct differences in the spectra between the alkyl substituted Phthalocyanine (Pc) compounds. In contrast to PcZn and (but)<sub>8</sub>PcZn, the spectra of (hep)<sub>8</sub>PcZn and (dec)<sub>8</sub>PcZn show two additional features in the spectral range between 3700 and 3000 cm<sup>-1</sup>, which are discussed in detail.

© 2005 Elsevier B.V. All rights reserved.

PACS: 78.30.Jw

Keywords: Phthalocyanine; Thin films; FTIR-ATR spectroscopy

## 1. Introduction

Phthalocyanines (Pc's) are among the most intensely studied molecular materials due to their unique properties [1]. They represent one of the most promising candidates for ordered organic thin films, as these systems possess advantageous attributes, such as chemical stability and excellent film growth, which

can result in optimized electronic properties [2–4]. Thus, Pc's are not only a model system for the entire class of low molecular weight, organic molecules — in particular in the field of organic semiconductors they are attractive for numerous applications, such as organic light emitting diodes (OLED), displays, organic field effect transistors (OFET) and solar cells [2,4–9].

A very high degree of orientation in evaporated Pc films was recently observed on several substrates, the films can be prepared by evaporation or from solutions. A low-cost preparation from solution,

\* Corresponding author. Tel.: +49 7071 2976931;

fax: +49 7071 295490.

E-mail address: [peisert@ipc.uni-tuebingen.de](mailto:peisert@ipc.uni-tuebingen.de) (H. Peisert).

however, requires at least a partial solubility, thus only substituted Pc's are applicable. In recent years, efforts have been made to synthesize Pc derivatives with alkoxy, alkyl and other lipophilic substituents [10–13]. Here, we report on investigations of vibration properties in thin films in dependence on the chain lengths of alkyl substituents in Pc's using attenuated total reflection – Fourier transform infrared (ATR-FTIR) spectroscopy.

## 2. Experimental

All ATR spectra were recorded using a Bruker FTIR-spectrometer (IFS66v) with a separate high vacuum chamber ( $\sim 1 \times 10^{-7}$  mbar) and an ATR unit (Harrick Scientific). The spectra were taken with a resolution of  $2 \text{ cm}^{-1}$ . The substituted Pc's were synthesized according Ref. [13]. The powder source materials ( $(\text{hep})_8\text{PcZn}$  and  $(\text{dec})_8\text{PcZn}$ ) were additionally characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) using a FTIR-spectrometer (Equinox 55). Thin films (2–50 nm) of the organic materials (1,4-octa-alkyl substituted and unsubstituted zinc phthalocyanines (PcZn)), were evaporated directly on ZnSe ATR-crystals (a double-pass plate with single aperture and cocked end) in a separate UHV chamber. The film thicknesses were determined using a quartz micro-balance. In order to keep the influence of air exposure low, the samples were directly transferred to the spectrometer from the evaporation unit.

## 3. Results and discussion

Fig. 1 shows the spectra of nominally 50 nm thick films of unsubstituted and 1,4-octa-alkyl substituted zinc phthalocyanines with different alkyl chain lengths [alkyl: (but)<sub>8</sub>, (hep)<sub>8</sub> and (dec)<sub>8</sub>] in the spectral range between 1700 and  $675 \text{ cm}^{-1}$ . The PcZn spectrum at the bottom exhibits the characteristic spectral features to be expected for Pc molecules, e.g. the asymmetrical C–N=C vibration ( $1486 \text{ cm}^{-1}$ ), C–C stretching modes of pyrrole ( $1334, 1165, 1118 \text{ cm}^{-1}$ ) and the C–N bending mode ( $1092 \text{ cm}^{-1}$ ) [14]. In case of the substituted Pc's additionally a strong absorption structure ( $1470$ –

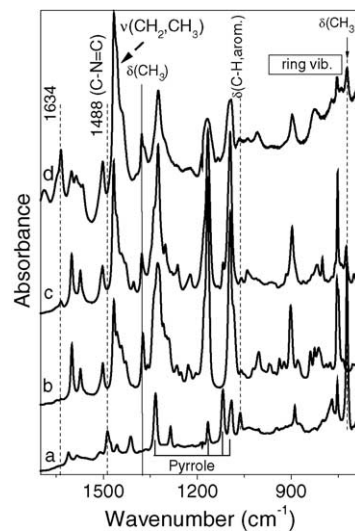


Fig. 1. Spectra of unsubstituted ZnPc (a), 1, 4-octa-alkyl substituted ZnPc, where alkyl chains are butyl (b), heptyl (c) and decyl (d) in the fingerprint spectral range.

$1430 \text{ cm}^{-1}$ ) occurs which systematically increases with alkyl chain length. These features correspond to different vibration modes of the  $\text{CH}_2/\text{CH}_3$  groups. The deformation mode of  $\text{CH}_3$  groups appears in the spectra at  $1373 \text{ cm}^{-1}$ . In the spectral range between 900 and  $740 \text{ cm}^{-1}$ , several weak structures, mostly attributed to Pc breathing modes, appear. They are evidently affected by the particular substitution. The absorption band at  $723 \text{ cm}^{-1}$  is assigned to C–H out of plane deformation mode ( $\delta_{\text{C-H, o.o.p.}}$ ). The appearance of an absorption band at  $1634 \text{ cm}^{-1}$  in the spectra of  $(\text{hep})_8$  and  $(\text{dec})_8\text{PcZn}$  could be a hint of the formation of C–C double bond (C–C stretching mode).

Further changes in the spectra of differently 1,4-octa-alkyl substituted PcZn have to be recognized at higher wavenumbers (see Fig. 2) in the spectral range characteristic for aromatic and aliphatic C–H vibrations ( $3100$ – $3000$  and  $3000$ – $2800 \text{ cm}^{-1}$ , respectively). The spectra in the range of the aromatic modes are much weaker ( $\times 10$ ) and appear less affected by the substitution. For the aliphatic vibrations distinct variations of both absolute and relative intensities of the absorption bands are observed. As expected from the chemical composition, in particular the intensity ratio of  $\text{CH}_2$ -related ( $\nu_{\text{as}(\text{CH}_2)}$   $2923 \text{ cm}^{-1}$ ,  $\nu_{\text{s}(\text{CH}_2)}$   $2852 \text{ cm}^{-1}$ ) and  $\text{CH}_3$ -stretching modes ( $\nu_{\text{as}(\text{CH}_3)}$   $2954 \text{ cm}^{-1}$ ,  $\nu_{\text{s}(\text{CH}_3)}$

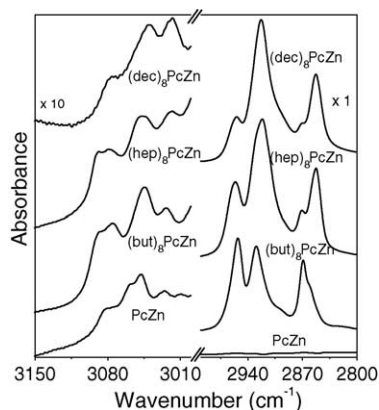


Fig. 2. Comparison of the 1,4-octa-alkyl substituted zinc phthalocyanines showing the vibrations of aromatic and aliphatic C–H stretching modes.

2871  $\text{cm}^{-1}$ ) changes significantly due to the increasing alkyl chain length.

In case of substituted Pc's two additional absorption bands with different half width at half maximum appear at 3525, 3396  $\text{cm}^{-1}$  and the broad background absorption grows with increasing chain length between these two absorption bands (see Fig. 3, left). This region is characteristic for the N–H or O–H related species, whereas O–H vibration modes usually appear at higher wavenumbers. Of course, overtones may be also present at higher wavenumbers. Tentatively, we assign these features to N–H stretching modes. The appearance of two absorption bands with a distance of more than 100  $\text{cm}^{-1}$  may point to different N–H vibrations, or to ionic structures. Similar intermolecular N–H interactions were recently also

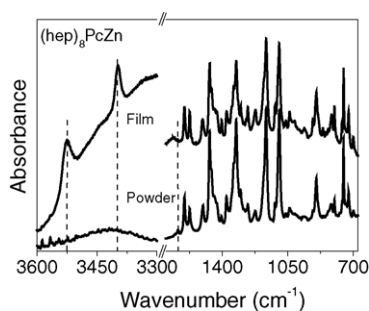


Fig. 3. Comparison of (hep)<sub>8</sub>PcZn (film, ATR-FTIR) and (hep)<sub>8</sub>PcZn (powder, DRIFT) spectra in the spectral range of 3600–3000  $\text{cm}^{-1}$  (left, typical for N–H and O–H vibrations) and of 1700–675  $\text{cm}^{-1}$  (right).

observed in other related aromatic nitrogen containing compounds [15].

However, from the chemical structure of the Pc molecule N–H bonds cannot be expected. Thus, the observations above raise questions regarding the origin of these features. Different explanations are conceivable, for instance: a contamination by traces of other organic materials, alterations of the substituted Pc's during the evaporation process, specific interactions of the substituted Pc's at the substrate interface, interactions with air during the transport of the sample from the evaporation chamber to the measurement chamber or specific interactions between substituted Pc molecules in ultra thin films related to the growth process.

In order to demonstrate the cleanliness of the substituted Pc materials we have additionally taken powder spectra for (hep)<sub>8</sub>PcZn (Fig. 3) and (dec)<sub>8</sub>PcZn (not shown) using the DRIFT technique. Since the N–H vibration is not present in the corresponding powder spectrum in Fig. 3, a contamination of the Pc's can be ruled out. Accompanying in situ experiments using high-resolution photoemission spectroscopy did not provide hints for a modification of the Pc's during the evaporation process.

On the other hand, the appearance of the N–H group and the C=C double bond may point to a drastical conversion of the substituted PcZn molecules, where H atom from the substituent is attached to the N atom of the inner ring of the Pc molecule. It seems that molecules with longer substituents can be modified more easily. However, the true chemical origin of these modes calls for further detailed studies. The investigation of the influence of oxygen is currently in progress in our lab.

#### 4. Conclusion

Thin film unsubstituted and 1,4-octa-alkyl substituted zinc phthalocyanines with different alkyl chain lengths were characterised using ATR-FTIR spectroscopy. Distinct differences in the spectra between the different PcZn compounds can be directly explained by additional contributions from the alkyl chains. However, in contrast to PcZn and (but)<sub>8</sub>PcZn, the spectra of (hep)<sub>8</sub>PcZn and (dec)<sub>8</sub>PcZn show two additional features in the spectral range between 3700

and  $3000\text{ cm}^{-1}$ , which may indicate specific intermolecular interactions due to the substitutions.

### Acknowledgement

Technical support from W. Neu is gratefully acknowledged.

### References

- [1] N. Kobayashi, J. Porphyryns Phthalocyanines 4 (2000) 377.
- [2] S.R. Forrest, *Chem. Rev.* 97 (1997) 1793 (and references cited therein).
- [3] M. Hanack, M. Lang, *Adv. Mater.* 6 (1994) 819.
- [4] M. Knupfer, H. Peisert, *Phys. Status Solidi (a)* 201 (2004) 1055.
- [5] C.W. Tang, S.A. VanSlyke, *Appl. Phys. Lett.* 51 (1987) 21.
- [6] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A. Dos Santos, J.L. Bredas, M. Löglund, W.R. Salaneck, *Nature* 397 (1999) 121.
- [7] D.C. Dimitrakopoulos, R.L. Melenfant, *Adv. Mater.* 14 (2002) 99.
- [8] P. Peumans, A. Yakimov, S.R. Forrest, *J. Appl. Phys.* 93 (2002) 3693.
- [9] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, *Adv. Funct. Mater.* 11 (2001) 15.
- [10] S. Vagin, M. Hanack, *Eur. J. Org. Chem.* 3 (2004) 600.
- [11] M. Hanack, *Synth. Met.* 55 (1993) 873.
- [12] I. Chambrier, M.J. Cook, M. Helliwell, A.K. Powell, *J. Chem. Soc., Chem. Commun.* (1992) 444.
- [13] M.J. Cook, M.F. Daniel, K.J. Harrison, N.B. McKeown, A.J. Thomson, *J. Chem. Soc., Chem. Commun.* (1987) 1086.
- [14] H. Günzler, H.-U. Gremlich, *IR-Spektroskopie*, Wiley-VCH, Weinheim, 2003.
- [15] J. Schnadt, J. Schiessling, J.N. O'Shea, S.M. Gray, L. Patthey, M.K.-J. Johansson, M. Shi, J. Krempaský, J. Åhlund, P.G. Karlsson, P. Persson, N. Mårtensson, P.A. Brühwiler, *Surf. Sci.* 540 (2003) 39.