

# Design of Molecular Interactions in Pigment Particles to Control the Emission Yield of Thin Films

Derck Schlettwein<sup>1</sup>, Harald Graaf<sup>1</sup>, Hisao Yanagi<sup>2</sup>, Nils Jaeger<sup>1</sup>, and Dieter Wöhrle<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Bremen, D- 28334 Bremen, Germany

<sup>2</sup>Faculty of Engineering, Kobe University, Kobe 657- 8501, Japan

## Abstract

Perylene- and phthalocyanine-pigment molecules were systematically modified and consequences were studied for their solid state properties. Thin films (1- 100 nm) of these compounds were prepared by physical vapor deposition on Si- based interdigitated microelectrode arrays or transparent insulating substrates such as (amorphous) glass or (single crystalline) alkali halides. Intermolecular interactions were probed by optical measurements in absorption and emission as well as by measurements of the electrical conductivity and the field effect (OFET). The morphology of films was studied by transmission electron microscopy (TEM) and atomic force microscopy (AFM).

Different interactions among the molecules and with the substrate surfaces allowed to prepare either crystalline or amorphous films. Crystalline films were characterized by strong chromophore coupling leading to characteristic splitting, well- defined shifts of optical absorption bands and emission mainly from excimeric species whereas the chromophore coupling in the amorphous films was suppressed sufficiently to provide a significantly increased photoemission yield from uncoupled monomeric states.

## Introduction

The growth of organic thin films of well-defined and adjustable structure represents a fundamental prerequisite to discuss basic principles underlying a number of properties of organic thin films that are of significant relevance in a number of established and emerging technologies. The ability to prepare films of well-defined molecular arrangement in the solid is in turn needed to develop and optimize devices based on organic thin films. Films of well-ordered pigment particles are therefore preferred as photoconductors in electrophotography,<sup>1</sup> for studies of organic diodes and transistors,<sup>2,3</sup> for the construction of organic photovoltaic cells<sup>4,5</sup> and chemical sensors.<sup>6,9</sup> Phthalocyanines (Pc) and perylene tetracarboxylic acid bisimides (PTCDI) represent two groups of pigments that are of particular interest.<sup>10,11</sup> Aside from these crystalline films some groups of materials which are of equal or even higher relevance in some applications do not rely upon a highly ordered growth. Films of molecules or metal

complexes which form amorphous rather than crystalline solids<sup>12-14</sup> can be very efficient layers for charge transport or light emission.

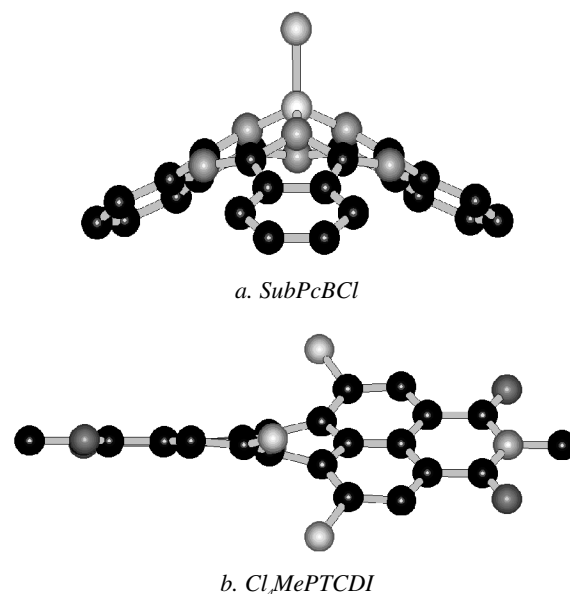


Figure 1. Structures of studied molecules as obtained following geometry optimization by semiempirical quantum chemical calculations (AM1 parameter set). Deviations from planarity of the aromatic systems are clearly seen.

In the present contribution results obtained at chemically modified Pc and PTCDI that lead to a decreased chromophore interaction as otherwise mainly observed for amorphous films will be presented and discussed. Subphthalocyaninatochloroboron (SubPcBCl) and 1,6,7, 12-tetrachloro-N,N'-dimethyl perylene tetracarboxylic acid diimide (Cl<sub>4</sub>MePTCDI) were chosen as examples (see figure 1) to study the effect of distortion of the aromatic core<sup>15-18</sup> on molecular interactions and chromophore coupling in vapor-deposited thin films when compared to the widely flat aromatic systems as typical for Pc and unsubstituted N,N'-dimethyl perylene tetracarboxylic acid diimide (MePTCDI).<sup>10,11,19-21</sup>

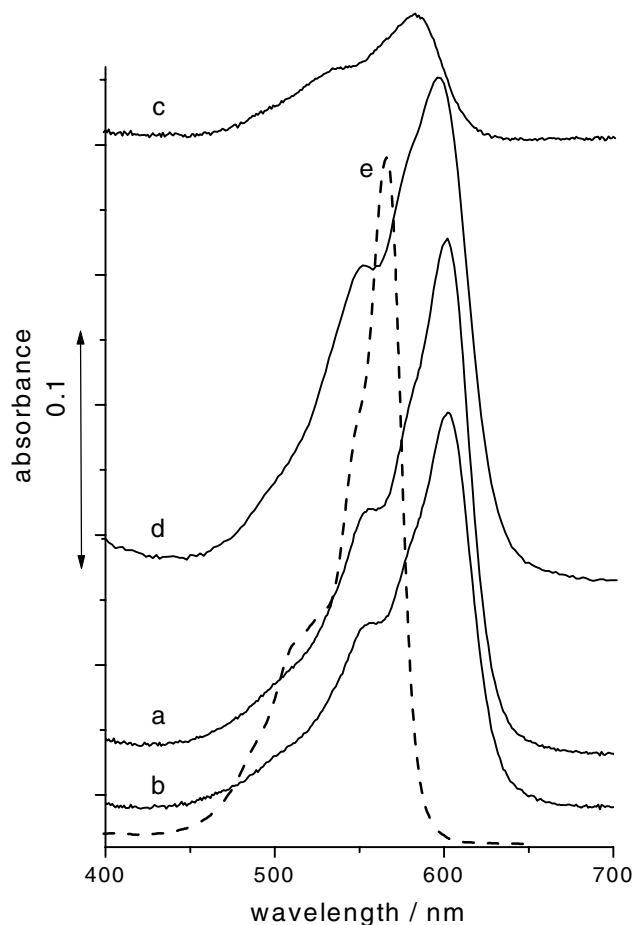


Figure 2. Optical absorption spectra of SubPcBCl as observed in transmission of (a) 11 nm on KBr, (b) KCl, (c) glass and (d) 23 nm on glass as compared to (e) a solution spectrum in DMF.

### SubPcBCl - A Modified Phthalocyanine

Regular phthalocyanines (Pc) are generally considered flat aromatic systems with a central group either within that same plane (for the metal-free Pc and metallated complexes with small divalent metal atoms) or sticking out of the plane for larger metal atoms like Pb or metals of higher valence which carry additional axial ligands (e.g. InCl, TiO, VO).<sup>4,10</sup> Subphthalocyaninato-chloro-boron (SubPcBCl) on the other hand is known to form a cone-shaped molecule<sup>16-18</sup> as also revealed by a semiempirical quantum chemical geometry optimization using the AM1 parameter set starting from a structure optimized by molecular mechanics calculations (MM<sup>+</sup> force field) as shown in figure 1a. This molecular structure leads to a bulk crystal structure which is characteristically different from those of regular Pc.<sup>16,17</sup>

Also in thin films characteristically different intermolecular interactions were obtained. Figure 2 shows the optical absorption spectra of the films as compared to a solution of SubPcBCl in DMF. For all thin films bands are found in the Q-band region which are only slightly broadened and shifted relative to that in solution. The shape,

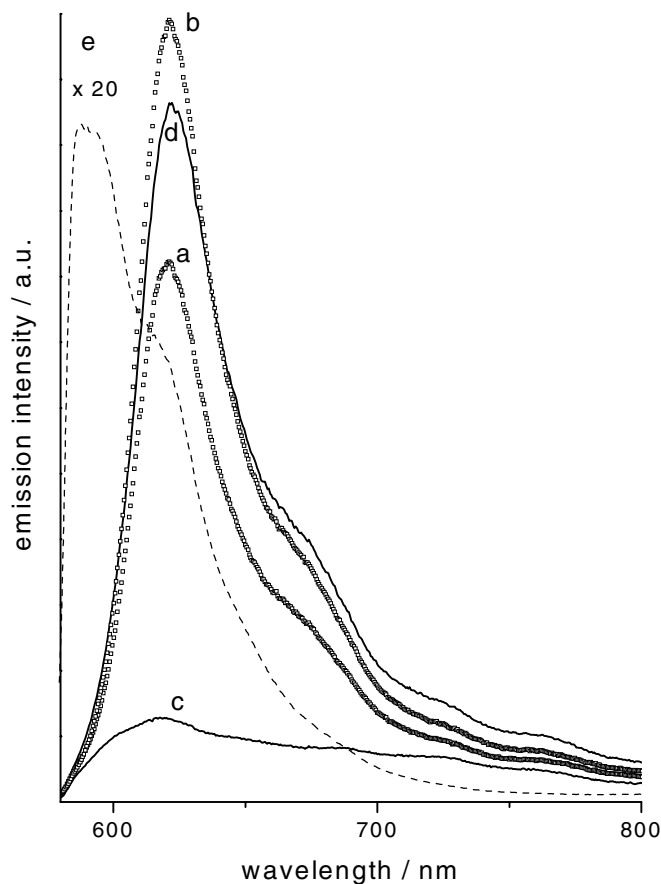


Figure 3. Optical emission spectra of SubPcBCl collected vertical to the film surface for (a) 11 nm on KBr, (b) KCl, (c) glass and (d) 23 nm on glass as compared to (e) a solution spectrum (optical absorption 0.1) in DMF.

however, is preserved. Especially noteworthy, there is no prominent splitting of bands as often seen previously for Pc thin films.<sup>10,21</sup> This observation indicates a small coupling of chromophores and hence negligible inter-molecular interactions in the solid. The observed shift to lower transition energy as often observed in solid Pc films is caused by an increased stabilization of molecules in the excited state relative to the stabilization of molecules in the ground state which is caused by the solid matrix when compared to the solvent shell. The shift increases in a row 11 nm / glass (c) < 23 nm / glass (d) < 11 nm / KBr (a) = 11 nm / KCl (b). This row approximately reflects the level of crystallinity as it would be assumed from transmission electron microscopy of the films.<sup>22</sup> Although the films prepared by deposition in UHV stem from the same deposition step and hence contain exactly identical amounts of SubPcBCl the absorption is found at a considerably smaller value for the film deposited on glass when compared to the absorption of the films on KBr or KCl. A preferential arrangement of the optical transition moments of the molecules and hence different overlap with the dipole vector of the incoming light beam is thereby indicated. As

the light passed perpendicular to the sample surface it is concluded that the transition moment of the molecules on KBr and KCl has a stronger tendency to be oriented parallel to the surface than is the case for the molecules on glass. In a three-dimensional random film still one third of the transition moments would show an overlap with a light beam in any direction. The difference in the integral absorption of the film on KBr and that on glass, however is larger than a factor of three. To explain this both has to be assumed, an arrangement of transition moments preferentially parallel to the substrate surface in the case of the film on KBr and an arrangement preferentially vertical to the surface in the case of the thin film on glass. It is interesting to note that the film of 23 nm on glass deposited at higher temperature and at a faster deposition rate shows an integral absorbance which, normalized for the increased average film thickness, falls in between those of that of the thinner films on glass and alkali halide surfaces discussed so far. An intermediate level of the orientation of molecular transition moments is thereby indicated.

In *figure 3* the emission spectra following Q-band excitation are plotted for the films, again compared to the signal from a solution. Comparing to thin films of regular phthalocyanines a high emission intensity could be collected from the films of SubPcBCl. As in the case of the absorption spectra, also the emission spectra were only shifted to lower energy and even the vibrational fine structure as observed for the free molecule in solution is preserved. Self-quenching which for regular Pc in the solid state is known to be efficient enough to quench the emission almost completely is found at a considerably lower level in the present experiments as an emission intensity only about a factor of 50 lower in the case of the film on KCl compared to that of the molecules in solution is detected. The emission intensity of the films on KCl and KBr is found at clearly higher values than that of the films on glass. This is especially clear for the 11 nm film prepared in the same deposition as the films on KCl and KBr, but also for the film prepared under HV conditions if its higher film thickness is considered. The preferentially parallel orientation of transition moments in the films deposited on the alkali halides would give rise to this observed difference. For the 11 nm film on glass additional radiationless deactivation pathways in that film by its very low emission yield.

### Cl<sub>4</sub>MePTCDI - A Modified Perylene Pigment

Perylene pigments that are unsubstituted at the central aromatic core are known to align in widely parallel stacks of molecules in the solid state and hence produce a rather strongly split absorption spectrum due to chromophore coupling.<sup>1,23,24</sup> As an example a spectrum obtained for a thin film of N,N'-dimethyl perylene tetracarboxylic acid diimide (MePTCDI) is compared to a solution of a solubilized derivative (the longer alkane chain is known to have no influence on the isolated chromophore)<sup>15</sup> in *figure 4*. A spectrum typical for solid MePTCDI is seen for the thin film and can be explained in a model based on coupling of transition dipoles.<sup>20</sup> The intermolecular transition dipole

interactions are strongly perturbed by introduction of four Cl atoms to the central aromatic core of the molecule leading to Cl<sub>4</sub>MePTCDI. Although the solution spectrum (*figure 5*) is very similar to that of the unsubstituted MePTCDI,<sup>15</sup> the spectrum of the thin film shows a characteristic difference: the solution spectrum is widely preserved also in the solid state. The reason for this is seen in the twisted shape of the Cl<sub>4</sub>MePTCDI molecule as concluded from the structure of a crystal precipitated from benzene solution and confirmed by force field and molecular orbital calculations (*figure 1*). No splitting can be observed for the thin film spectra of Cl<sub>4</sub>MePTCDI, and the observed red-shift (0.07 eV for the 0-0 transition) is again explained based on van-der-Waals intermolecular energies that stabilize the excited state relative to the ground state more in the solid than in the solution. The relative stabilization of the excited state in the solid as compared to solutions is larger than those found for MePTCDI (0.02 eV).<sup>20</sup> A stronger stabilization of the excited state relative to the ground state in solid Cl<sub>4</sub>MePTCDI is also reflected in an influence on the molecular vibrational structure of the excited state. The transition energies for the transitions from the vibrational ground state of the electronic ground state to the different vibrational states of the first excited electronic state (*figure 5*) are therefore more strongly spaced in energy.

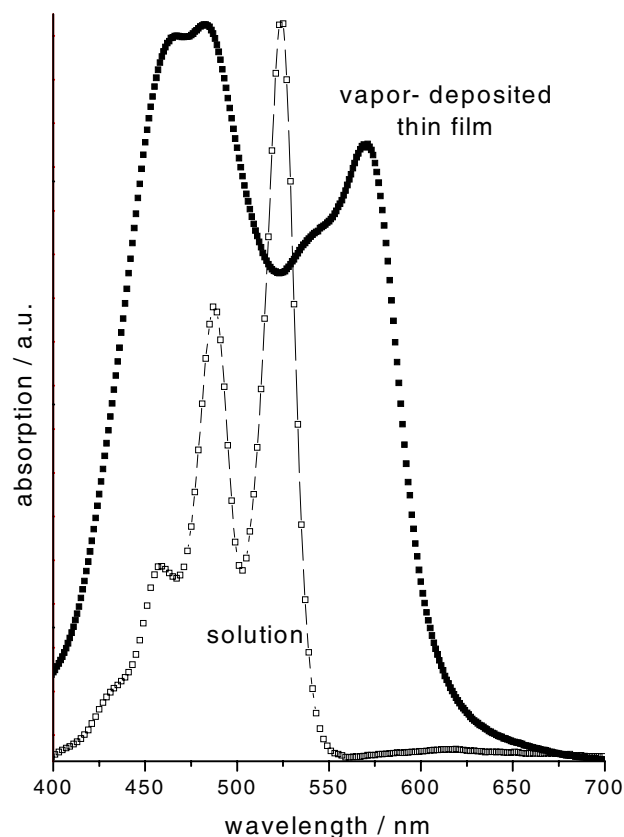


Figure 4. Optical absorption spectra of 30 nm MePTCDI deposited on glass at 50°C (■) and of a solution of C<sub>16</sub>PTCDI (alkane chain to increase solubility) in CH<sub>2</sub>Cl<sub>2</sub> (□)

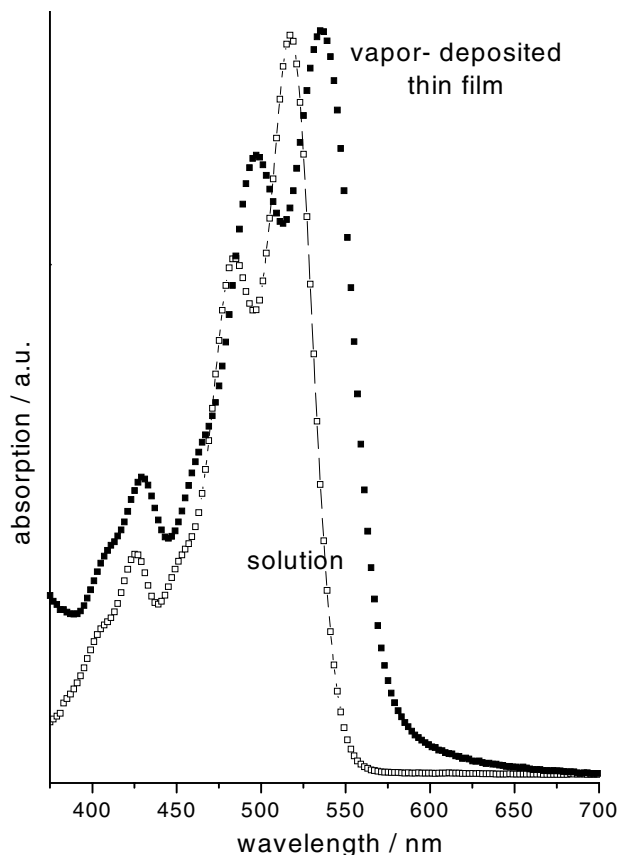


Figure 5. Optical absorption spectra of 30 nm  $\text{Cl}_4\text{MePTCDI}$  deposited on glass at  $45^\circ\text{C}$  (■) and of a solution in  $\text{CH}_2\text{Cl}_2$  (□)

The lower degree of intermolecular interactions in thin films of  $\text{Cl}_4\text{MePTCDI}$  concluded from the optical absorption is clearly reflected also in a comparison of emission spectra (figure 6). Thin films of unsubstituted perylene pigments are characterized by a strongly quenched monomer emission due to excimer formation.<sup>19,25,26</sup> Due to successful competition of radiationless decay the subsequent emission from the excimer is weak enough to give the strongly attenuated emission spectrum as seen in figure 6 for the thin film of MePTCDI. The thin film of  $\text{Cl}_4\text{MePTCDI}$ , however, shows a strong emission indicating strongly blocked pathways of excimer formation and radiationless decay and hence less aggregation quenching. This is again seen as a consequence of the twisted aromatic core of the molecule (figure 1) that suppresses excimer formation that relies upon a parallel arrangement of chromophore  $\pi$ -systems.<sup>27</sup> When the integral emission of the  $\text{Cl}_4\text{MePTCDI}$  thin film and solution is normalized to the

respective absorption, a lower limit (no correction for different scattering) for the quantum efficiency of  $\text{Cl}_4\text{MePTCDI}$  in the film of 54 % can be estimated based on the value of 85%<sup>15</sup> reported for a solution of  $\text{Cl}_4\text{MePTCDI}$ . Such a high value of the quantum efficiency for a pure pigment material without any matrix to isolate the chromophores appears noteworthy and might even be of technical relevance.

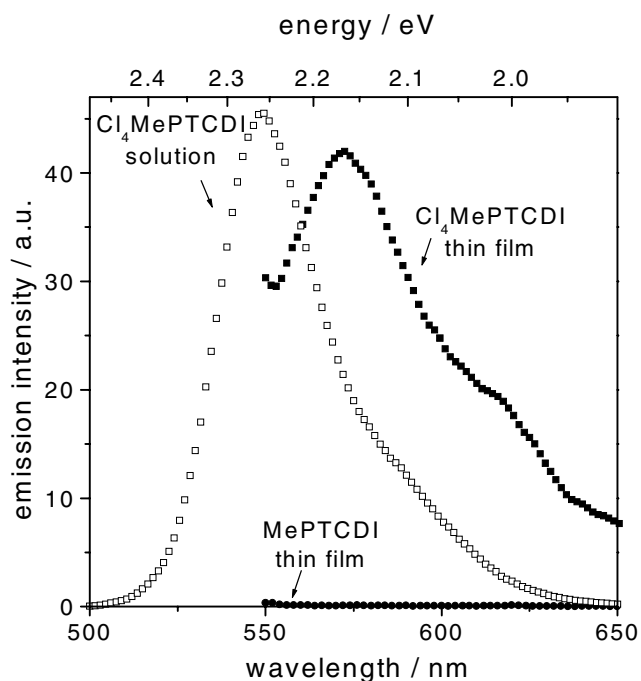


Figure 6. Optical emission spectra (excitation wavelength 520 nm) of vapor deposited films of  $\text{Cl}_4\text{MePTCDI}$  (30 nm, glass substrate of  $45^\circ\text{C}$ ) (■ ■ ■) and MePTCDI (20 nm, glass substrate of  $50^\circ\text{C}$ ) (● ● ●) and of a solution (□) of  $\text{Cl}_4\text{MePTCDI}$  in  $\text{C}_6\text{H}_5\text{Cl}$  (excitation at 480 nm)

The smaller intermolecular interaction in thin films of  $\text{Cl}_4\text{MePTCDI}$  as revealed by attenuated chromophore coupling in optical absorption and emission relative to thin films of MePTCDI also leads to significant differences in the morphology of films (figures 7 and 8). MePTCDI crystallizes in needles which easily reach lengths in the  $\mu\text{m}$  range even for films as thin as 30 nm (figure 7).  $\text{Cl}_4\text{MePTCDI}$  on the other hand, forms flat round-shaped dots of material that are more reminiscent of amorphous than crystalline growth which would be in line with the smaller intermolecular interaction detected in the optical experiments.

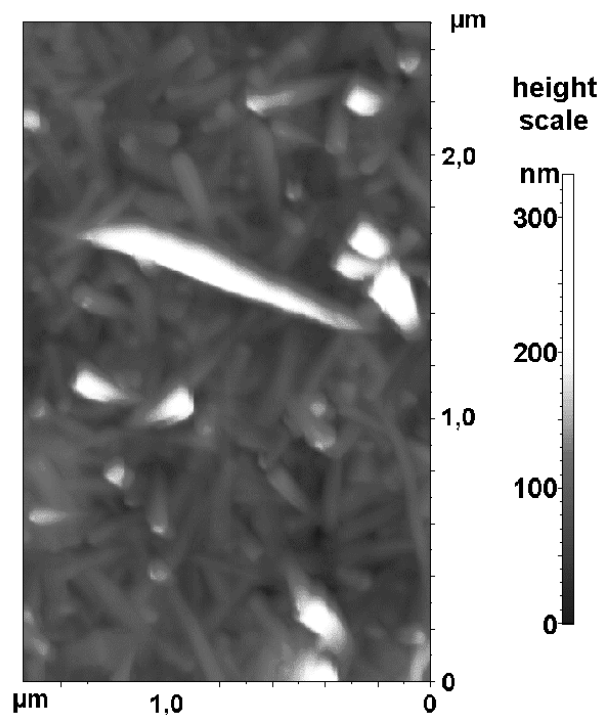


Figure 7. Morphology of a 30 nm film of MePTCDI grown on amorphous SiO<sub>2</sub> (modified Si surface) at 50°C as revealed by AFM in resonant mode

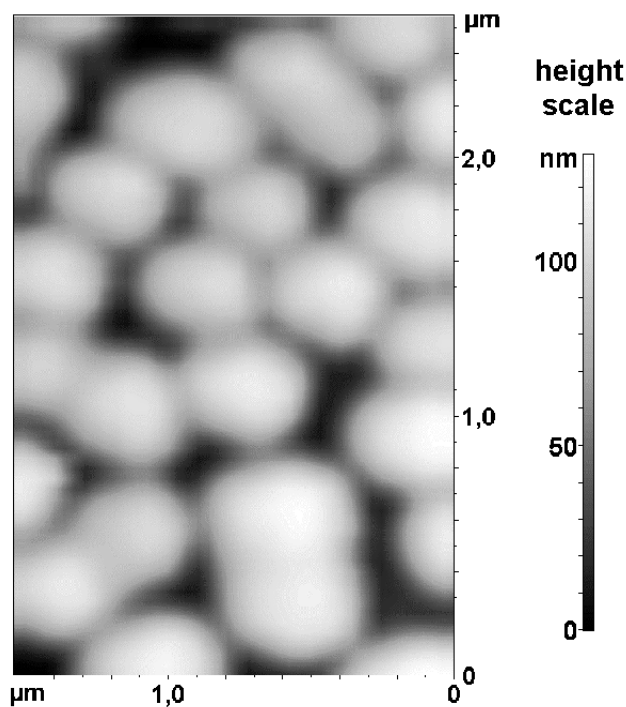


Figure 8. Morphology of a 30 nm film of Cl<sub>4</sub>MePTCDI grown on a glass slide at 45°C as revealed by AFM in resonant mode

## Conclusions

By chemical modifications at the aromatic core the molecular shape of phthalocyanines as well as perylene pigments can be distorted sufficiently to significantly alter the intermolecular interactions in the solid state. The coupling of chromophores which normally leads to strongly split absorption spectra and almost completely quenched emission for both groups of materials in the solid state can thereby be decreased widely. Monomer-like absorption and emission spectra were observed for SubPcBCl and Cl<sub>4</sub>MePTCDI, two examples of this strategy. Significantly increased emission intensities and hence quantum efficiencies of emission could be obtained in both cases when compared to the regular phthalocyanine and perylene pigments which can otherwise only be obtained for these groups of materials, if dilute solid solutions in matrix hosts (polymers, sol-gel oxides etc.) are studied. In the field of organic light-emitting diodes strongly emissive pure layers are well-known and mostly consist of amorphous phases. A change towards an amorphous growth is also indicated by the present experiments at Cl<sub>4</sub>MePTCDI, but a crystalline structure is well-known for SubPcBCl. Further experiments are on the way to discuss the role of crystallinity in these films in a more detailed way.

## References

1. K.-Y. Law *Chem. Rev.* **93**, 449 (1993).
2. C. Rompf, D. Ammermann and W. Kowalsky *Mater. Sci. Technol.* **11**, 845 (1995).
3. Z. Bao, A.J. Lovinger and J. Brown *J. Am. Chem. Soc.* **120**, 207 (1998).
4. J. Simon and J.-J. Andre *Molecular Semiconductors: Photoelectrical Properties and Solar Cells*, Springer, Berlin (1985).
5. D. Wöhrle, L. Kreienhoop and D. Schlettwein in *Phthalocyanines- Properties and Applications vol.4* (Edited by C.C. Leznoff and A.B.P. Lever) Verlag Chemie, New York, Weinheim, Cambridge, (1996).
6. J.D. Wright *Prog. Surf. Sci.* **31**, 1 (1989).
7. A.W. Snow and W.R. Barger in *Phthalocyanines, Properties and Applications* (Edited by C.C. Leznoff and A.B.P. Lever) p. 341. VCH, New York (1989).
8. R. Zhou, F. Josse, W. Göpel, Z.Z. Öztürk and Ö. Bekaroglu *Appl. Organomet. Chem.* **10**, 557 (1996).
9. M.J. Cook *J. Mater. Chem.* **6**, 677 (1996).
10. A. Schmidt, L.K. Chau, A. Back and N.R. Armstrong in *Phthalocyanines: Properties and Applications* (Edited by C.C. Leznoff and A.B.P. Lever) p. 307. VCH, New York (1996).
11. S.R. Forrest *Chem. Rev.* **57**, 1793 (1997).
12. F. Garnier *Pure & Appl. Chem.* **68**, 1455 (1996).
13. S.R. Forrest, P.E. Burrows, V. Bulovic, V. Kozlov, Z. Shen and M.E. Thompson *Mat. Lett.* **34**, 103 (1998).
14. 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. Lögdlund, et al. *Nature* **397**, 121 (1999).

15. M. Sadrai, L. Hadel, R.R. Sauer, S. Husain, K. Krogh-Jespersen, J.D. Westbrook and G.R. Bird *J. Phys. Chem.* **96**, 7988 (1992).
16. H. Kietaihl *Monatsh. Chem.* **105**, 405 (1974).
17. M.K. Engel, J. Yao, H. Maki, H. Takeuchi, H. Yonehara and C. Pac *Report Kawamura Inst. Chem. Res.* **9**, 53 (1998).
18. H. Yanagi, D. Schlettwein, H. Nakayama and T. Nishino *Phys. Rev. B* **61**, 1959 (2000).
19. D. Schlettwein, A. Back, T. Fritz, B. Schilling and N.R. Armstrong *Chem. Mater.* **10**, 601 (1998).
20. D. Schlettwein, H. Graaf, J.-P. Meyer, T. Oekermann and N.I. Jaeger *J. Phys. Chem. B* **103**, 3078 (1999).
21. D. Schlettwein, H. Tada and S. Mashiko *Langmuir* **16**, 2872 (2000).
22. D. Schlettwein and H. Yanagi *Annual Report of Venture Business Laboratory, Kobe University* **4**, 160 (1999).
23. G. Klebe, F. Graser, E. Hädicke and F. Berndt *Act. Cryst.* **B45**, 69 (1989).
24. P.M. Kazmaier and R. Hoffman *J. Am. Chem. Soc.* **116**, 9684 (1994).
25. U. Gomez, M. Leonhardt, H. Port and H.C. Wolf *Chem. Phys. Lett.* **268**, 1 (1997).
26. K. Puech, H. Fröb and K. Leo *J. Luminescence* **72**, 524 (1997).
27. J.B. Birks *Organic Molecular Photophysics*, Wiley, London (1975).

## Biography

Derck Schlettwein was born 1962 in Hanover, Germany. He studied chemistry at the universities of Muenster and Bremen, Germany (Diploma 1988, Dr. rer. nat. 1991). Since 1991 he works as Senior Research Assistant, DFG Research Fellow and lecturer in Physical Chemistry and Electrochemistry at the University of Bremen. His "Habilitation" in Physical Chemistry is going to be issued in October 2000. Fields of interest are focussed on organic thin films: molecular order, electrical and optical properties, molecular electronics, electrochemistry and photoelectrochemistry.