

# Intermolecular charge transfer transitions in 4-tert-butylphenyl-diester of N-(4-Carboxyphenyl)-trimellitimide

A. Lorenc, C. Spies, R. Gehrke and H.R. Kricheldorf<sup>1</sup>

HASYLAB at DESY, Notkestr. 85, 22603 Hamburg, Germany

<sup>1</sup>Institut für Technische und Makromolekulare Chemie, Universität Hamburg, Bundesstr. 45, 20146 Hamburg, Germany

Aromatic copoly(ester-imides) are materials with useful properties [1]. In order to interpret the complex fluorescence behaviour of copoy(ester-imides) different model substances, representing different parts of the polymer chain, have been investigated. Their fluorescence can be compared with the observed fluorescence of the copoly(ester-imides). In this contribution we report on the intermolecular charge transfer (ICT) transitions in the model substance 4-*tert*-butylphenyl-diester of *N*-(4-carboxyphenyl)-trimellitimide (NCTB). The chemical structure of NCTB is shown in fig. 1.

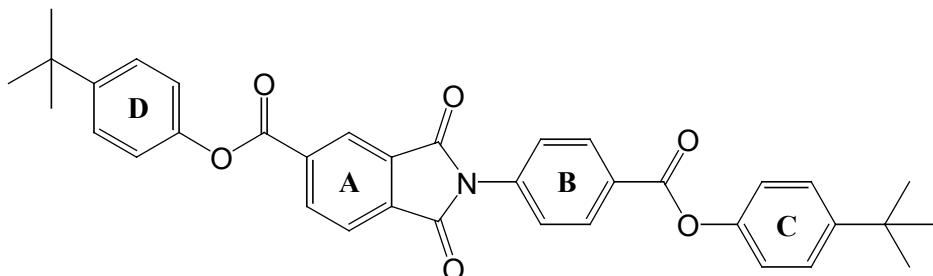


Figure 1: Chemical structure of NCTB. Parts of the molecule are highlighted (A, B, C, and D) to show which electron transitions between the different aromatic rings take place when ICT-species are formed.

Figure 2 shows the UV absorption spectrum, the fluorescence excitation spectrum at  $\lambda_{\text{em}} = 490$  nm and the emission spectrum at  $\lambda_{\text{ex}} = 260$  nm of a saturated solution ( $c < 10^{-4}$  mol/l) of NCTB in cyclohexane. Furthermore, a fluorescence emission spectrum of the dibutylester of *N*-(4-carboxyphenyl)-trimellitimide (NCTD) in cyclohexane solution ( $c = 10^{-4}$  mol/l) at  $\lambda_{\text{ex}} = 250$  nm is depicted. From investigations of NCTD it was evident, that the emission band with the maximum intensity at 480 nm arises from an ICT-species. This ICT-species is realised after excitation of one of the molecule-moieties. In the excited state the ICT-species of NCTD is formed by an electron transfer from *N*-4-carboxyphenyl (donor-moiety) to trimellit (acceptor-moiety). Because there is a good correspondence between the emission spectrum of NCTD and the one of NCTB shown in fig. 2, we conclude, that the majority of fluorescence intensity at 480 nm arises from the same ICT-species of NCTB (electron transfer from B to A, see fig. 1). On the basis of good correspondence of the UV absorption and fluorescence excitation spectra (fig. 2) we assume, that the building mechanism of the ICT-species in NCTB is the same as it is in NCTD, because the UV absorption spectrum arises mainly from the absorption of each individual molecule moiety. Time-resolved fluorescence measurements were performed in order to elucidate why the full width at half maximum of the emission band of NCTB is larger than that of the emission band of NCTD.

Figure 3 shows fluorescence decay curves of a saturated ( $c < 10^{-4}$  mol/l) solution of NCTB in cyclohexane observed at an excitation wavelength of  $\lambda_{\text{ex}} = 300$  nm and at different emission wavelengths:  $\lambda_{\text{em}} = 450$  nm (a) and  $\lambda_{\text{em}} = 500$  nm (b). By fitting the decay curves with a sum of two exponential functions the decay times of two different emitting species were calculated. The first decay time is 1.1 ns. This decay time was also observed for the ICT-species in NCTD. The second decay time is 3.5 ns and its amplitude was 13% at an emission wavelength of  $\lambda_{\text{em}} = 450$  nm and 42% at  $\lambda_{\text{em}} = 500$  nm. The different amplitudes at different emission wavelengths can be attributed to a bathochromic shift of the emission of ICT'-species with the decay time of 3.5 ns relative to the emission of the ICT-species with the decay time of 1.1 ns. We assume, that in the ICT'-species the electron deficiency is on moiety C (fig. 1) and the excess of electrons on the moiety A of the NCTB molecule. Because all investigated amplitudes are positive, it is evident, that the building processes of both emitting species is in the range of picoseconds or even faster. The building process of ICT'

proceeds after two electron transfers in accordance with an electron hopping mechanism [2]. In the NCTB the excited acceptor chromophore (moiety A,  $\lambda_{\text{ex}} = 300 \text{ nm}$ ) is consecutively attached to two donor moieties (B and C). After the excitation an electron proceeds first from the donor B to the acceptor A and then from the donor C to the donor B. The emitting ICT'-species formed in this way has a electron deficiency on moiety C and an excess of electrons on moiety A.

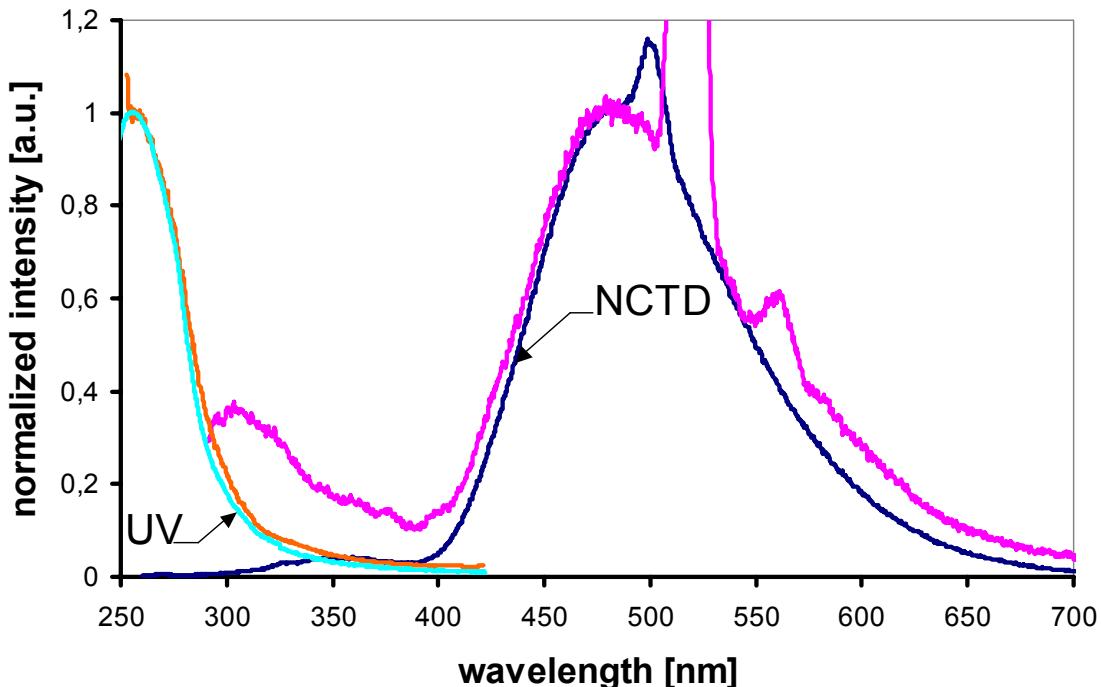
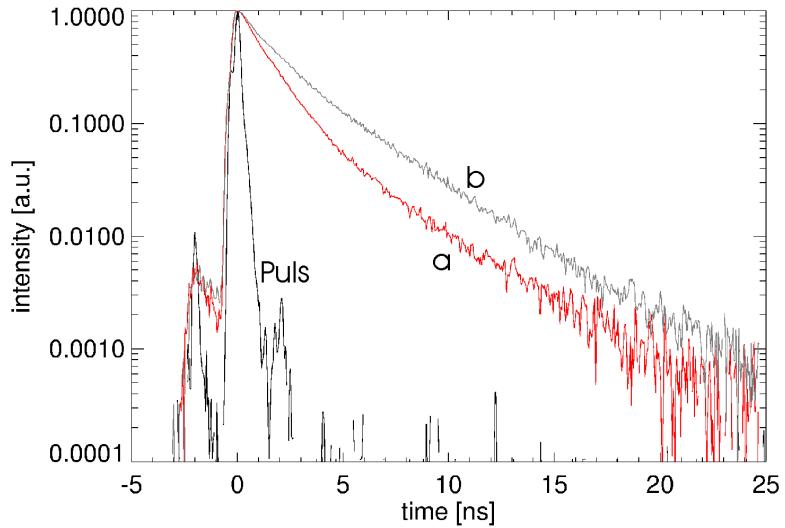


Figure 2: UV absorption spectrum, fluorescence excitation spectrum at  $\lambda_{\text{ex}} = 490 \text{ nm}$  and emission spectrum at  $\lambda_{\text{ex}} = 260 \text{ nm}$  of a saturated solution ( $c < 10^{-4} \text{ mol/l}$ ) of NCTB in cyclohexane and a fluorescence emission spectrum of dibutylester of the *N*-(4-Carboxyphenyl)-trimellitimide (NCTD) in a cyclohexane solution ( $c = 10^{-4} \text{ mol/l}$ ) at  $\lambda_{\text{ex}} = 250 \text{ nm}$ . The spectra are normalized to maximum intensity.

Figure 3: Fluorescence decay curves of a saturated ( $c < 10^{-4} \text{ mol/l}$ ) solution of NCTB in cyclohexane observed at an excitation wavelength of  $\lambda_{\text{ex}} = 300 \text{ nm}$  and different emission wavelengths:  $\lambda_{\text{em}} = 450 \text{ nm}$  (a) and  $\lambda_{\text{em}} = 500 \text{ nm}$  (b). The curves are normalized to maximum intensity.



## References

- [1] H. R. Kricheldorf, Mol. Cryst. Liq. Cryst. 254, 87 (1994)
- [2] G. J. Kavarnos, N. J. Turro, Chem. Rev. 86, 401 (1986)