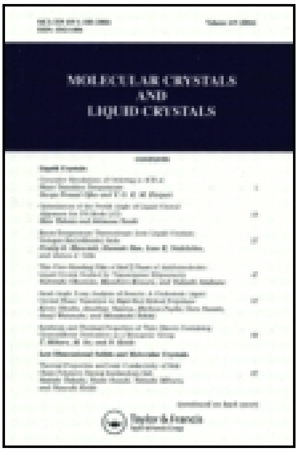

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Triplet States of Oligothiophenes and Electron Transfer to C_{60}: A Pulsed EPR Investigation

M. Bennati [a] , A. Grupp [a] , P. Bäuerle [b] & M. Mehring [a]
[a] 2. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, D-70569, Stuttgart, Germany
[b] Institut für Organische Chemie, Universität Stuttgart, Germany

To cite this article: M. Bennati , A. Grupp , P. Bäuerle & M. Mehring (1994): Triplet States of Oligothiophenes and Electron Transfer to C_{60}: A Pulsed EPR Investigation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 751-756

To link to this article: http://dx.doi.org/10.1080/10587259408039320

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 751–756
Reprints available directly from the publisher
Photocopying permitted by license only

TRIPLET STATES OF OLIGOTHIOPHENES AND ELECTRON TRANSFER TO C_{60}: A PULSED EPR INVESTIGATION

M.BENNATI, A.GRUPP, P.BÄUERLE* AND M.MEHRING
2.Physikalisches Institut, Universität Stuttgart
Pfaffenwaldring 57, D-70569 Stuttgart, Germany
* Institut für Organische Chemie, Universität Stuttgart, Germany

Abstract Triplet states of oligothiophenes and C_{60} were excited by a pulsed laser light using a Nd:YAG laser. The finestructure values D, E of different endcapped oligothiophenes (EC3T, EC4T, and EC5T) were determined from pulsed EPR-spectra. Time resolution was applied to study the kinetics and relaxation times.

A photoinduced electron transfer from EC4T to C_{60} in liquid solutions was investigated in detail. Fourier transform of the free induction decays results in spectra of the transient triplet state and of the transient C_{60} monoradical anion. Electron transfer rates were deduced from the observed triplet quenching rates at different temperatures.

INTRODUCTION

The investigation of the photoexcitation in oligomers molecules with well defined chain length represents a useful approach for the understandig of the electronic properties in the corresponding polymers. Particularly time resolved EPR spectroscopy can give informations about the nature, the relaxation processes and the lifetime of an electronic excitation.

The end-capped thiophene oligomers[1] are of high interest as model compounds for polythiophene and for photoinduced electron transfer processes with electron acceptor molecules[2]. Spectroelectrochemical investigations show that oxidation-potentials and the $\pi - \pi^*$ excitation energy vary systematically with the chain length. Furthermore the compounds with chain length $n \geq 4$ undergo two stable, reversible oxidized states at room temperature[3]. C_{60} fullerene on the other hand represents also a new molecular system with very unusual electronic properties. After light excitation the lowest triplet state of the molecule is populated with a quantum yield of nearly one which indicates that the system would be an ideal component in photochemical devices. The electron affinity is so high that C_{60} can be reduced chemically as well as electrochemically with up to six electrons[4]. In order to study the properties of some end-capped oligothiophenes (n = 3 - 5) and C_{60} as a new donor/acceptor system we performed a pulsed EPR investigation of their lowest photoexcited triplet states in glassy matrix. Furthermore we investigated the dynamics of an electron transfer process from EC4T to $^3C_{60}$ in liquid solution.

EXPERIMENTAL

Toluene solutions ($c \approx 1{*}10^{-3}$ mol/l) of the end-capped oligothiophenes (EC3T, EC4T, EC5T), C_{60} and C_{60} in mixture with EC4T were degassed by several freeze-thaw cycles and sealed off on a high vacuum line. The samples were irradiated at $\lambda = 355$ nm by a Nd:YAG-laser with an energy of $\simeq$ 20 mJ per pulse at a pulse frequency of 30 Hz.

The EPR measurements were carried out using a home built electron spin echo spectrometer with a slotted tube resonator and an helium flow cryostat. The triplet EPR powder spectra were recorded at T = 10 K with a Hahn-echo microwave pulse sequence by integrating the echo signal while sweeping the magnetic field. The lineshape of the spectra corresponds directly to the EPR line and should not be confused with standard EPR spectra recorded with field modulation. The time evolution of the EPR-line was obtained by varying the delay time between laser and first microwave pulse. Free induction decays were recorded using quadrature detection. The short deadtime of the spectrometer after the microwave pulse ($\tau_D \simeq$ 70 ns) allowed to Fourier transform the data set to give the EPR spectrum after a frequency proportional phase correction.

OLIGOTHIOPHENE TRIPLETS

The samples containing the glassy toluene solutions of the end-capped oligomers were irradiated at T = 10 K. We observe highly polarized EPR spectra in all samples when starting the Hahn-echo detection sequence at t $\simeq$ 20 ns after the laser pulse. The spectra are represented in figure 1. All signals grow up in a time scale shorter than the spectrometer time resolution. This is expected because the lowest excited triplet state of the molecule is populated during the laser flash via highly excited singlet states by mean of the spin orbit interaction in a time scale of $\tau_{ISC} = 10^{-8}$ - 10^{-9} s. The intersystem crossing causes a selective population of the zero field energy levels which depends on the molecular symmetry. Since the high field Zeeman wave functions are linear combinations of the zero field wave functions the population of the triplet Zeeman levels do not correspond to the Boltzmann equilibrium population but shows polarization patterns typical for the given molecular symmetry.

In this case all spectra show the same polarization pattern, i.e. emissive peaks at the low field side and absorptive peaks at the high field side. The polarization was determined by comparing the triplet signal phase with the one of a stable radical measured simultaneously.

Triplet EPR powder spectra are characterized by their total spectral width which is correlated with the finestructure parameter D. We notice that the spectral width (edge to edge) decreases with increasing oligomers chain lengths. This indicates that we are observing the intrinsic triplet state on the molecule and not a local excitation of a thiophene ring. The finestructure parameters D and E which characterize the strength and the asymmetry of the electron dipolar coupling can not be determined directly from the spectra because the high field approximation is not valid for large D and E values. Therefore we simulated the EPR powder spectra using the solution for the eigenvalues of the Hamilton-operator:

$$\hat{\mathbf{H}} = g\beta\mathbf{SB} - (XS_x^2 + YS_y^2 + ZS_z^2)$$

where X, Y, Z are the eigenvalues of the finestructure tensor in the tensor principal axis. The polarization for every transition was calculated from the population of the zero field energy levels, the transition probabilities were considered for a microwave field perpendicular to the magnetic field. The lineshape of the powder spectra computed for a static triplet do not correspond exactly to the experimental one. Obviously the intensity of transitions in orientations between the principal axis is much weaker than expected for a powder pattern. Measurements of the spectra at different delay time after the laser pulse show that the low field side decays much faster than the high field side and the spectra become absorptive after a time delay of $\tau \simeq 30\ \mu s$. This indicates that the spin lattice relaxation is on the order of few microseconds and may also affect the spectra recorded 500 ns after the laser pulse. For this reason we considered anisotropic T_1 relaxation in the spectra calculation. Spin lattice relaxation in a three level system is biexponential with the rates k_1 = 3*w and k_2 = -(w+2*W). w and W are the probabilities for $\Delta m = 1$ and $\Delta m = 2$ transitions respectively. The angular dependence of w and W can be obtained from the matrix elements of the Hamilton-operator in the laboratory axis system which are proportional to the $S_\pm$and $S_\pm^2$ operators respectively. For the simulations at low temperature it can be assumed that $\omega_0\tau_c \gg 1$ and therefore the spectral densities for w and W are related by $J_1 \simeq 4*J_2$. The spectra simulations are represented in figure 1 by the solid lines. The obtained finestructure values and zero field populations are listed in table 1.

TABLE 1: Triplet state finestructure values and populations of EC3T, EC4T, EC5T

	$\mid D \mid$ $[cm^{-1}]$	$\mid E \mid$ $[cm^{-1}]$	P_x	P_y	P_z
EC3T	0.0738	0.0046	0.31	0.18	0.51
EC4T	0.0682	0.0023	0.35	0.21	0.44
EC5T	0.0607	0.0023	0.35	0.25	0.4

It is not possible to determine the absolut sign of the D value from the calculation. Considering the particular structure of the oligomers with a stretched one-dimensional π-system we suggest a prolate triplet spin density distribution which corresponds to a negative D-value.

Comparing the experimental with the calculated spectra we notice small deviations in the case of the EC3T. This could be due to the anisotropic hyperfine interaction which can lead to anisotropy in the linewidth. A computation of the spectra including hyperfine coupling may be performed if the anisotropic hyperfine tensor (from single crystal measurements) is known which is currently not the case.

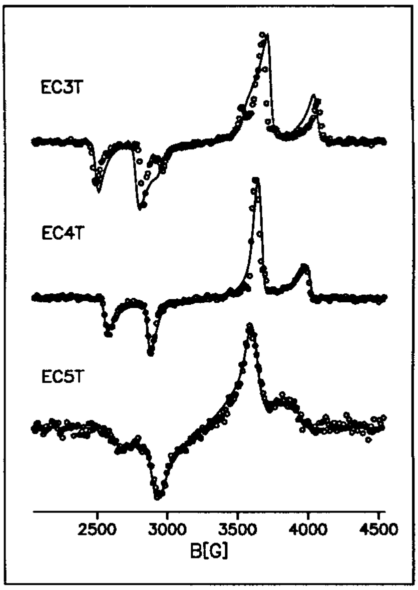

FIGURE 1: Triplet EPR powder spectra of the end-capped oligothiophenes EC3T, EC4T, EC5T

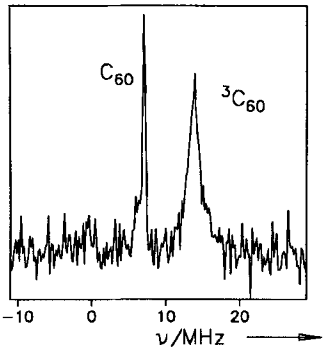

FIGURE 2: Fourier transform spectrum of $^3C_{60}$ and C_{60}^-

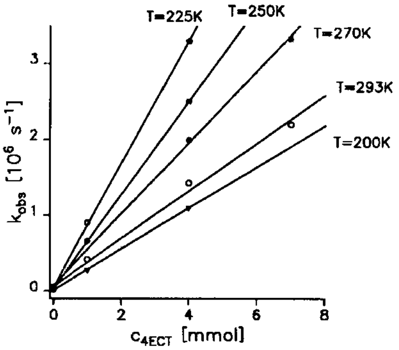

FIGURE 3: Stern-Volmer plots of the observed triplet decay rates

ELECTRON TRANSFER FROM EC4T TO $^3C_{60}$

Toluene solutions containing mixtures of EC4T and C_{60} in different concentration ratios were irradiated in a temperature range T = 200 - 300 K. A free induction decay (FID) was observed after the laser pulse. The Fourier transform of the FID gives a spectrum with two narrow absorptive EPR lines at g = 2.0014 and g = 1.9999. The EPR spectrum is shown in figure 2. We assign the first line to the triplet state of C_{60} and the second line to C_{60} radical monoanion according to the following analysis of the kinetics.

The build-up and decay of the C_{60} triplet EPR line can be described by a biexponential relation which considers only T_1 relaxation and pseudo first order kinetics for the electron transfer as dominant processes. The time evolution of the triplet EPR line at different temperatures was fitted with the equation:

$$S(t) \sim M_B(-exp[-t/T_1] + exp[-k_{obs}t])$$

We observe that the triplet decay rate k_{obs} depends on the concentration of the added donor EC4T. When plotting k_{obs} versus the concentration of EC4T we obtain for a given temperature a linear correlation (figure 3). The quenching follows the Stern- Volmer relation:

$$k_{obs} = k_T + k_q[EC4T]$$

where k_T is the triplet decay rate without quencher. The determined quenching rate k_q increases with decreasing temperature. We estimated a negative activation energy of $E_a \simeq$ -10 kJ/mol which is in contrast to the model of a diffusion controlled or thermally activated electron transfer process according to the theory of Marcus. A second quenching mechanism has to be considered which includes the formation of an exciplex intermediate before the charge separation takes place[5]:

$$D + A^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^*[{}^+D-A^-] \xrightarrow{k_{ip}} D^+ + A^-$$

In this path the equilibrium constant $K_{exc} = k_1/k_{-1}$ involves exciplex dissociation which for a bound complex is expected to be strongly temperature dependent. If the exciplex formation enthalpy is larger than the ion pair solvation enthalpy ($\Delta H_{ip} < -\Delta H_{exp}$) the activation energy is indeed negative as observed here.

The second component of the EPR spectrum has a g-factor which corresponds to that found in electrochemically prepared C_{60} radical monoanions[4]. The assignment of this transient to C_{60}^- is also supported by the analysis of the signal polarization. The signal is absorptive at all times as is expected from the radical pair mechanism: the polarization of radicals formed from a non polarized triplet exciplex is positive for the transient with the lower g-factor[6], i.e. for C_{60}^- (compared to g = 2.0024 for EC4T). We determined the temperature dependence of the linewidth for C_{60}^- and $^3C_{60}$ by fitting the EPR lines with a Lorentz line shape function. The $1/T_2$ values are plotted versus temperature in figure 4.

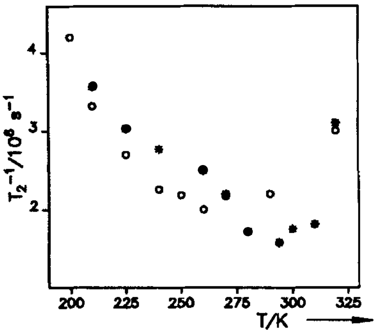

FIGURE 4: Temperature dependence of the EPR-linewidth ($1/T_2$) of (o) $^3C_{60}$ and (*) C_{60}^-

The relaxation rates of the two transients show the same temperature dependence. This suggests that T_1, T_2 are determined by the same relaxation mechanism for both $^3C_{60}$ and C_{60}^- which we attribute to the spin rotation interaction.

Acknowledgements: Financial support by the Deutsche Forschungsgemeinschaft (SFB 329) and the Fonds der Chemischen Industrie is gratefully acknowledged.

REFERENCES

1. P. Bäuerle, Adv. Mat., 102, 4 (1992)
2. P. Bäuerle et al., Synthetic Metals, 61, 71 (1993)
3. P. Bäuerle, U. Segelbacher, A. Maier, M. Mehring, J. Am. Chem. Soc., 115, 10217 (1993)
4. D. Dubois, M. J. Jones, K. M. Kadish, J. Am. Chem. Soc., 114, 6446 (1992)
5. A. Weller in M. Gordon and W.R. Ware, The Exciplex (Academic Press New York, 1975)
6. F. J. Adrian, J. Chem. Phys., 54, 3918 (1971)