

Spectrochimica Acta Part A 56 (2000) 2729-2739

SPECTROCHIMICA ACTA PART A

www.elsevier.nl/locate/saa

Photoinduced electron transfer between C_{70} fullerene and 3,3',5,5'-tetramethylbenzidine studied by electron paramagnetic resonance

Vlasta Brezová *, Dana Dvoranová, Peter Rapta, Andrej Staško

Department of Physical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

Received 29 February 2000; accepted 23 May 2000

Abstract

Electron paramagnetic resonance (EPR) in situ spectroscopy was applied in the study of photoinduced electron transfer between 3,3',5,5'-tetramethylbenzidine (TMB) and C_{70} in different solvent systems. The changes found in UV-vis spectra pointed at ground state charge transfer complex formation { C_{70} -TMB} in benzonitrile. Upon selective excitation of C_{70} using steady-state monochromatic irradiation with a wavelength of 546 nm, two EPR singlets were observed, which were assigned to C_{70} mono- and di-anion. In the photochemical and cathodic in situ reductions, identical EPR spectra of anion radicals were obtained. C_{70} mono-anion was investigated also in frozen 1,2-dichlorobenzene solutions within the temperature range from 110 to 210 K, and at 110 K the anisotropic EPR spectrum of C_{70} mono-anion was simulated assuming an axially symmetric g-matrix with $g_{\parallel} - g_{\perp} = 0.00165$. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Anion radicals; C70 fullerene; Electron paramagnetic resonance; Photoinduced electron transfer

1. Introduction

Numerous investigations of the unique photochemical and photophysical properties of fullerenes have been carried out in recent years [1–14]. The electron transfer to fullerene C_{60} was intensively studied by electron paramagnetic resonance (EPR) [15–21], UV-vis-Near-IR spectroscopy [17,19,22] and laser flash techniques [1,2,4,10–14]. In our previous EPR and Near-IR (NIR) investigations the formation of C_{60} anion radicals was observed [24–26], induced either by electron transfer from photoactivated TiO₂ particles [23], or by quenching the photoexcited triplet state of fullerene C_{60} and its derivatives. On the other hand, there is only limited information on the generation of anion radicals of C_{70} and their characterization [27–34].

Fullerene C_{70} , similarly to C_{60} , occurs in solutions in a number of oxidation states including

^{*} Corresponding author. Tel.: +421-7-52926032; fax: +421-7-52493198.

E-mail address: brezova@cvtstu.cvt.stuba.sk (V. Brezová).

 C_{70}^+ , $C_{70}^{-\bullet}$ up to $C_{70}^{-6\bullet}$ [15,35–37]. NIR spectroscopy represents a powerful tool in the identification of individual C_{70} species, as each oxidation state possesses characteristic absorption bands [36,38]. The experimental absorption spectrum of $C_{70}^{-\bullet}$ with a maximum at 1368 nm was explained by assuming that the addition of one electron to the C_{70}^{\bullet} skeleton caused a lowering of the symmetry from D_{5h} to C_{5v} , and consequently that C_{70} exists as a dipolar anion [38]. The enhanced reactivity Of C70° as compared to C60 in the photoinduced electron transfer from 1-benzyl-1,4dihydronicotineamide was similarly ascribed to the higher local densities of unpaired electron and negative charge in C_{70}^{-} due to the loss of symmetry [39]. The photoinduced electron transfer between tetrathiafulvalenes and C₇₀ in polar and nonpolar solvents was investigated by nanosecond laser photolysis combined with transient absorption spectroscopy in the visible and NIR regions [40]. The formation of C_{70}^- was monitored at 1380 nm [40]. Similar techniques were applied also in the photoinduced electron transfer between C_{60}/C_{70} and zinc tetraphenylporphyrin [41], or 1,1'-binaphthyl-2,2'-diamine [42]. Baumgarten et al. prepared different C_{70}^{\bullet} anions in toluenetetrahydrofuran solutions by contact with a potassium mirror, and the EPR and vis-NIR spectra were recorded [36]. Mono-anion $C_{70}^{-\bullet}$ characterized in EPR by g = 2.0022 and a line width of 0.07 mT was identified in NIR spectra by an absorption maximum at 1370 nm. Paramagnetic C_{70}^{2-} was described in EPR by a singlet with g = 2.0026, a line width of 0.06 mT, and a NIR absorption band at 1171 nm [36]. Friedrich et al., applying electrochemical in situ reduction of C_{70} , measured one narrow EPR line for $C_{70}^{-\bullet}$ characterized by g = 2.0019 and a line width of 0.019 mT [43]. Reduction of C_{70} by interaction with 1amino-3-propanol and 1,5-diaminopentane was evidenced by EPR and vis-NIR spectroscopy [44,45]. The monitored NIR-characteristic absorptions for $C_{70}^{-\bullet}$ and C_{70}^{2-} are in good agreement with data published in [36,38], while the EPR spectrum of $C_{70}^{-\bullet}$ measured at 333 K was here described by two lines, with g-values of 2.0004 and 2.0001, and an EPR spectrum of $C_{70}^{-\bullet}$ observed at 12.5 K was simulated applying $g_{\parallel} =$ 2.0000 and $g_{\perp} = 1.994$ [44,45].

Our study was motivated by the differing data in the EPR spectra of C_{70} anion radicals found in the literature. Therefore, we investigated the photoinduced electron transfer between C_{70} and an electron-donating substrate TMB, applying monochromatic excitation ($\lambda = 546$ nm) of fullerene molecules in solvent systems with a different polarity, and we also generated C_{70} anion radicals in the cathodic reduction.

2. Experimental

2.1. Materials

Fullerene C₇₀ (Gold Grade) was purchased from Hoechst (Germany) and TMB from Aldrich applied. was The organic solvents 1.2dichlorobenzene (DCB), benzonitrile (BN), acetonitrile (ACN) of analytical grade and tetrabutylammonium hexafluorophoshate $((TBA)PF_6)$ salt were obtained from Fluka.

2.2. Photochemical reduction

The solutions with the desired concentrations of C_{70} and TMB were prepared immediately prior to irradiation, carefully purged by argon and transferred into a quartz flat cell optimized for the Bruker standard rectangular cavity. The cell was placed in the Bruker TM cavity and continuously irradiated by monochromatic light with wavelength of 546 nm, which was selected from the radiation flux of a medium-pressure mercury lamp (Applied Photophysics, UK) using a glass filter (Schott Glaswerke, Germany).

2.3. Cyclic voltammetry

Cyclic voltammograms were measured at 295 K under argon in 0.05 mM C_{70} fullerene, 0.1 M (TBA)PF₆ in DCB or BN solutions using a PAR 270 (Princeton Applied Research) electrochemical system with the standard three-electrode cell with platinum working and counter electrodes and a saturated calomel reference electrode (SCE) at scan rate of 100 mV s⁻¹.

2.4. Photochemical in situ EPR

A Bruker 200D EPR spectrometer, assembled with an Aspect 2000 computer was used to measure EPR spectra. The solutions of fullerene C_{70} and TMB were continuously irradiated ($\lambda = 546$ nm) in the cavity of the spectrometer and the EPR spectra were monitored in situ. The standard EPR experiments were performed at 290 K. Typical settings for the series of EPR experiments were as follows: gains $10^4 - 10^5$; time constant 50 or 100 ms; sweep time 20 or 50 s; modulation amplitude 0.005-0.05 mT; microwave power 10 mW. The g-value was determined with an uncertainty of +0.0001 using a marker containing 1,1-diphenyl-2-picrylhydrazyl (DPPH) built into the spectrometer. EPR spectra were simulated using Bruker WIN-EPR SimFonia.

The measurements of EPR spectra at low temperatures were carried out in 3 mm o.d. quartz EPR tubes. In situ irradiation of fullerene solution was performed at 200 K. Immediately after



Fig. 1. UV-vis spectra of individual compounds: [TMB] = 1.4 mM (1); $[C_{70}] = 0.34$ mM (2) measured under argon in BN solutions, along with spectra observed at constant $[C_{70}] = 0.34$ mM and variable TMB concentrations: 0.05 (3); 0.12 (4); 0.24 (5) and 0.48 mM (6). The inset shows the dependence of absorbance at $\lambda = 470$ nm evaluated from spectra 2–6 on TMB concentration.

generation of a sufficiently high concentration of the radical species of interest, the sample temperature was lowered to 110 K using a Bruker variable temperature control unit ER 4111 VT. The EPR spectra were recorded without further irradiation raising the temperature to the desired values in the temperature range from 110 to 210 K.

2.5. Electrochemical in situ EPR

Amperostatic cathodic reduction was carried out directly in the cavity of the EPR spectrometer with solutions as specified in the cyclic voltammetry section, using a Varian electrolytic cell with platinum net working, gold counter, and Ag/AgCl reference electrodes. This galvanostatic procedure allows a better potential control at the entire platinum grid than by standard potentiostatic techniques.

2.6. UV-visible spectroscopy

UV-vis spectra of C_{70} and TMB solutions were recorded under argon using a diode array UV-vis spectrometer PC 1000 (Ocean Optics).

3. Results and discussion

Fig. 1 shows the individual UV-vis spectra of C_{70} and TMB in BN, along with the spectra of the solutions measured under argon at a constant C_{70} concentration and at the changed TMB concentrations. The formation of charge-transfer complexes between the ground state in C₇₀ and also in C₆₀ fullerenes and amines was previously demonstrated by UV-vis spectroscopy, as the absorption spectra of fullerenes undergo characteristic changes upon the addition of amines to the solution [46-50]. Spectra presented in Fig. 1 indicate absorption spectra of C70 alteration similar to those observed previously in the presence of different electron donating substrates [47-50]. The detected spectral changes caused by the presence of TMB pointed at ground state charge transfer complex formation between C70 and TMB in BN solvent. As TMB has only negligible absorption in the range 500-600 nm (Fig. 1), in the steady-state



Fig. 2. EPR spectra obtained at 290 K during continuous irradiation ($\lambda = 546$ nm) of 0.48 mM TMB in BN solutions containing various concentrations of C₇₀: (a) 0 mM; (b) 0.23 mM; (c) 0.34 mM.

photochemical experiments using monochromatic light of 546 nm, only C_{70} molecules were selectively excited.

Fig. 2 shows EPR spectra measured before and during a continuous irradiation ($\lambda = 546$ nm) of TMB solutions in BN containing various concentrations of C₇₀. The TMB molecule is not excited by the applied radiation in fullerene-free solutions, and no EPR signals are evident (Fig. 2a). Adding C₇₀ to such donor solutions, a sharp EPR singlet M, characterized by g-value, $g_M = 2.0004$ and peak-to-peak line-width, pp_M = 0.013 mT, can be observed already before starting irradiation, and it increased upon progressing irradiation (Fig. 2b,c). We assigned this signal to C_{70} mono-anion, taking into account the fact that the UV-vis experiments provided evidence of ground state charge transfer complex {C/70(SUB)-TMB} formation in BN (Fig. 1). This solvent is characterized by a relative permittivity of 25.7, and allows the ground state separation and stabilization of $C_{70}^{-\bullet}$ according to Eq. (1) [14]:

$$C_{70} + TMB \leftrightarrow \{C_{70} - TMB\} \leftrightarrow C_{70}^{-} + TMB^{+}$$
(1)

Upon starting the radiation, the intensity of the EPR signal M increased, and formation of a new

radical D ($g_D = 2.0007$; pp_D = 0.011 mT) is evident, which is attributed to C₇₀ di-anion (Fig. 2b,c). The formation of C₇₀ di-anion under the given experimental conditions can be explained either by C₇₀^{-•} excitation and subsequent electron transfer from TMB (Eq. (2)) or by C₇₀^{-•} disproportionation [16,20] (Eq. (3)):

$$C_{70}^{-,\text{TMB, hv}} \xrightarrow{} C_{70}^{2-} \tag{2}$$

$$2C_{70}^{-} \leftrightarrow C_{70} + C_{70}^{2-} \tag{3}$$

The intensities of EPR signals M and D in BN sensitively reflected the solution composition (C_{70} and TMB initial concentrations), as well as the irradiation period. It should be noted here that radicals M and D photogenerated in BN solutions were relatively stable after the cessation of radiation (half-times $\tau_{\rm M} = 12$ min and $\tau_{\rm D} = 5$ min, respectively). The high stability in polar BN solvent supported our assignment of EPR signals to C_{70} anion radicals, because the EPR signals of photogenerated radical adducts on C70 are transient, and decayed immediately after stopping illumination [51]. Additionally, when we exposed the irradiated C_{70}/TMB solutions to oxygen, both EPR signals disappeared, due to the well-known electron transfer from fullerene anions to molecular oxygen, forming super-oxide anion radical [20,40,52] (Eq. (4)):

$$C_{70}^{-1} + O_2 \rightarrow C_{70} + O_2^{-1}$$
 (4)

Replacing BN by less polar DCB ($\varepsilon_r = 9.95$) significantly lowered the intensity of both C_{70} anion radicals, as well as their stability. Fig. 3 illustrates a set of EPR spectra recorded upon continuous irradiation ($\lambda = 546$ nm) of fullerene C_{70} solutions in DCB with various concentrations of TMB. The excitation of TMB-free solutions of C_{70} at 290 K by monochromatic light caused the excitation of C_{70} to the paramagnetic triplet state [3,5]. However, in our cw-EPR experiments at 290 K the triplet state cannot be observed (Fig. 3a), because of its low intensity and large line width [5]. The analogous situation was described in a study of the photochemical reactions of fullerenes with anthracenes [51]. The detection of the C_{70} triplet state requires application of pulsed EPR techniques [3,5]. Photoexcitation in the presence of TMB in our experiments resulted in the formation of C_{70} anion radicals M and D (Fig. 3b,c). Despite higher concentrations of electron donating TMB (~10⁻³ M) used in the DCB solvent, the relative intensities of EPR signals M and especially D are low (Fig. 3d). This low efficiency of electron transfer is presumably caused predominantly by the low stability of C_{70} anion radicals in DCB.

Because the solvent polarity and relative permittivity determine the stability of ion radicals [39–42,53], we attempted to improve the electron transfer efficiency by the addition of ACN or salt with a large cation as (TBA)PF₆ to DCB. The relative permittivity of binary solvents DCB/ACN was calculated by algebraic averaging based on the mole fraction, as recommended by Sun et al. [54].

The time dependence of mono-anion M formation during irradiation ($\lambda = 546$ nm) and after stopping irradiation in DCB and DCB/ACN (6:1; v/v) solutions of C₇₀/TMB monitored by EPR is shown Fig. 4. The relative EPR intensity of signal M reached a stationary value after 1 min in DCB solvent, and its fast decay after stopping irradiation can be observed, characterized by a half-time of 5.3 s. The presence of ACN in DCB significantly enhanced the relative mono-anion M intensity during irradiation (Fig. 4). The decay profiles of signal M in both solvent systems were analyzed by the non-linear minimization procedure of leastsquares using the program SCIENTIST (Micro-Math) in order to determine decay kinetics (inset in Fig. 4). In DCB solutions the best results were obtained by the application of first-order kinetics (fit correlation = 0.986), but in binary solvent DCB/ACN (6:1; v/v) a better fit was calculated by the combination of first-order and second-order kinetics (fit correlation = 0.992).

Sasaki et al. investigated photoinduced electron transfer between C_{60} and TMB in different solvents by nanosecond laser photolysis [53]. In nonpolar and less polar solvents they confirmed that $C_{60}^{-\bullet}$ and TMB^{+•} decline with first-order kinetics, indicating that the back electron transfer reaction take place within the ion pair $(C_{60}^{-\bullet}, \text{TMB}^{+\bullet})_{\text{ion}}$

pair. On the other hand, in the polar media $C_{60}^{-\bullet}$ and TMB^{+•} the decay kinetics changed to secondorder, indicating that the back electron transfer reaction occurred on separate solvated anions C60^{-•} and TMB^{+•} [53]. Our results here using $C_{70}^{-\bullet}$ agree well with these suggestions; consequently we proposed that in less polar DCB solvent photogenerated ions exist as ion pairs ($C_{70}^{-\bullet}$, TMB^{+•})_{ion pair}. However, an increased solvent polarity boosted the $C_{70}^{-\bullet}$ and TMB^{+•} solvation and separation. This is illustrated in Fig. 5 where the EPR-relative intensities of mono-anion M are higher in the mixed DCB/ACN solvents, and they increased upon progressing irradiation. Analogously, the additional saturation of DCB solvent with (TBA)PF₆ salt stabilized $C_{70}^{-\bullet}$ and further improved the yield of mono-anion formation (Fig. 5).

Mono-anion radical M was also generated at low temperature by electron transfer between C_{70}



Fig. 3. EPR spectra measured at 290 K during continuous irradiation ($\lambda = 546$ nm) of 0.4 mM C₇₀ in DCB solutions containing various concentrations of TMB: (a) 0 mM; (b) 2 mM; (c) 3 mM; (d) 4 mM.



Fig. 4. The time dependence of the EPR-relative intensity of line M observed during irradiation (\uparrow , $\lambda = 546$ nm) and after stopping irradiation (\downarrow) in 0.8 mM C₇₀ and 1 mM TMB solutions in different solvent systems: DCB (1); DCB/ACN (6:1; v/v; $\varepsilon_r = 16.31$) (2). The inset shows the experimental (\bigcirc , \Box) and calculated (—) dependence of radical M intensity in different solvent systems after stopping irradiation: DCB (\bigcirc) and DCB/ACN (6:1; v/v; $\varepsilon_r = 16.31$) (\Box).

and TMB irradiating ($\lambda = 546$ nm) frozen DCB solution at 200 K (Fig. 6a). The quartz tube containing the sample was irradiated for 6 min, and at that moment the sample temperature was immediately lowered to 110 K. Then, the solid state EPR spectra were recorded without further irradiation raising the temperature to the desired value in the temperature range from 110 to 210 K (over 210 K the EPR line M expired without irradiation in DCB solvent). As can be seen from Fig. 6b, upon lowering the temperature, the EPR line M became broader and asymmetric. Consequently, the corresponding simulations of lowtemperature EPR spectra were performed assuming g-value and line-width anisotropy (Fig. 6b). The data extracted from simulations are presented in Fig. 7. The lower temperatures enhanced the $g_{\parallel} - g_{\perp}$ difference (Fig. 7a), hence at 110 K the experimental EPR spectrum was simulated by an axially symmetric g-matrix with $g_{\parallel} - g_{\perp} =$ 0.00165, whereas at 210 K this difference is only 0.00025. The temperature dependence of the perpendicular peak-to-peak line width obtained from simulations of line M is plotted in Fig. 7b. With increased temperature the line M became narrower, and a fit of the temperature dependence of the peak-to-peak width by least-squares analysis resulted in an activation energy of 11 meV.

The low-temperature EPR spectrum of C_{70}^{-} measured at 120 K in frozen CH₂Cl₂ glass by Dubois et al. was quite anisotropic, and was interpreted using three g-values at g = 2.007, 2.003 and ~ 2.000 [15]. The greater anisotropy for C_{70}^{-} comparing with C_{60} was explained in view of the lowered symmetry of C_{70} molecule [15]. Lobach et al. investigated the EPR spectra of C_{70}^{-} in a large temperature range from 12 to 350 K. At the lowest temperature they observed an axial anisotropy of g-factor; however above 70 K the anisotropy was averaged out, presumably by Jahn-Teller distorsions [44,45].

In order to prove that in the photochemical in situ EPR experiments C_{70} anion radicals were generated, we completed these investigations with a cathodic reduction.



Fig. 5. The time dependence of the EPR-relative intensity of line M observed during irradiation ($\lambda = 546$ nm) in 0.4 mM C₇₀ and 0.74 mM TMB solutions in different solvent systems: DCB (**I**); DCB/ACN (5:2; v/v; $\varepsilon_r = 21.36$) (**O**); DCB/ACN (4:3; v/v; $\varepsilon_r = 25.17$) (**A**); DCB saturated with by (TBA)PF₆ (\Box).



Fig. 7. The temperature dependence of g_{\parallel} and g_{\perp} -values (a) and perpendicular peak-to-peak line width (b) extracted from the simulations of the anisotropic EPR line M measured in the frozen DCB solutions within the temperature range from 110 to 210 K.



Fig. 6. (a) EPR spectra generated upon continuous monochromatic irradiation ($\lambda = 546$ nm) at 200 K in frozen DCB solutions containing 0.4 mM C₇₀ and 4 mM TMB. (b) Experimental (solid line) and simulated (dotted line) EPR spectra of photogenerated radical M observed at different temperatures in frozen DCB solutions.

In Fig. 8 the EPR spectra measured by in situ cathodic reduction of C_{70} in DCB solvent in the region of the first reduction wave, were compared with those measured by photoinduced electron transfer from TMB. The inset in Fig. 8 represents the corresponding cyclic voltammogram measured under argon in 0.05 mM C_{70} DCB solution in the presence of (TBA)PF₆ supporting electrolyte at 295 K. Under the given experimental conditions,

in DCB, as well as in BN solvents, three reversible redox waves were observed, characterized by the half-wave potentials: $E_{1/2}$ (C₇₀ in DCB) = -0.57; -0.97 and -1.39 V versus SCE; $E_{1/2}$ (C₇₀ in BN) = -0.47; -0.87 and -1.30 V vs. SCE. The shift in half-wave potentials probably reflects different properties of the solvent used, as already reported in the study of solvent, and supporting electrolyte, effects on the electrochemical proper-

ties of C_{70} [37]. The simulations of spectra unambiguously confirmed that the EPR spectra generated in both (photochemical and electrochemical) systems are identical and originate from C_{70} anion radicals.

4. Conclusions

The photoexcitation of fullerene C_{70} by monochromatic light ($\lambda = 546$ nm) in the presence of electron donating substrate 3,3',5,5'-te-



Fig. 8. Experimental (solid line) and simulated (dotted line) EPR spectra measured at 290 K by in situ photochemical electron transfer in 0.4 mM C₇₀ and 0.74 mM TMB in DCB/ACN (4:3;v/v; $\varepsilon_r = 25.17$), along with the EPR spectra obtained by in situ cathodic reduction of 0.05 mM C₇₀, 0.1 M (TBA)PF₆ in DCB in the region of the first reduction wave (*). The inset represents the cyclic voltammogram obtained in 0.05 mM C₇₀, 0.1 M (TBA)PF₆ in DCB under argon at 295 K (scan rate of 100 mV s⁻¹).

tramethyl-benzidine resulted in the charge transfer, quenching the fullerene excited states and forming the corresponding C_{70} anion radicals. The detected changes in UV-vis spectra of C_{70} in the presence of TMB pointed at ground state charge transfer complex formation between C_{70} and TMB in BN solvent.

Two EPR signals were observed upon in situ irradiation of C_{70} /TMB solutions in the cavity of an EPR spectrometer. The EPR singlet M, characterized by g-value, $g_{\rm M} = 2.0004$ and peak-to-peak line width, $pp_M = 0.013$ mT, was assigned to the C_{70} monoanion. Signal D ($g_D = 2.0007$; $pp_D =$ 0.011 mT) was attributed to the C_{70} di-anion. The stabilization of photogenerated anion radicals is significantly dependent on solvent polarity. The shortest lifetime of the radicals was found in DCB, and it increased considerably upon the addition of (TBA)PF₆ salt or ACN to the C_{70}/DCB solution, or if DCB was replaced by BN. The concentration of radicals M and D formed during irradiation sensitively reflected the composition of the solution irradiated (solvent, C₇₀ and TMB concentrations) and the irradiation period.

Mono-anion M was generated also in the solid state, irradiating frozen C_{70} and TMB solutions in DCB at a temperature of 200 K. Lowering the temperature, the EPR line M became broader and asymmetric. At 110 K the observed EPR spectrum can be simulated by an axially symmetric g-matrix with $g_{\parallel} - g_{\perp} = 0.00165$.

The EPR spectra recorded by the in situ cathodic reduction and also by the in situ photochemical reduction of C_{70} in DCB are in both experimental systems identical, and consequently, justify their assignment to the anion radicals of C_{70} .

Acknowledgements

We thank the Slovak Grant Agency (Project VEGA 1/4206/97) for financial support.

References

 A.Z. Sension, G.R. Szarka, G.R. Smith, R.M. Hochstrasser, Chem. Phys. Lett. 185 (1991) 179.

- [2] P.V. Kamat, J. Am. Chem. Soc. 113 (1991) 9705.
- [3] M.R. Wasielewski, M.P. O'Neil, K.R. Lykke, M.J. Pellin, D.M. Gruen, J. Am. Chem. Soc. 113 (1991) 2774.
- [4] J.W. Arbogast, C.S. Foote, M. Kao, J. Am. Chem. Soc. 114 (1992) 2277.
- [5] G.L. Closs, P. Gautam, D. Zhang, P.J. Krusic, S.A. Hill, E. Wasserman, J. Phys. Chem. 96 (1992) 5228.
- [6] D.M. Guldi, H. Hungerbühler, E. Janata, K.-D. Asmus, J. Phys. Chem. 97 (1993) 11258.
- [7] M.R. Fraelich, R.B. Weisman, J. Phys. Chem. 97 (1993) 11145.
- [8] C.A. Steren, H. van Willigen, K.-P. Dinse, J. Phys. Chem. 98 (1994) 7464.
- [9] P.V. Kamat, I. Bedja, S. Hotchandani, J. Phys. Chem. 98 (1994) 9137.
- [10] C.S. Foote, Top. Curr. Chem. 169 (1994) 347.
- [11] O. Ito, Res. Chem. Intermed. 23 (1997) 389.
- [12] H.N. Ghosh, D.K. Palit, A.V. Sapre, J.P. Mittal, Chem. Phys. Lett. 265 (1997) 365.
- [13] F. Prat, R. Stackow, R. Bernstein, W. Qian, Y. Rubin, C.S. Foote, J. Phys. Chem. A 103 (1999) 7230.
- [14] M. Fujitsuka, C. Luo, O. Ito, J. Phys. Chem. B 103 (1999) 445.
- [15] D. Dubois, K.M. Kadish, S. Flanagan, R.E. Haufler, L.P.F. Chibante, L.J. Wilson, J. Am. Chem. Soc. 113 (1991) 4364.
- [16] D. Dubois, M.T. Jones, K.M. Kadish, J. Am. Chem. Soc. 114 (1992) 6446.
- [17] M.M. Khaled, R.T. Carlin, P.C. Trulove, G.R. Eaton, S.S. Eaton, J. Am. Chem. Soc. 116 (1994) 3465.
- [18] S.S. Eaton, G.R. Eaton, Appl. Magn. Reson. 11 (1996) 155.
- [19] M. Baumgarten, A. Gügel, L. Gherghel, Adv. Mater. 5 (1993) 458.
- [20] J. Stinchcombe, A. Pénicaud, P. Bhyrappa, P.D.W. Boyd, C.A. Reed, J. Am. Chem. Soc. 115 (1993) 5212.
- [21] P.D.W. Boyd, P. Bhyrappa, P. Paul, et al., J. Am. Chem. Soc. 117 (1995) 2907.
- [22] M.A. Greaney, S.M. Gorun, J. Phys. Chem. 95 (1991) 7142.
- [23] A. Staško, V. Brezová, S. Biskupič, K.-P. Dinse, P. Schweitzer, M. Baumgarten, J. Phys. Chem. 99 (1995) 8782.
- [24] V. Brezová, A. Staško, P. Rapta, G. Domschke, A. Bartl, L. Dunsch, J. Phys. Chem. 99 (1995) 16234.
- [25] A. Staško, V. Brezová, P. Rapta, K.-P. Dinse, Fullerene Sci. Technol. 5 (1997) 593.
- [26] A. Staško, V. Brezová, P. Rapta, K.-P. Dinse, A. Gügel, Res. Chem. Intermed. 23 (1997) 453.
- [27] J.W. Arbogast, C.S. Foote, J. Am. Chem. Soc. 113 (1991) 8886.
- [28] N.M. Dimitrijević, P.V. Kamat, J. Phys. Chem. 96 (1992) 4811.

- [29] R.V. Bensasson, T. Hill, C. Lambert, E.J. Land, S. Leach, T.G. Truscott, Chem. Phys. Lett. 206 (1993) 197.
- [30] P.J. Surján, K. Németh, M. Kállay, J. Mol. Struct. (Theochem) 398-399 (1997) 293.
- [31] P.A. Lane, X. Wei, Z.V. Vardeny, J. Partee, J. Shinar, Phys. Rev. B 53 (1996) 7580.
- [32] H.T. Etheridge, III, R.B. Weisman, J. Phys. Chem. 99 (1995) 2782.
- [33] X.L.R. Dauw, O.G. Poluektov, J.B.M. Warntjes, M.V. Bronsveld, E.J.J. Groenen, J. Phys. Chem. A 102 (1998) 3078.
- [34] V.N. Semkin, N.V. Drichko, A.V. Talysin, et al., Synth. Metals 93 (1998) 207.
- [35] Q. Xie, E. Pérez-Cordero, L. Echegoyen, J. Am. Chem. Soc. 114 (1992) 3978.
- [36] M. Baumgarten, L. Gherghel, Appl. Magn. Reson. 11 (1996) 171.
- [37] L. Fan, Y. Li, Y. Li, D. Zhu, Fullerene Sci. Techn. 5 (1997) 1563.
- [38] D.R. Lawson, D.L. Feldheim, C.A. Foss, et al., J. Phys. Chem. 96 (1992) 7175.
- [39] S. Fukuzumi, T. Suenobu, T. Hirasaka, et al., J. Phys. Chem. A 103 (1999) 5935.
- [40] M.A. Alam, A. Watanabe, O. Ito, Bull. Chem. Soc. Jpn. 70 (1997) 1833.
- [41] T. Nojiri, A. Watanabe, O. Ito, J. Phys. Chem. A 102 (1998) 5215.
- [42] M. El-Kemary, M. Fujitsuka, O. Ito, J. Phys. Chem. A 103 (1999) 1329.
- [43] J. Friedrich, P. Schweitzer, K.-P. Dinse, P. Rapta, A. Staško, Appl. Magn. Reson. 7 (1994) 415.
- [44] A.S. Lobach, N.F. Goldshleger, M.G. Kaplunov, A.V. Kulikov, Chem. Phys. Lett. 243 (1995) 22.
- [45] A.S. Lobach, N.F. Goldshleger, M.G. Kaplunov, A.V. Kulikov, Russ. Chem. Bull. 45 (1996) 93.
- [46] R. Seshadri, C.N.R. Rao, H. Pal, T. Mukherjee, J.P. Mittal, Chem. Phys. Lett. 205 (1993) 395.
- [47] Y.-P. Sun, B. Ma, G.E. Lawson, Chem. Phys. Lett. 233 (1995) 57.
- [48] N.A. Nadtochenko, N.N. Denisov, P.P. Levin, Russ. Chem. Bull. 44 (1995) 1038.
- [49] V.A. Nadtochenko, N.N. Denisov, I.V. Rubtsov, A.P. Moravsky, Russ. Chem. Bull. 45 (1996) 1091.
- [50] M.C. Rath, H. Pal, T. Mukherjee, J. Phys. Chem. A 103 (1999) 4993.
- [51] R. Klemt, E. Rodunert, H. Fischer, Acta Chim. Scand. 50 (1996) 1050.
- [52] V. Brezová, A. Gügel, P. Rapta, A. Staško, J. Phys. Chem. 100 (1996) 16232.
- [53] Y. Sasaki, Y. Yoshikawa, A. Watanabe, O. Ito, J. Chem. Soc., Faraday Trans. 91 (1995) 2287.
- [54] Y.-P. Sun, B. Ma, C.E. Bunker, J. Phys. Chem. A 102 (1998) 7580.