6. SUMMARY

The purpose of the presented work was to align group V endohedral fullerenes in a solid matrix and to perform basic quantum computation experiments on this system using electron spin resonance (ESR and ENDOR). These fullerenes were continuously produced and enriched and some of their properties were thoroughly investigated in polycrystalline form as well as when they are embedded in a solid state matrix.

$N@C_{60}$ and $P@C_{60}$ were produced by ion implantation and enriched using HPLC. A $P@C_{60}/C_{60}$ mixture was enriched up to 30 % for the first time in this work. Full purification of the sample was not achieved, possibly due to the lower stability of the enriched material which seems to decompose on the HPLC column. It was shown that $P@C_{60}$ can be chemically modified with the Bingel type reaction at room temperature. The ESR spectra of these adducts can be qualitatively simulated using anisotropic g-factor and hyperfine constant A in contrast to chemically modified $N@C_{60}$. In the latter a well resolved zero-field splitting (ZFS) is observed, which cannot be detected in $P@C_{60}$ adducts.

Quantum computer architectures based on group V endohedral fullerenes require alignment of the qubits in an array on a solid state surface. However, such implementations require single electron spin detection which remains a big challenge at present. Therefore ensemble experiments were performed in this work with the aim to further understand the properties of theses endohedrals. We could show that $N@C_{60}$, $N@C_{70}$ and $P@C_{60}$ can be incorporated as guests in the host solid state matrix of BrPOT. Two different crystal modifications - hexagonal and rhombohedral were obtained.

In the hexagonal structure, fullerenes are situated together with solvent molecules in parallel channels formed by BrPOT molecules. The ESR spectral lines are inhomogeneously broadened compared to those of non-encapsulated ("bulk") fullerenes with no observable fine structure in the case of crystals obtained from toluene solution. For hexagonal crystals obtained from CS_2 solution of $N@C_{60}$ and BrPOT, there is a small ZFS of about $D = 1$ MHz.

In the rhombohedral crystal modifications of $N@C_{60}$ and $P@C_{60}$ in BrPOT the fullerenes are fully oriented in individual pockets formed by the BrPOT molecules,

hence there are no channels and no solvent inclusion is observed. The ESR spectra show significant fine structure with $D = 8.01$ MHz and $D = 127$ MHz for $N@C_{60}$ and $P@C_{60}$, respectively. The presence of ZFS means that the degeneracy of the electron spin $S = 3/2$ system is lifted and the absence of an E-term indicates a purely axial deformation of the fullerene carbon cage.

Distant proton ENDOR measurements of $P@C_{60}$ in BrPOT reveal coupling of the three p electrons of the endohedral atom to the abundant protons of the BrPOT matrix. This coupling most probably causes the observed ESR line broadening. From the line splitting in the H-ENDOR spectrum an average electron-proton distance $\bar{r} = 5.85\,\mathring{A}$ is estimated. The latter is in rough agreement with the values calculated from the XRD measurements, which reveal larger distances of about 6.7 $\mathring{A}$. The discrepancy is attributed to a shortcoming of the simple point-dipole model used here.

Controlling the coherence time of qubits is very important since this is the time that limits the performance of the quantum computer. To study the coherence time of polycrystalline $P@C_{60}$, several polycrystalline samples with low spin concentrations were prepared. The phase memory time T_m and the spin-spin relaxation time T_2 were measured using the Hahn echo and Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences, respectively. T_m increases from 11.2 μs to 113.25 μs upon decreasing the spin concentration, where the latter is the maximum achieved value at a spin concentration of 6.3×10^{13} spins/cm^3. The T_2 time measured with the CPMG pulse sequence shows a similar trend, but the values are larger and T_2 varies from 11.2 μs up to 417 μs. It was found that instant diffusion does not significantly influence the spin-spin relaxation and that the phase memory time is determined mainly by spectral diffusion.

The spin relaxation of rhombohedral $P@C_{60}$ in BrPOT has been studied at various temperatures in W-band. Spin-lattice relaxation times were measured using inversion recovery and all time traces were found to be best fitted with a double exponential function. As observed previously in polycrystalline ("bulk") $P@C_{60}$, the two longitudinal relaxation times T_1^a and T_1^b have similar temperature dependence, but they are much shorter than in bulk $P@C_{60}$.

The presence of fine structure allowed the transition selective measurement of relaxation. While no transition dependence was found for the spin-lattice relaxation times, the spin-spin relaxation shows characteristic differences for the transitions. The coherence time $T_m^{3/2}$ of transitions with $m_s = -1/2 \leftrightarrow m_s = -3/2$ and $m_s = +3/2 \leftrightarrow m_s = +1/2$ is equal, but could not be measured between room temperature and $T = 150$ K. Below this temperature, T_m increases up to 17 μs at $T = 30$ K where it is longer than $T_m^{1/2}$ measured on transitions with

$m_s = +1/2 \leftrightarrow m_s = -1/2$. $T_m^{1/2}$ is measurable from room temperature down to $T = 10$ K and shows a minimum at $T = 210$ K. It seems that fluctuations of the ZFS cause the spin-spin relaxation, since the ZFS changes rapidly at this temperature, hence its fluctuations increase.

A subsystem of four states from the total eight levels of P@C$_{60}$ in BrPOT was selected for quantum computing experiments. In this subsystem pseudo-pure states were prepared and their diagonal matrix elements were measured with the help of Rabi oscillations. The experimental density matrices deviate slightly (~ 3 %) from the theoretically calculated ones due to pulse imperfections.

Pseudo-entanglement was created in this subsystem using the prepared pseudo-pure states. Electron and nuclear spin phase rotations were used for the detection of the entanglement. The lifetime of the entangled state depends on the type of states used for its creation. For two states with $|m_S| = 1/2$, the coherence time was so short that the entanglement between them was partially destroyed during the preparation. If one of the energy levels has $|m_s| = 3/2$, pseudo-entanglement can be prepared with a decay time of $T_2^{ent} \approx 55$ ns. This is much shorter than the electron spin coherence time at that temperature, $T_m = 17$ μs. A possible reason for the fast decay could be the coupling of the endohedral electrons to protons in the BrPOT matrix.

In summary, a new solid state matrix was found for the orientation of group V endohedral fullerenes. The orientation lifts the degeneracy of the electron spin $S = 3/2$ system and allows transition selective addressing. This was used to (i) to measure level specific spin-spin relaxation times which proved the influence of fluctuations in zero-field splitting on T_2, and (ii) to create different entangled states between electron and nuclear spins. These are the first quantum computation measurements of oriented endohedral fullerenes and the results show that, pseudo-pure states can be very well prepared. Pseudo-entangled states were also created, although with very short decay time possibly due to matrix-coupling (as determined by matrix ENDOR) together with very long radio frequency pulses.

The short coherence time of the entanglement hinders implementation of quantum computation algorithms. In order to reduce the matrix-coupling, several experimental approaches can be taken: (i) experiments with endohedrals encapsulated in a per-deuterated BrPOT matrix and (ii) decoupling of the neighboring protons from the endohedral atom. The inclusion of doubly filled dimers (P@C$_{60}$-P@C$_{60}$, N@C$_{60}$-N@C$_{60}$) in BrPOT could make possible entanglement between two electron spin systems, a necessary step for a scalable quantum computer based on electron spins.