

Contents

Acknowledgements	v
Abstract	vii
Zusammenfassung	ix
List of figures	xiv
List of tables	xvii
Introduction and outline	1
I Triplet DNP of pentacene:naphthalene crystals: methodology and its application as a neutron spin filter	5
1 Overview of triplet DNP and its application	7
1.1 Dynamic nuclear polarization by photo-excited triplet states	7
1.2 The system pentacene:naphthalene	9
1.3 Polarized proton target as a neutron spin filter	12
2 Apparatus for triplet state DNP	15
2.1 Introduction	15
2.2 Cryostat with optical access	16
2.3 Optical excitation	17
2.4 X-band pulse ESR spectrometer	20
2.5 ESR resonator	22
2.6 DNP schemes	24
2.7 NMR system	24
2.8 ESR on photo-excited triplet states of pentacene	25
2.9 Choice of the proper excitation light source	26
2.10 Target sample	28
2.10.1 Determination of pentacene doping concentration	28
2.10.2 Manufacture of target sample	29

3	DNP via the integrated solid effect using pentacene-d_{14} I: theory	33
3.1	The Hamiltonian	34
3.2	Evolution of the electron spin polarization	36
3.3	The Integrated Solid Effect (ISE)	38
3.3.1	Applying Landau-Zener theory	39
3.3.2	Polarization transfer	42
4	DNP via the integrated solid effect using pentacene-d_{14} II: experiments	45
4.1	The spin Hamiltonian	45
4.2	Polarization transfer	49
4.3	Experimental methods	50
4.4	Experimental results	52
4.5	Polarization transfer above the Hartmann-Hahn condition	57
4.5.1	Proton spins on the pentacene molecule	58
4.5.2	Higher order transitions	59
5	Studies on the photophysics of pentacene:naphthalene crystals	61
5.1	Model of photo-excitation of the pentacene triplet state	62
5.2	Optical parameters of pentacene:naphthalene crystals	65
5.2.1	Absorption bands of pentacene	65
5.2.2	Absorption cross section $\sigma(\omega)$	65
5.2.3	Fluorescence lifetime τ_f and intersystem crossing efficiency ϕ_{ISC}	68
5.2.4	Optical tensor of naphthalene	68
5.3	Theoretical calculations	69
5.3.1	The saturation intensity I_{sat} and weak field absorption length z_{abs}	69
5.3.2	Simulation of the triplet state distribution in pentacene:naphthalene crystals	69
5.3.3	Photobleaching of pentacene:naphthalene crystals	70
5.4	Secondary order effects	72
5.4.1	Amplified spontaneous emission within fluorescence spectrum	72
5.4.2	Photoabsorption within the triplet manifold	74
5.4.3	Reabsorption of fluorescence light	74
6	DNP performance using the triplet state of pentacene-d_{14}	77
6.1	Introduction	77
6.2	Optimization of DNP parameters	78
6.3	Experimental results	80
6.3.1	Theoretical polarization buildup	83
6.3.2	Proton polarization profiles	83
6.4	Spin filter performance and outlook	85
6.4.1	Neutron focusing optics	86
6.4.2	Proposed novel ISE sequence	87

II Photo-induced non-persistent radicals in frozen endogenous materials for dissolution DNP	89
7 Photo-induced radicals in α-keto acids for dissolution DNP	91
7.1 ESR spectra of UV-irradiated α -keto acids	92
7.2 Performance and feasibility of the method in dissolution DNP	98
7.2.1 Radical generation in frozen pyruvic acid	98
7.2.2 Solid-state DNP measurements	98
7.2.3 ^{13}C signal decay in a hyperpolarized pyruvic acid solution	100
7.2.4 High-resolution NMR spectra of the pyruvic acid substrate	100
7.2.5 Sample preparation for an optimized radical density	103
8 Hyperpolarization of pyruvic acid without persistent radicals for <i>in vivo</i> real-time metabolic imaging	105
8.1 Results and discussion	105
8.2 Methods	108
8.2.1 Dissolution and transfer of DNP-enhanced pyruvic acid	108
8.2.2 Animal preparation	108
8.2.3 <i>In vivo</i> hyperpolarized ^{13}C MRS and imaging measurements	109
Conclusion and outlook	111
A Appendix	113
A.1 Optical nuclear polarization of pentacene:naphthalene crystals	113
A.2 MATLAB [®] code for photo-excitation in pentacene:naphthalene crystals	116
A.2.1 Main m-file	116
A.2.2 Function file	118
A.3 Simulation of saturation and bleaching in pentacene:naphthalene crystals by photo-excitation	119
A.3.1 Two-level system	119
A.3.2 Three-level system	120
A.4 Triplet decay of deuterated pentacene in naphthalene	121
A.5 DNP with UV-irradiated azo compounds	122
A.6 Photographs of the triplet DNP experiment	125
A.6.1 Laser setup	125
A.6.2 Triplet DNP Apparatus	126
A.6.3 The SING facility at PSI	127
A.6.4 The triplet DNP experiment at the BOA beamline	128
A.6.5 Pentacene:naphthalene crystal	130
A.7 Photographs of the dissolution DNP experiment	131
A.7.1 Sample preparation	131
A.7.2 Dissolution DNP setup at CIBM, EPFL	132

Contents

Bibliography	142
Curriculum Vitae	143
Publications, conference proceedings, patent & public outreach	145