PHENYLENE ETHYNYLENE FOLDAMERS:
FROM SYNTHESIS TO TUBULAR SCAFFOLDING
AND PHOTOSWITCHABLE HELICES

INAUGURAL – DISSERTATION

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Anzar Ul Haque Khan
aus Khamgaon, Indien

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1. Gutachter: Dr. Stefan Hecht
2. Gutachter: Prof. Dr. Rainer Haag
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The objective of the work presented in this thesis is to develop more efficient methods for the synthesis of artificial backbones capable to adopt a stable helical conformation in solution. The motivation for such efforts is to gain a profound understanding of the backbones’ folding behavior and to utilize the reversible helix-coil transition for tubular scaffolding and for the design of stimuli-responsive materials.

The general introduction, provided in Chapter 1, describes some representative examples of helical oligomers and polymers reported in the literature. While Chapter 2 is focused on the synthesis of high molecular weight meta-linked poly(phenylene ethynylene)s (PPE)s by a novel in-situ activation/coupling protocol, the extension of this newly developed method to the preparation of new helically folding ortho-linked PPEs is outlined in Chapter 3. In Chapter 4, the synthesis of cinnamate-based meta-linked PPEs and the first example of an intramolecular helical crosslinking reaction to furnish covalently stabilized tubular nano-objects is described. The synthesis and photoresponsive behavior of the first prototype of a photoswitchable foldamer, in which the helix-coil transition can be triggered by light, is described in Chapter 5. Finally, Chapter 6 details the synthesis of site-isolated, defect-free, and water-soluble conjugated para-linked PPEs, which display remarkably high fluorescence efficiencies in water.
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Appendix

Symbols and Abbreviations

d doublet (NMR)
DBU 1,8-diazabicyclo[5. 4. 0]undec-7-ene
DCC dicyclohexylcarbodiimide
dd doublet of doublet (NMR)
DIB dibromoisocyanuric acid
DIPA diisopropyl ethyl amine
DMF dimethylformamide
EA elemental analysis
EI electron ionisation (MS)
FAB fast atom bombardment (MS)
Φ fluorescence quantum yield
g gram
GPC gel permeation chromatography
HPLC high-performance liquid chromatography
J coupling constant in Hz
k rate constant
m multiplet (NMR)
M molar
[M]+ molecular ion peak
MALDI-TOF matrix assisted laser desorption ionization- time of flight (MS)
m/e mass to charge ratio in mass spectrometry
mg milligram
mmol millimol
MS mass spectrometry
OEG oligo(ethylene glycol)
TEA triethyl amine
Tg triglyme monomethyl ether
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<td>tetrahydrofurane</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
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<tr>
<td>TMSA</td>
<td>trimethylsilyl acetylene</td>
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<tr>
<td>UV</td>
<td>ultraviolet</td>
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Versicherung