

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

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**BY
ANZAR UL HAQUE KHAN**

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

THF	tetrahydrofurane
TMS	trimetylsilyl
TMSA	trimetylsilyl acetylene
UV	ultraviolet

Versicherung

Hiermit versichere ich, Anzar Khan, geb. 1. Januar 1978, die vorliegende Arbeit selbständig und nur mit Hilfe der angegebenen Mittel verfasst zu haben.