

Summary of PhD thesis

Synthesis and characterization of light-emitting compounds

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1. Introduction and aims

Fluorescent compounds are essential reagents in medical diagnosis and bioanalytics. Structure, interactions of biomolecules, biologically active materials labeled by various fluorescent dyes can be determined, and their location can be monitored in the organs. The so-called solvatochromic dyes have particular importance, since the wavelength and the intensity of their emitted fluorescent light depends on the polarity of the environment around the molecule. The reason for the phenomenon is that the ground and the excited state of the light-absorbing molecule solvates differently in various media. Most important field of application for solvatochromic dyes are bioanalytics and fluorescent microscopy, where the parts of cells and tissues with different polarity can be easily differentiated by the color of their emitted fluorescent light.

Light emitting polymers can also be sorted among fluorescent materials (typically there are aromatic chromophores in both groups). Excitation of their most important members, conjugated polymers can be not only by light but also with electric current due to their semiconducting properties. Therefore there are intensive research for the application of them in displays. Special needs can be easily solved by using these materials, due to their advantageous properties (flexibility, toughness, solubility, malleability) and the ease of processibility (particularly in solution). Among light emitting polymers the ones capable of blue light-emission are the most important, since blue light can be converted to any color with lower energy.

Therefore the aim of our research was the synthesis of novel blue light-emitting polymers, and the investigation of their fluorescence properties, the possibility of their self-assembly. One of our aims was to synthesize phenanthroline-terminated poly(ethylene glycol)s and polyisobutylenes. In these polymers phenanthroline is responsible not only for the light-emitting chromophore, but also gives the possibility for the self-assembly and the formation of ionomer networks by metal ions due to its complex forming property.

An other goal was the synthesis of novel glycosylated naphthalene-phenylene copolymer, since naphthalene-based light emitting polymers have advantageous luminescent and electrical properties, most of them emit blue light. The bulky glucose substituents give a simple and economical way to increase solubility, while the polymer to be formed is able to emit blue light with good intensity.

The synthesis of blue light-emitting isoindole-based polymers by novel methods was also aimed, since isoindoles are less studied, however they have promising properties. A novel, simple, catalyst-free polycondensation method was aimed to be developed, based on the reaction widely used in analytics for the quantitative analysis of amines by phthalaldehyde. In addition, during the test-reaction to synthesize 1-carboxamidoisoindoles with similar structure to the above mentioned one, one of the monomers, 1-amino-5-isocyanonaphthalene showed interesting solvatochromic fluorescent behavior. Since there was no example in the literature for that behavior in the case of molecules with similar structure, its thorough investigation was also aimed.

2. Experimental methods

Synthesis of small molecules was monitored by thin layer chromatography, gel permeation chromatography was used in the case of polymers. Synthesized compounds were purified by column chromatography. Structure of the materials prepared were proved by using ^1H -NMR, ^{13}C -NMR and ESI as well as MALDI-TOF mass spectrometry methods. Optical properties of fluorescent materials were studied by UV-Vis spectrophotometry and spectrofluorimetry. Self-assembly properties were described by dynamic light scattering measurements and with optical as well as with transmission electron microscopy.

3. Novel scientific achievements

3.1. Synthesis of new amino-isocyanonaphthalene based fluorophores and investigation of their solvatochromic properties

A new fluorophore was prepared by the reaction of 1,5-diaminonaphthalene with dichlorocarbene in basic chloroform solution. The resulting 1-amino-5-isocyano-naphthalene showed strong positive solvatochromic effects. Unlike in the case of the starting 1,5-diamino- and the subsequent 1,5-diisocyanonaphthalene, the emission maxima fell in almost every case in the visible region of the spectrum (Figure 1). The lowest value of 409 nm belonged to the hexane solution, while the highest at 513 nm to the most polar solvent applied, which was water. The fluorescence quantum efficiency varied between $\Phi_F=0.95$ in 1,4-dioxane and $\Phi_F=0.04$ in water, and was found to decrease with increasing solvent polarity.

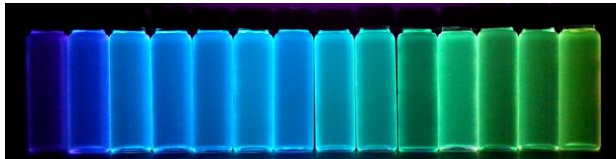


Figure 1. Demonstration of the fluorescence properties of 1-amino-5-isocyanonaphthalene (ICAN) in different solvents

The shape of the absorption spectra in different media was calculated using time-dependent density function quantum chemical model. The calculated and measured spectra are in good correlation. The Lippert-Mataga plot was applied to describe the solvent polarity effect on the emission spectra; however the Kamlet-Taft equation turned out to give the best results. Samples dissolved in DMF, pyridine and PEG resulted almost the same excitation spectra in the range of 250-450 nm indicating, that the shape of the excitation spectrum can be independent of the acidity parameter of the solvent. The phenomenon of preferential solvation was detected in cyclohexane/THF solutions of ICAN. The radiative decay rates of the excited state were determined by laser light flash photolysis experiments. The shortest and the longest life-times were observed in hexane (6.4 ns) and

dimethyl sulfoxide (16.3 ns), respectively and were in the order of 10 ns for most of the solvents studied.

Derivatives with alkyl substituents have similar properties to that of the starting compound, however their solvatochromic emission region is slightly shorter. The differences in the spectral properties of the dialkylated molecules can be explained by the lack of the free amine N-H hydrogens, therefore the missing ability to form hydrogen bonds.

Due to its molecular character ICAN prefers nonpolar environments. Based on this property it was demonstrated that ICAN can be applied for the cmc determination of surfactants such as sodium lauryl sulfate (SLS) with long nonpolar chain. Above cmc ICAN is located in the nonpolar core of the micelles resulting in a significant blue-shift in emission and increased quantum efficiency.

3.2. Synthesis of phenanthroline-functionalized polymers and their Fe (II)-complexes

Mono and diphenanthroline-terminated poly(ethylene glycol)s and polyisobutylenes were prepared using the Williamson synthesis. The polymers were characterized by MALDI-TOF MS and ^1H -NMR methods. It was shown that both PIB and PEG-phenanthrolines form strong complexes with Fe^{2+} ions. The complex formation was studied by UV-vis spectrophotometry for PEG-phenanthrolines. The complex formation was quantitative in each case, the ratio of the phenanthroline termini and Fe^{2+} ions was 3:1. Molar absorption coefficients were determined for PEG complexes and were found to be $\epsilon=11090 \text{ M}^{-1}\text{cm}^{-1}$ and $\epsilon=10300 \text{ M}^{-1}\text{cm}^{-1}$ for phen-PEG-phen and mPEG-phen, respectively. These values are in good agreement with the ones published previously for ferriin.

Phen-PEG-phen was shown to form cross-linked structure with Fe^{2+} ions as supported by ESI-TOF measurements. mPEG-phen was found to form aggregates in water. The critical micelle concentration and hydrodynamic radius of the aggregates were determined by dynamic light scattering measurements.

The complex formation of the mono phenanthroline-terminated polymers was investigated by ESI-TOF mass spectrometry. In the case of monofunctional ligands the single complexes can be clearly identified in the mass spectra. A red-colored rubbery polymer network was created from phen-PEG-phen and the Mohr's salt, the general formula of the polymer network can be given as $(\text{NH}_4)_4[(\text{phen-PEG-phen})_3\text{Fe}_2](\text{SO}_4)_4$. A well-defined microstructure was found according to optical microscopic studies of the layer. The network is stable in air and was found to be stabilizing Fe^{2+} ions from oxidation as is the case for all of the ligands prepared. Well controlled structure was prepared from phen-PIB-phen and Fe^{2+} ions in a heterophase reaction. The formation of a large amount of gel was observed which lost water over time. The dry polymer network could not be dissolved in solvents common for PIB derivatives. The PIB-phenanthroline Fe^{2+} complexes are soluble in apolar solvents, whereas the PEG-phenanthroline Fe^{2+} complexes are soluble in both polar and apolar solvents. The wide range of solubility makes these complexes promising candidates in the field of phase transfer catalysis.

3.3. Synthesis and characterization of an amphiphilic blue light-emitting glycosylated polynaphthalene-phenylene copolymer

A glucosylated naphthalene-phenylene-type copolymer was prepared by the Suzuki polycondensation of 1,6-dibromo-2-naphthyl tetra-O-acetyl- β -D-glucoside and benzene-1,4-diboronic acid (Figure 2).

In the first step poly(2-(tetra-O-acetyl-glucopyranosyl)-1,6-naphthalene-1,4-phenylene) was obtained which was deacetylated to obtain poly(2-glucopyranosyl-1,6-naphthalene-1,4-phenylene). The polymer was characterized by GPC and ^1H -NMR methods. It was found that the glucosylated copolymer was soluble in polar solvents such as methanol/tetrahydrofuran mixtures and even in water. The acetylated copolymer showed self-assembly behavior in MeOH/THF mixture and in aqueous media.

The formation of uniform sized nanospheres in solid phase having an average diameter of 460 nm was detected by transmission electron

microscopy. The nanospheres showed blue fluorescence under optical microscope. It was shown that the copolymer forms aggregates also in aqueous medium. Using dynamic light scattering method, the critical micelle concentration and hydrodynamic radius of the aggregates were determined.

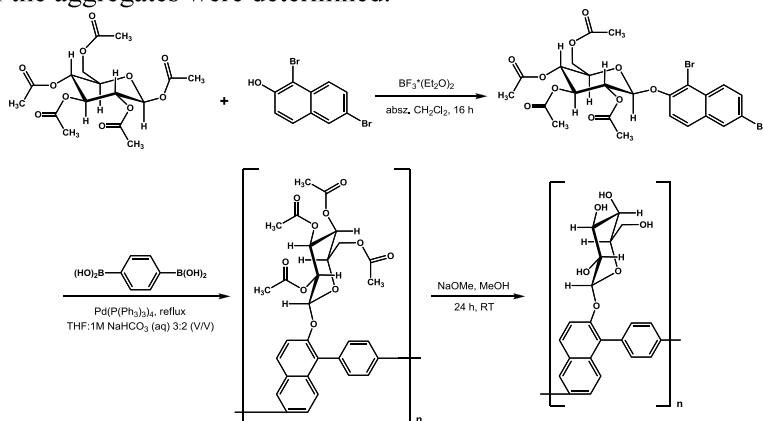


Figure 2. Synthesis of poly(2-(tetra-O-acetyl-glucopyranosyl)-1,6-naphthalene-1,4-phenylene

The fluorescence properties of the copolymer was also studied. Emission spectra were recorded and the emission maximum was determined. $\lambda_{\text{max}}=396$ nm was found for poly(2-(tetra-O-acetyl-glucopyranosyl)-1,6-naphthalene-1,4-phenylene) and $\lambda_{\text{max}}=403\text{--}405$ nm for poly(2-glucopyranosyl-1,6-naphthalene-1,4-phenylene) depending on the solvent applied. The emission maximum and the shape of the emission peak showed solvent-dependence that can be attributed to the self-assembly of the copolymer. It was shown that the red shift and broader emission peak can be attributed to a specific π -interaction between the polymer chains due to self-assembly. In short, the elevated solubility, the ability of the preparation of well-defined surfaces through self-assembly and the ability to alter the emission spectrum make this glucosylated copolymer a promising candidate in the field of blue light emitting polymers.

3.4. Novel, simple polycondensation method for the synthesis of sulfur-linked isoindole-phenylene based blue light-emitting copolymers

Poly[(1,2-isoindolene)-(1-sulfane-4-phenylene)] and poly[(1,2-isoindolene)-(1-sulfane-3-phenylene)] new isoindole based copolymers were prepared in a simple polycondensation reaction between ortho-phthalaldehyde and 4- or 3-aminothiophenol. The reaction proceeds under mild conditions without the presence of any catalyst. The reaction gives the pure copolymers with high yields. The polycondensation was found to be largely solvent dependent. It proceeds well only in acetonitrile in the presence of trace amounts of water. Unfortunately, the copolymers are insoluble in acetonitrile therefore the obtainable molecular weight is limited. The other molecular weight limiting factor can be cyclization when meta-aminothiophenol is applied.

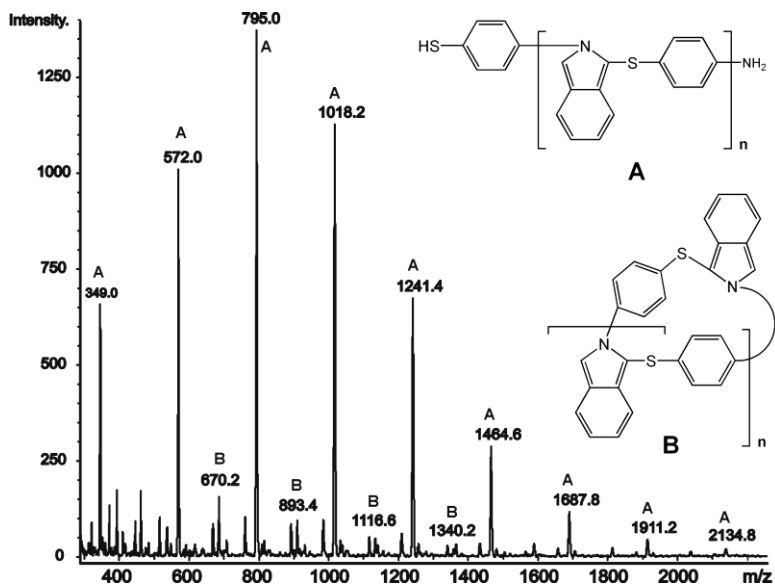


Figure 3. MALDI-TOF mass spectrum of poly[(1,2-isoindolene)-(1-sulfane-4-phenylene)]

The polycondensation is not too sensitive to the monomer ratio, however the large excess of OPA should be avoided. Unlike their low molecular weight derivative isoindoles, the copolymers proved to be stable for several weeks. MALDI-TOF MS investigation showed the presence of amino and thiophenyl endgroups, while the formation of cyclic product could also be detected (Figure 3). NMR studies indicated a largely twisted structure, where orthogonal σ - π interactions (two orthogonal aromatics ring facing each other and a CH bond is affected by the electron current of the other ring) are present.

Optical study of the copolymers showed blue-light emission in solution with $\lambda_{\text{em}}=448$ nm for the 1,4- and $\lambda_{\text{em}}=426$ nm for the 1,3-copolymer. In short, these copolymers can serve as good model compounds for the synthesis of new and versatile isoindole containing light emitting polymers.

4. Possible applications of the results

1-amino-5-isocyanonaphthalene and its derivatives provide an excellent alternative for fluorescent dyes used nowadays in molecular biology, fluorescent microscopy. Their simple synthesis, high quantum yields, great sensitivity to the polarity can be also advantageous in the preparation of organic photovoltaic devices.

Fluorescent polymers synthesized can serve an excellent base for the construction of polymer-based light emitting diodes. The emitted blue light can be converted to any color of the visible spectrum by effective dyes. Furthermore, color of the emitted light can be influenced by complex formation or self-assembly in the case of compounds capable of that.

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Ph.D. List of Publications

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List of publications related to the dissertation

Hungarian scientific article(s) in Hungarian journal(s) (3)

1. **Rácz D.**, Nagy M., Zsuga M., Kéki S.: Szolvatokróm polimerek.
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4. Nagy, M., **Rácz, D.**, Lázár, L., Purgel, M., Dítői, T., Zsuga, M., Kéki, S.: Solvatochromic Study of Highly Fluorescent Alkylated Isocyanonaphthalenes, Their π -Stacking, Hydrogen-Bonding Complexation, and Quenching with Pyridine.
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14. Lázár, L., Nagy, M., **Rácz, D.**, Zsuga, M., Kéki, S.: Synthesis of fluorescent fluorene-isindole-containing mono- and oligomers.
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DOI: <http://dx.doi.org/10.1016/j.tet.2014.04.018>
IF:2.817 (2013)

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