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SHORT COMMUNICATION

Naphthyridine Derivatives as a Model System for Potential Lithium–Sulfur Energy-Storage Applications

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Naphthyridines have been identified as structural elements in sulfurized polyacrylonitrile, which is a common electrode material in lithium–sulfur batteries. Some dibenzonaphthyridine derivatives with a fused dithiolo moiety were prepared as model compounds for battery studies. These heterocyclic systems were prepared via the corresponding diphenyldi-

Introduction

In the past decade, great efforts went into the development of high-density lithium battery storage systems.^[1] To increase the battery capacity compared to commercially available lithium-ion batteries, a suitable cathode material needs to be developed.^[2] A promising candidate for a highdensity cathode material is sulfur, because of its high theoretical energy density of 2600 Wh kg⁻¹ and its general abundance.^[3,4] The major drawback of elemental sulfur for the application in energy-storage systems lays in its insulating nature, which makes conductive additives necessary, but this also lowers the energy density of the final device.^[5]

Several concepts were elaborated over the past years to overcome this drawback.^[4,6] The elegant concept published by Wang et al. in 2002 embedded sulfur inside a conducting polymeric matrix by pyrolizing polyacrylonitrile (PAN) with elemental sulfur.^[7] The resulting composite, referred to as sulfurized polyacrylonitrile (SPAN, Figure 1), was analyzed over the past years, and a covalent bond between sulfur and a polymeric, conducting backbone was found.^[8,9]

Owing to the insoluble nature of the polymer, only fragments of the polymeric structure could be elucidated. To obtain further insight into that structure, we identified the 9,10-dithiolonaphthyridine moiety as a structural feature of the polymer and elaborated the synthesis of a model com-

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carbamide intermediate. Followed by naphthyridione forma-

tion, stepwise installation of the dithiolane subunit occurred

in a straightforward manner. In the solid state, the heteroaro-

matic system is completely planar and was thoroughly char-

acterized. Initial battery cycling tests indicated a potential

use of such structural motifs in sulfur-lithium systems.

Figure 1. Postulated polymeric structure of SPAN.^[10]

pound exhibiting this structural feature (Scheme 1). The analytical data of **1a** allow structural and electronic comparison of SPAN with the model compound.



Scheme 1. Elaborated structure for the model compound.

Results and Discussion

As the starting compound for our synthesis towards dithiolo dibenzonaphthyridine derivative 1, we selected dibenzonaphthyridione 2, as through benzannulation better solubility properties and less potential side reactions were anticipated. The naphthyridine moiety of 2 was constructed within three steps by following modified procedures known in the literature. We decided to construct parent compound 2a (Figure 2) and dibromo derivative 2b, which opened up potential applications.

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Figure 2. Selected compound as central intermediate for our synthesis.

Phenyl isothiocyanate derivative **3** was converted into symmetric N,N'-diphenylthiourea derivative **4** in up to 90% yield by simple heating with substituted or unsubstituted aniline derivative **5** in ethyl acetate for 1 h (Scheme 2).^[11] The formation of N,N'-diphenylcarbodiimide derivatives **6** was performed by following the protocol of Ali, and this provided the desired products in good yields up to 75%.^[12] The addition of diethyl malonate at the central carbon atom yielded condensation product malonate derivative **7** in good yields up to 73%. The twofold Conrad–Limpach synthesis in diphenyl ether resulted in the formation of 5H,6Hdibenzo[b,g]-1,8-naphthyrine-11,12-dione derivative **2** in yields up to 89%.^[13]



Scheme 2. Synthetic pathway for the synthesis of dithiolo naphthyridines **1**.

Owing to the low solubility and reactivity of naphthyridione derivatives **2**, it was not possible to accomplish the direct transformation towards desired compound **1** (Scheme 3).



Scheme 3. Direct transformation of naphthyridione **2** into disulfide derivative **1**.

To overcome the poor reactivity of **2**, we chlorinated the molecule in the 9-position by using an excess amount of PCl₅ in boiling POCl₃. Resulting chloronaphthyridone derivative **8** was isolated in excellent yields up to 96%.

The slightly improved solubility of **2** in nonpolar solvents offered us the possibility for further transformations. We installed the first sulfur atom for the target molecule by nucleophilic substitution by using benzylthiol, which resulted in 6H-12-(benzylsulfanyl)dibenzo[b,g]-1,8-naphthyridin-11-one (**9**) in good yields up to 77%. The final product, dibenzo[b,g]-1,2-dithiolo[3,4,5-d,e]-1,8-naphthyridine (**1**), was synthesized by a thionation reaction under reflux conditions in chlorobenzene by using a mixture of P₄S₁₀ and Na₂CO₃.

After the successful synthesis of desired model compound **1a**, we extended our synthetic approach towards dibromo-substituted naphthyridione derivative **1b**. For further use of the target structure, for example, polymeric energy-storage structures, the halide substituent offers the possibility for additional functionalization mostly on the basis of transition-metal catalysis.^[14] To generate a compound even more similar to SPAN, it is possible to subject **1b** to polymerizing coupling reactions such as the Yamamoto reaction or Suzuki-type reactions.

Model compound **1a** was investigated by UV/Vis, IR, and NMR spectroscopy, and a suitable single crystal was analyzed by X-ray diffraction. The electrochemical properties of **1a** were investigated by cyclic voltammetry as well as by application of the material in a prototype Li-battery cell system.

The diffraction study of a suitable single crystal by using X-ray diffraction offered us the possibility to determine the length of the S–S bond at 2.07 Å, which is in the range of an average disulfide bond. The polycyclic core of the molecule is flat, with a small distortion of 2° towards the plane (Figure 3). The average C–C bond inside the molecule has a length of 1.40 Å, which fits the average of a typical aromatic C–C bond.



Figure 3. Molecular structure of **1a** by X-ray diffraction analysis of a suitable single crystal: Top view (left) and side view (right).

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Naphthyridine derivatives **1a**, **8a**, and **9a** were analyzed by UV/Vis absorption spectroscopy (Figure 4). All three derivatives show their strongest absorption band at around 300 nm. Naphthyridone derivatives **8a** and **9a** show a lower degree of resonance stabilization, owing to a blueshift in the absorption band at 450 nm. Dithiolo naphthyridine derivative **1a** displays a fully conjugated polycyclic aromatic system, which appears in the UV/Vis spectrum as four different absorption bands in the 500–620 nm range. The same additional absorption behavior in the visible spectrum can be found in the absorption spectrum of SPAN, which is indicative of the striking similarity of the fully conjugated backbone structure.^[15]



Figure 4. UV/Vis absorption spectra of naphthyridine derivatives 1a, 8a, and 9a.

Analysis of final compound **1a** by IR transmission spectroscopy shows two characteristic absorption bands for the disulfide structure at $\tilde{v} = 514.1$ for v(S–S) and 672.7 cm⁻¹ for v(C–S). Three absorption bands at $\tilde{v} = 1514.1$; 1536.5, and 1552.1 cm⁻¹ correspond to a thioamide moiety, in which the sulfur atom has the same oxidation state as that in sulfides. Compared to SPAN, it is plausible that inside a statistical polymeric structure, these bands superimpose and form a broad intense absorption band, as observed by several other groups.^[9,10,15,16]

Owing to the sufficient solubility of **1a** in DMSO, it was possible to record and analyze the solution NMR spectra of the product by using 1D and 2D NMR techniques. The ¹³C NMR spectroscopy data of the product revealed a signal at $\delta = 152.3$ ppm, which was assigned to carbon atoms in positions 4a and 6a of the aromatic structure. The carbon atoms in positions 11 and 12 were equivocally assigned only by ¹H–¹³C HMBC spectroscopy at $\delta = 161.1$ ppm. By comparing these data with the magic-angle solid-state ¹³C NMR spectroscopy data of SPAN, a broad peak at $\delta =$ 150 ppm with a shoulder at a higher chemical shift represent the consistent equivalent. The quaternary carbon atoms at 5a and 11a could not be resolved within the spectra, owing to the relative low solubility of sulfanyl derivative **1a** and the poor signal intensity for these atoms. The electrochemical properties of naphthyridine derivae **1a** were investigated by cyclic voltammetry (CV, Fige 5). The experiments were conducted at room tempera-

tive **1a** were investigated by cyclic voltammetry (CV, Figure 5). The experiments were conducted at room temperature in DMF solutions containing tetra-*n*-butylammonium tetrafluoroborate (0.1 M) as a supporting electrolyte. A glassy carbon electrode tip (d = 2 mm) was used as the working electrode and a glassy carbon rod was employed as the counter electrode. The data was measured against Ag/AgCl in a saturated LiCl/EtOH solution and was recorded at a scan rate of 200 mV s⁻¹. Additionally, peak potentials were referenced against ferrocene. As expected, dithiolo derivative **1a** shows two reversible reduction/oxidation waves at -354 and -594 mV versus Ag/AgCl.



Figure 5. Cyclic voltammogram of 1a in 0.1 M Bu₄NBF₄/DMF vs. satd. Ag/AgCl, sweep rate 200 mV s⁻¹.

Naphthyridine derivative **1a** was applied to a battery test cell setup. The cathode consisted of 70% **1a**, 15% carbon black, and 15% binder. LiPF₆ (1 M) was dissolved in a mixture of ethylene carbonate, diethyl carbonate, and dimethyl carbonate (2:2:1) as supporting electrolyte. As anode material, lithium metal was chosen. The setup was charged and discharged with a C rate of C/10 for 20 cycles. Figures 6 and 7 show the charge and discharge profiles of the first five charging/discharging cycles. The reversible redox reaction of the disulfide bond can be found at a cell potential of 2.25 V, which is consistent with CV analysis.^[17] The decreasing cell capacity can be rationalized with the low, but still existing, solubility of the active material in the supporting electrolyte.

Moreover, upon reduction of 1, dramatically enhanced solubility in the electrolyte system was expected. With every cycle, a little amount of the active material migrates and cannot be used for subsequent cycles. Although the cell capacity fades, it is possible to charge and discharge a battery setup consisting of the model system for several cycles, which proves its similarity to SPAN (Figure 8). One of the future projects to overcome the capacity fading due to solubility is the polymerization of substituted naphthyridine derivative **1b**.

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Figure 6. Charging profile of the first five charging cycles.



Figure 7. Discharge profile of the first five discharge cycles.



Figure 8. Specific capacity for the model compound 1a charged at C/10.

Conclusions

We developed a synthetic strategy for the synthesis of 4,5-dithiolo-1,8-naphthyridine derivatives 1 by using dibenzonaphthyridione-based compounds 2 as starting materials. Resulting compound 1a was fully characterized and investigated for its electrochemical properties. The cell potential during charge and discharge cycles was comparable to that of SPAN. As a potential building block for polymer synthesis, we extended our synthetic approach towards substituted dibenzonaphthyridone derivatives, which resulted in compound 1b. This molecule can be applied to Suzuki cross-coupling and Yamamoto coupling reactions to overcome the solubility drawback of the single naphthyridine moiety.

Experimental Section

Supporting Information (see footnote on the first page of this article): General procedures, characterization data, and copies of the ¹H NMR and ¹³C NMR spectra

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The structure of a polyacrylonitrile-derived sulfur composite is elucidated by a bottomup approach. New naphthyridine derivatives are synthesized as model systems for analytical comparison. The IR, NMR, and



UV/Vis spectroscopy data indicate a strong correlation between this simple model compound and sulfurized polyacrylonitrile polymer. S. Resch, A.-R. Schneider, R. Beichler, M. B. M. Spera, J. Fanous, D. Schollmeyer, S. R. Waldvogel* 1–6

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