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Technical Notes

Continuous Production of a Near Infrared Absorbing Chromophore

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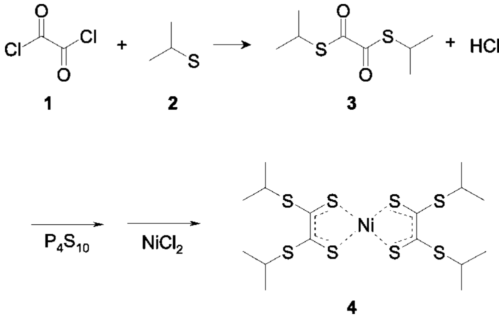
Abstract:

The nickel dithiolene complex-type near-infrared chromophore, nickel bis-(1,2-diisopropylthioethane-1,2-dithiolene), was synthesized in three reaction steps and applied to a near-infrared cutoff filter for PDP TV. A microreactor was employed in the strong exothermic reaction of 2-propanethiol and oxalyl chloride. A 90% yield of *S,S′*-diisopropyl dithiooxalate was obtained with a 75% reduction in solvent usage. Thionation of *S,S′*-diisopropyl dithiooxalate with the use of tetraphosphorus decasulfide and aluminum hydroxide provided a clean dithiolene feed for the next continuous step. The final product was efficiently produced in a microreactor and a tubular reactor in series using nickel chloride solution and dithiolene synthesized from thionation in a batch reactor.

Introduction

The dithiolene complexes of transition metals show intense electronic transition in the near-infrared region with high thermal and photochemical stability. Since the first syntheses of a type of dithiolene were reported in the early 1960s,[1−3] syntheses have continued in the search for a dithiolene complex with a broad absorption range in the near-infrared (near-IR) spectrum.[4−10] The use of dithiolene has received increased attention within various areas such as telecommunication, medicine, semiconductors, and near-IR lasers. [11−13] Another use of chromophores with near-infrared absorption is as an optical filter for plasma display panel television (PDP TV). Near-IR rays that radiate from PDP can cause malfunctions of near-IR remote control devices for home electronic appliances. Accordingly, an optical filter is provided on the front surface of PDPs to reduce the transmittance of near-IR rays of 850−1100 nm.

Scheme 1. **Synthesis of nickel bis-(1,2-diisopropylthioethane-1,2-dithiolene)**



The reaction scheme for nickel dithiolene complex is shown in Scheme 1. In this study, microreaction technology was applied to the highly toxic and exothermic reaction of 2-propanethiol and oxalyl chloride to produce the intermediate of a near-IR absorption chromophore. Microchannels with a high surface-to-volume ratio can improve the rate of heat and mass transfer so that the reaction can be operated isothermally and also provide safe operation with toxic chemicals.[14,15] The second thionation step generally has a low yield and a high content of impurities, which make separation difficult and prevent the crystallization of a final product. Optimization of the thionation step is also studied for the synthesis of the nickel dithiolene complex.

Experimental Section

All reagents and solvents were obtained from Sigma Aldrich Co. and used without further purification. HPLC analyses were performed on reversed-phase columns (Prevail C18, 3 μm, 50 mm × 4.6 mm column) with UV detection at 254 nm using a gradient system with elution from 30% acetonitrile to 100% over 20 min at a flow rate of 0.5 mL/min. ^{1}H NMR spectra were recorded on a 500 MHz spectrometer. Absorption spectra were obtained using a UV−vis spectrophotometer (Shimadzu UV-2450). HPLC analysis results are described as area % (AP).

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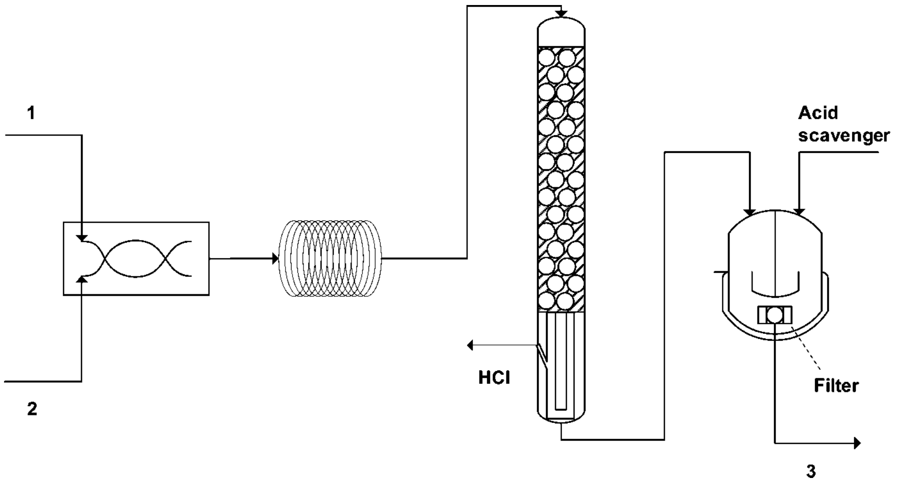

Figure 1. **Experimental setup.**

Preparation of Nickel Bis-(1,2-diisopropylthioethane-1,2-dithiolene) in a Batch Reactor. 2- Propanethiol (0.60 mol) and pyridine (0.60 mol) were mixed in dry carbon tetrachloride (400 mL) and cooled to −10 °C. Oxalyl chloride (0.30 mol) was then added dropwise to the 2-propanethiol pyridine mixture solution (30 mL) for 1 h. The reaction mixture was stirred for 2 h at room temperature. This reaction step is highly exothermic; therefore, the amount of solvent, the starting temperature, and the feeding rate of oxalyl chloride described above were carefully determined by trial and error to minimize the process time at its maximum conversion. When the rate of heat generation exceeded the rate of cooling, either due to a high starting temperature or due to a high feeding rate with a small amount of solvent, an increase in temperature was observed. This led to a faster evaporation of the reactants and resulted in the loss of the overall yield. The boiling temperatures of the two reactants, 2-propanethiol and oxalyl chloride, are 57 and 63.5 °C, respectively. Pyridine hydrochloride salt and the remaining nickel chloride were washed with water. After evaporating the 1,4-dioxane from the resulting solution, *S*,*S*′-diisopropyl dithiooxalate was obtained in 85% yield. Tetraphosphorus decasulfide (0.24 mol) and *S*,*S*′-diisopropyl dithiooxalate (0.26 mol) were then mixed in 1,4-dioxane (425 mL) and refluxed for 3 h at 120 °C under a nitrogen atmosphere. The resulting solution was cooled to room temperature. Nickel chloride hexahydrate (0.15 mol) in 250 mL of water was then added to the batch resultant of thionation and refluxed for 3 h at 120 °C. The product was isolated by the following workup procedure. After 1,4-dioxane was evaporated from the resulting solution, the crude residue was dissolved in chloroform (500 mL). The nickel chloride in the residue was washed with water. After the chloroform was evaporated, the *S*,*S*′-diisopropyl dithiooxalate was crystallized within the methanol. The final yield was 14%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.13 (septet, 4H, $J = 6.71$ Hz), 1.50 (d, 24H, $J = 6.71$ Hz).

Preparation of *S*,*S*′-Diisopropyl Dithiooxalate in a Microreactor. Two HPLC pumps were used to feed the two reactants with a total flow rate above 1.842 mL/min. One feed was 2-propanethiol (1.97 mol). The other feed consisted of oxalyl chloride (0.89 mol) in carbon tetrachloride (105 mL). The two feeds were pumped at the same flow rate (0.92 mL/min) such that they mixed in a microreactor (HPIMM with Hasteloy high pressure mixer inlays, channel width 45 μm, Institut für Mikrotechnik Mainz GmbH, Germany). The reaction mixture was passed through the extension tube (o.d. 3.18 mm, 30 m long) and discharged into a packed bed column (0.850 bar). HCl gas was removed from the packed bed outlet as shown in Figure 1, and the product flowed into a continuously stirred tank reactor where the remaining HCl was removed by the feeding of a pyridine solution (1.24 mol pyridine in 105 mL of carbon tetrachloride) at a flow rate of 1 mL/min. The product solution was then transferred through an in-line filter into a receiving vessel using a peristaltic pump, and the precipitated pyridine-HCl salt was separated from the product. *S*,*S*′-Diisopropyl dithiooxalate was obtained in 95% yield (AP 95%). ^{1}H NMR (500 MHz) δ: 3.70 (septet, 2H, $J = 6.90$ Hz,) 1.38 (d, 12H, $J = 6.90$ Hz).

Preparation of Nickel Bis-(1,2-diisopropylthioethane-1,2-dithiolene). Tetraphosphorus decasulfide (0.37 mol) and aluminum hydroxide (0.20 mol) were ground in a ball mill for 6 h. A fine homogeneous powder was obtained. *S*,*S*′-Diisopropyl dithiooxalate (0.4 mol) was then mixed in 1,4-dioxane (718 mL) with the fine homogeneous powder and refluxed for 3 h at 120 °C under a nitrogen atmosphere. The resulting solution was cooled to room temperature, and unreacted tetraphosphorus decasulfide was filtered.

Nickel chloride hexahydrate solution (0.6 M) and the filtrate of the thionation reaction were fed into the micromixer (CPIMM-V2-1000, Institut für Mikrotechnik Mainz GmbH, Germany) at flow rates of 1 and 3 mL/min, respectively. The reaction mixture was then introduced into a tubular reactor (o.d. 3.175 mm) for 1 h in an oil bath at 80 °C. The product was isolated by the same procedure as the batch described above. The final yield was 35% (AP 93.47%). The near-infrared spectra of **4** was measured in 2-butanone (Figure 2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.13 (septet, 4H, $J = 6.71$ Hz), 1.50 (d, 24H, $J = 6.71$ Hz).

Results and Discussion

Continuous Production of *S*,*S*′-Diisopropyl Dithiooxalate Using a Microreactor. The reaction of 2-propanethiol and oxalyl chloride is an equilibrium reaction. The simultaneous removal of hydrogen chloride is considered an effective tool to promote *S*,*S*′-diisopropyl dithiooxalate synthesis. In the case

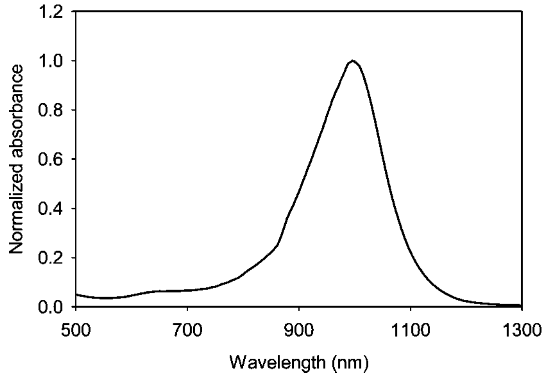

Figure 2. **Near-IR absorption spectra of 4.**

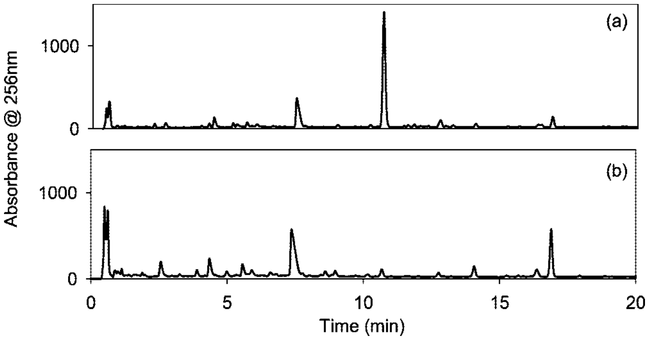

Figure 3. **Thionation without aluminium hydroxide. (a) HPLC analysis taken 30 min after batch start-up (b) HPLC analysis taken 2 h after batch start-up.**

of the batch reaction, an acid scavenger like pyridine is used to remove the free hydrogen chloride. The reaction shows vigorous exothermic behavior, so the reactant, oxalyl chloride is added dropwise at a low temperature; otherwise, the reaction heat can cause the reactants to evaporate into gases. When the reaction is conducted with a microreactor in continuous mode, the large surface to volume ratio provides excellent heat transfer and improves the mixing of the reactants. Thus, the reaction was carried out at room temperature with a microreactor while the batch reaction should keep the starting temperature below −10 °C to avoid the evaporation of reactants. The reaction time was reduced from 4 h in the batch reactor to 40 min in the microreactor. The chemical equilibrium conversion of 98% was estimated using Aspen Plus, release 10.2, with UNIQUAC parameters. The continuous microreactor shows 95% yield of *S,S′*-diisopropyl dithiooxalate, while the batch reactor shows 85% conversion. In the continuous microsystem, the acid scavenger, pyridine, could not be used since the pyridine salt formation could plug the microreactor channels. However, the hydrogen chloride was effectively removed in the gas phase by reduced pressure conditions in a packed bed column right after the reaction was complete at the extension loop, as shown in Figure 1. The microreactor reduced solvent usage by up to 75% since the heat of reaction was removed efficiently in the closed system as discussed above. Further reduction of solvent usage makes the product precipitate during the reaction. In the batch reaction, the reactants are volatile, so an excess amount of solvent is required to prevent evaporation of 2-propanethiol or oxalyl chloride from the reaction mixture.

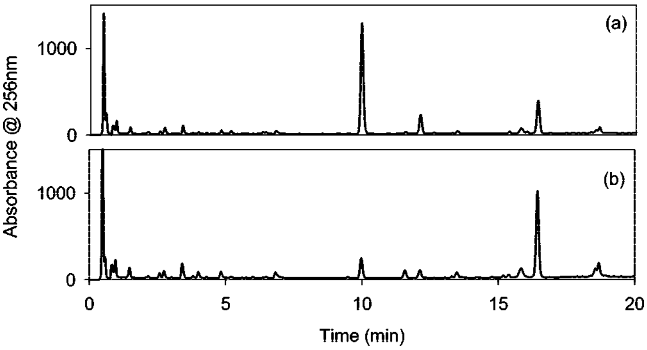

Figure 4. **Thionation with aluminium hydroxide. (a) HPLC analysis taken 30 min after batch start-up (b) HPLC analysis taken 2 h after batch start-up.**

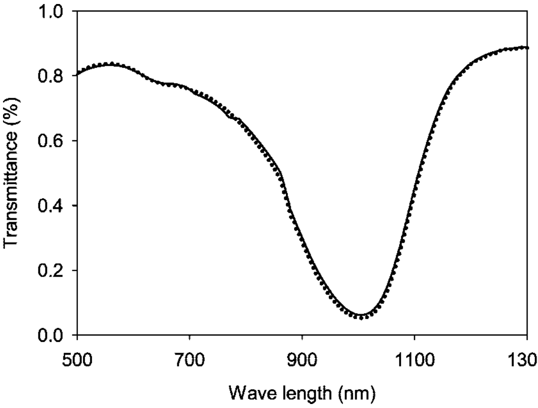

Figure 5. **Transmittance spectra of the near-IR optical filter. Durability test at 65 °C after 0 h (· · ·). Durability test at 65 °C after 500 h (—).**

Synthesis of Near-IR Absorption Chromophore from *S,S′*-Diisopropyl Dithiooxalate. Thionation of ketones to thioketones in *S,S′*-diisopropyl dithiooxalate was carried out using tetraphosphorus decasulfide. Since tetraphosphorus decasulfide is insoluble in most organic solvents, including 1,4-dioxane used in this experiment, the thionation reaction was performed in batch mode. The reactant was eluted at 10.7 min. As thionation proceeded, the product was formed in low yield at the retention time of 16.8 min. The byproduct was formed at the retention time of 7.4 min as shown in Figure 3a after 30 min, and the amount increased after 2 h (Figure 3b). The byproduct at the retention time of 7.4 min could not be removed from the reaction mixture.

To increase the reaction yield, thionation was carried out by refluxing the mixture of tetraphosphorus decasulfide with aluminum hydroxide. The yield of the thioketones was greater with the ground mixture of tetraphosphorus decasulfide and aluminum oxide than that with tetraphosphorus decasulfide alone.[16] Aluminum hydroxide also showed a scavenging action on impurities generated in the thionation reaction. Figure 4 clearly shows that the byproduct peak at retention time of 7.4 min disappeared from the mixture when aluminum hydroxide was used.

Nickel bis-(1,2-diisopropylthioethane-1,2-dithiolene) was produced continuously using a microreactor and a tubular reactor in series. The use of a continuous reaction has many

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advantages over a batch reaction. In particular, efficient temperature control in the microreactor and the tubular reactor prevent byproduct formation. The synthesized near-infrared-absorbing chromophore was subsequently bar-coated for durability testing. The minimum transmittance peak in the infrared region at 1000 nm is shown in Figure 5. Deterioration of the chromophore's transmittance in the near-infrared region at 1000 nm was less than 1% of its initial transmittance after 500 h in the high temperature test at 65 °C.

Conclusions

In this study, continuous production of *S*,*S*′-diisopropyl dithiooxalate was performed in a microreactor, and a 75% reduction in solvent usage was achieved with a total yield of 95%. Thionation of *S*,*S*′-diisopropyl dithiooxalate with the use of tetraphosphorus decasulfide and aluminum hydroxide provided clean dithiolene product compared to that with tetraphosphorus decasulfide alone. The nickel dithiolene complex was also continuously produced in a microreactor and a tubular reactor in series using nickel chloride solution and dithiolene synthesized from a batch reactor.

The nickel dithiolene complex-type near-infrared chromophore synthesized in this study exhibited strong absorption bands in the 850−1100 nm region and was applied as a near-infrared cutoff filter for PDP TV.

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