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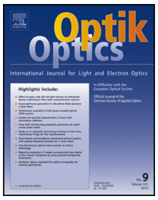

Original research article

Electrical and photoelectrical characterization of organic-inorganic heterostructures based on Ru-N-heterocyclic carbene complexes

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ABSTRACT

1,3-Bis(2-morpholinethyl)benzimidazoliumtrichlorido(η^6-*p*-cymene)-ruthenate(II), **2**, was synthesized and characterized by NMR spectroscopy and micro analysis. The organic-inorganic heterojunctions were fabricated by using n-type Si wafer and a series of Ru-*N*-heterocyclic carbene complexes, **3**–**5**, bearing sterically hindered aryl groups were documented for the first time. The thin films of the complexes are deposited on n-Si substrates using spin coating. Current-voltage (*I*–*V*) measurements of the devices in dark and illuminated environments were analyzed to determine electrical parameters of devices. Furthermore, the photoelectrical properties of the structures were investigated examined using *I*–*V* measurements under a solar simulator. Complexes **3** and **5** showed very low series resistance resulting in high rectification ratios which are promising results for the future electronic and photoelectronic applications.

1. Introduction

In the last decade, *N*-heterocyclic carbene (NHC) ligands have received remarkable attention after Arduengo's discovery on isolable free NHCs [1,2]. This discovery led researchers like Lappert [3], Grubbs [4,5], Herrman [6,7], Nolan [8,9], Cavell [10,11], Çetinkaya [12,13] to use NHCs as a ligand for transition metal complexes. The strong σ-donation-weak π-acceptor ability of NHCs stabilizes many transition metal centres. This spectacular property plays a key role in homogeneous catalysis fields such as hydrosilylation [14], transfer hydrogenation [15,16], olefin metathesis [17,18] and Pd-catalyzed cross-coupling reactions [19,20] catalyzed by metal-NHC complexes [21,22].

Electronic devices made by organic materials [23,24] such as solar cells [25,26], organic thin film transistors [27], Schottky diodes with organic interlayer [28] and organic light emitting diodes [29,30] have been attracted considerable concern for a

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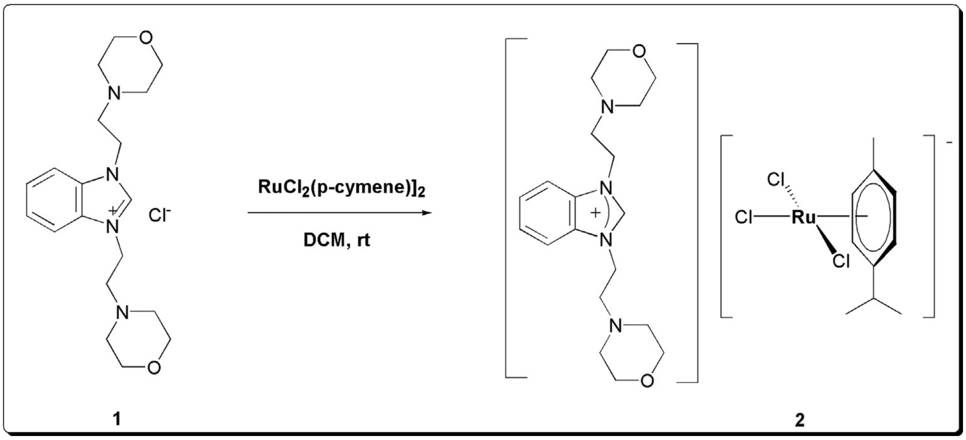

Fig. 1. Synthesis pathway of compound **2**.

few decades because of several advantages such as low cost, easy process and application to flexible substrates etc. Metal-semiconductor (MS) ultimate contacts have been a key issue in the electronic industry for decades. Contact properties such as the barrier height, series resistance and the states of the interface are important factors for continuous control of junction properties. The quality of the junction is determined by barrier height and ideally factor, *n*, which ideally equals to one, however, it deviates from ideal condition because of series resistance and interface states. When a metal is brought to contact with a semiconductor, charge exchange occurs between metal and semiconductor until the Fermi level is aligned. It has been shown that by introducing an organic interlayer between a metal and semiconductor electronic properties of the junction can be controlled [31]. The organic layer treats as a physical barrier through the MS contact, therefore, prevents metal to make direct contact with the inorganic semiconductor. For example, while the contact is biased under photo-illumination, electron-hole pairs are generated by incident photons, and this contributes net current. When electric field is applied to the junction; charges flow towards or through the organic layer. After all, the charge generation causes to change in the Fermi level and the potential barrier at the interface.

Herein, we reported the electrical and photoelectrical characterization of the Ru-NHC complexes based organic-inorganic heterojunctions. To show the usage of complexes for electrical and photoelectrical applications, current-voltage measurements of the devices fabricated using Ru-NHC complexes in the dark and under illumination were investigated. As far as we know, there are not any reports by using this kind of ruthenium-complexes as compound. The results showed that Ru- *N*-heterocyclic carbene complexes, **3**–**5**, bearing sterically hindered aryl groups are candidates for future electronic applications.

2. Experimental procedure

2.1. Materials and methods

Unless stated otherwise, all synthesis procedures were carried out under N_2 atmosphere. Chemicals and solvents were purchased from Sigma-Aldrich Co. (Dorset, UK) and used directly. ^1H NMR and ^{13}C NMR spectra were recorded using a Varian As 400 Merkur spectrometer operating at 400 MHz (^1H), 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. Coupling constants (*J*-values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, bs = broad singlet.

2.2. General method for the preparation of the NHC salts and ruthenium-NHC complexes

1 [21], **3** [13], **4** and **5** [15] were synthesized according to the literature. Complex **2** were synthesized by reaction of 10 mmol NHC ligand with 5 mmol $[RuCl_2(p\text{-cymene}]_2$ in 30 mL DCM. The mixture was stirred for 3 d at room temperature, and then the solution was filtered through celite, followed by crystallizing in DCM: diethyl ether (1:2) at room temperature (Fig. 1). The molecular structure of **2** was elucidated by NMR spectroscopy and micro analyses. The data of **2** are consistent with the literature [13].

2.2.1. 1,3-Bis(2-morpholinethyl)benzimidazoliumtrichlorido(η^6-p-cymene)-ruthenate (II)

m.p: 214–216 °C. Yield: % 60 (0.42 g). $\nu_{(CN)} = 1646\,cm^{-1}$. HRMS (ESI) for $C_{29}H_{43}N_4Cl_2O_2Ru$ $[M-Cl]^+$calcd. 651,1801, found 6,511,775. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.36 [d, *J* = 6.8 Hz, 6H, $p\text{-}CH_3C_6H_4CH(CH_3)_2$], 2.30 [s, 3H, $p\text{-}CH_3C_6H_4CH(CH_3)_2$], 2.56 [bs, 8H, $CH_2CH_2N(C\boldsymbol{H_2}CH_2)_2O$], 2.90 [bs, 4H, $CH_2C\boldsymbol{H_2}N(CH_2CH_2)_2O$], 3.16 [h, *J* = 6.9 Hz, 1H, $p\text{-}CH_3C_6H_4CH(CH_3)_2$], 3.63 [bs, 8H, $CH_2CH_2N(CH_2C\boldsymbol{H_2})_2O$], 4.81 [bs, 4H, $C\boldsymbol{H_2}CH_2N(CH_2CH_2)_2O$], 5.28 and 5.49 [d, *J* = 5.6 Hz, 4H, $p\text{-}CH_3C_6H_4CH(CH_3)_2$],