



# Synthesis of fluorescent fluorene–isoindole-containing mono- and oligomers



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## ABSTRACT

Novel fluorene–isoindole-containing light-emitting mono- and oligomers were prepared. The synthesis of the monomers *N*-(4-bromo-phenyl)-2-(7-bromo-9,9-diethylfluoren-2-yl)-isoindole-1-carboxamide, *N*-(7-bromo-9,9-dibutylfluoren-2-yl)-2-(7-bromo-9,9-dibutylfluoren-2-yl)-isoindole-1-carboxamide, and *N*-[7-bromo-9,9-bis(2-ethylhexyl)-fluoren-2-yl]-2-[7-bromo-9,9-bis(2-ethylhexyl)-fluoren-2-yl]-isoindole-1-carboxamide was carried out by a three-component reaction of *ortho*-phthalaldehyde with the corresponding amine and isocyanide partners. The Ni(0) mediated polymerization reactions of the obtained monomers gave the corresponding mixture of oligomers from two up to twelve repeat units. The optical properties were also studied and it was found that the phenylene-containing oligomer emitted green light in dichloromethane solution, while both difluorene-containing oligomers, under the same conditions, proved to be blue light-emitters with good quantum efficiency.

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## 1. Introduction

The development of organic light-emitting diodes (OLEDs) as base materials of future displays has attained much attention since the first report of electroluminescence from poly(*p*-phenylene vinylene)-based conjugated polymers by Burroughes et al. in 1990.<sup>1</sup> OLED based displays possess several advantages compared to their inorganic counterparts: they are flexible, transparent, light-weight and easily processable at lower temperatures. Blue light-emitting materials are the most important since blue light is easily converted to any other visible color.<sup>2,3</sup> The majority of efficient blue light-emitters contain polyaromatic backbones.<sup>4</sup> Fluorenes are considered important building blocks of polymers, which have the potential to act as both electroactive and photoactive materials.<sup>5–8</sup> The conjugation across the molecule allows for a reduced band gap the energy of which can be easily varied by the electron donating character of its substituents.<sup>9</sup>

The problem with polyfluorenes is that they often show both excimer and aggregate formation, which besides lowering the efficiency of the LEDs also causes a red shift in the emission spectrum.<sup>10</sup> These undesirable phenomena can be overcome in two ways (i) adding large substituents at the nine position of the fluorene unit,<sup>11</sup> (ii) copolymerizing polyfluorene with other fluorescent units.<sup>12</sup> A number of polyfluorenes with different homo- and heteroaromatic comonomers, such as anthracene,<sup>13</sup> carbazole,<sup>14</sup>

oxadiazole,<sup>15</sup> triphenyl-amine,<sup>16</sup> thiophene<sup>17</sup> have been prepared. Interestingly, we could not find any isoindole-containing polyfluorenes in the literature. This is peculiar considering that a number of aryl substituted isoindoles were characterized to show strong fluorescence and electroluminescence in *N,N*-dimethylformamide solution more than 40 years ago by Zweig et al.<sup>18</sup>

Substituted isoindoles, especially *N*-substituted ones, are of more interest because they are more stable than the non-substituted ones.<sup>19</sup> Preparation of phenyl substituted polyisoindoles is reported from dibenzoylbenzenes with anilines, which are highly fluorescent polymers with good thermal stability.<sup>20</sup> Condensation methods offer a simple way to obtain substituted isoindole derivatives. We recently reported the preparation of phenylene-containing polyisoindoles via the catalyst free polycondensation between *ortho*-phthalaldehyde (OPA) and amino-thiophenols.<sup>21</sup>

Zhang et al. recently published a three-component reaction yielding 1-carboxamido-isoindoles via the reaction of OPA, amines, and isocyanides.<sup>22</sup> It is noteworthy that there was no example for the use of an aromatic isocyanide component among the described three-component reactions. It is also important to note that the application of aromatic amine and isocyanide partners in the three-component reaction allows us to combine the 1-carboxamido-isoindole group with other fluorescent aromatic (e.g., phenylene, fluorene) or heteroaromatic (e.g., thiophene, pyridine) groups. Thus, employing bromo-substituted amine and isocyanide partners in the three-component reaction we can obtain a series of new fluorescent polymerizable monomers.

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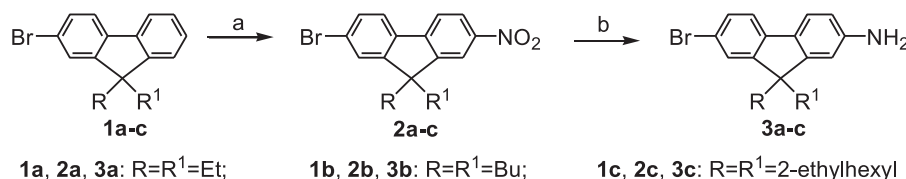
Here, we describe the synthesis of three new fluorene-1-carboxamido-isoindole-containing monomers. We also report the polymerization reactions of the obtained monomers by Yamamoto coupling.<sup>23</sup> Finally, the optical properties of the monomers are compared with those of the obtained oligomers.

## 2. Results and discussion

### 2.1. Synthesis of the monomers **7a–c** and oligomers **8a–c**

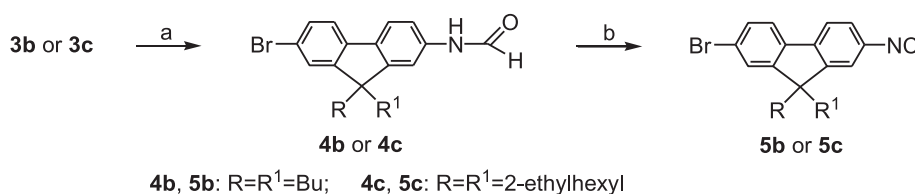
The preparation of the targeted polymerizable fluorene-1-carboxamido-isoindole-containing monomers **7a–c** was planned by the aforementioned three-component reaction.<sup>22</sup> First, the bromo-substituted amine (**3a–c**) and isocyanide (**5a–c**) components were synthesized.

The synthesis of the amines **3a**,<sup>24</sup> **3b**,<sup>25</sup> and **3c**<sup>26</sup> was accomplished by using the same strategy as shown in Scheme 1. The known 2-bromo-9,9-dialkylfluorenes **1a**,<sup>27</sup> **1b**,<sup>28</sup> and **1c**<sup>29</sup> were prepared started from the commercially available 2-bromo-fluorene as reported in the literature.<sup>30</sup> Compounds **1a–c** were nitrated using HNO<sub>3</sub> in the presence of a supported catalyst of SiO<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub><sup>31</sup> to afford the desired 2-bromo-9,9-dialkyl-7-nitrofluorenes **2a**, **2b**,<sup>32</sup> and **2c** with good regioselectivity. Reduction of nitrofluorenes (**2a–c**) by Fe/ammonium chloride<sup>33</sup> gave 7-bromo-9,9-dialkylfluorenyl-2-amines (**3a–c**) in good yields.



**Scheme 1.** Synthesis of the amines **3a–c**. Reagents and conditions: (a) SiO<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt, 10 min, 67% for **2a**, 63% for **2b**, 62% for **2c**; (b) Fe (powder), NH<sub>4</sub>Cl, EtOH/H<sub>2</sub>O (18:5), 85 °C, 2 h, 78% for **3a**, 76% for **3b**, 80% for **3c**.

In order to obtain the aromatic isocyanide partners for the 1-carboxamido-isoindole reactions amines **3b** and **3c** were converted into the isocyanide derivatives **5b** and **5c** by a two-step procedure (Scheme 2). N-Formylation of the amines **3b** and **3c** was carried out by applying the procedure established by Dawane et al.<sup>34</sup> Thus, compounds **3b** and **3c** were treated with 6 equiv of formic acid for 3 h at 70 °C affording the corresponding formamides **4b** and **4c** in excellent yields, respectively. Dehydration of the formamides **4b** and **4c** using phosphoryl chloride and diisopropylamine<sup>35</sup> resulted in the desired isocyanides **5b** and **5c** in high yields.



**Scheme 2.** Synthesis of the isocyanides **5b** and **5c**. Reagents and conditions: (a) HCOOH, 70 °C, 3 h, 91% for **4b**, 97% for **4c**; (b) POCl<sub>3</sub>, DIPA, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C, 1 h, 93% for **5b**, 91% for **5c**.

Next, we attempted to synthesize the target 1-carboxamido-isoindole-containing monomer **7a** using the general procedure described by Zhang et al.<sup>22</sup> Accordingly, a mixture of commercially available OPA (**6**), 1 equiv of amine **3a**, 2 equiv of 4-bromo-phenyl isocyanide (**5a**)<sup>36</sup> and 2 equiv of NaHSO<sub>3</sub> in DMSO/H<sub>2</sub>O (1:1) was

reacted for overnight at room temperature. After 12 h under these conditions, we did not observe any noticeable formation of the desired product **7a**. Prolonging the reaction time still failed to produce any desired product. Addition of acetonitrile in order to increase the solubility of the isocyanide **5a** proved to be also insufficient to obtain **7a**. Next we decided to increase the temperature, and after several attempts at different temperatures we found that the best conversion could be achieved in 4 h at 100 °C, and due to the low solubility of the isocyanide **5a** in the mixture of DMSO/H<sub>2</sub>O (1:1), the addition of 1 part of acetonitrile was also needed. Thus, we obtained the targeted compound **7a**, by employing the optimized conditions, in 65% isolated yield (Scheme 3).

The above established optimized conditions were used for the preparation of isoindoles **7b** and **7c** starting from the amines **3b**, **3c** and isocyanides **5b**, **5c**, respectively, as depicted in Scheme 3. In this case, the moderate to low isolated yields obtained for compounds **7b** and **7c** were the consequence of partial decomposition of the isoindole derivatives **7b** and **7c** during the work-up and purification procedures owing to their low stability in solution, in the presence of air and light (especially in the case of **7c**). We tried to overcome the undesirable decomposition by using neutral aluminum oxide in the purification step instead of silica gel chromatography, but even in these conditions the products (**7b** and **7c**) partially decomposed. It is noteworthy, however that below 0 °C, in the dark and under inert atmosphere, crystalline **7a** and **7b** or **7c** in the form of solid

spume can be stored for several months. Under these conditions we have not observed noticeable decomposition during our investigations.

Thereafter, we explored the possibility to polymerize the obtained monomers (**7a–7c**) via Ni(0) mediated Yamamoto coupling reaction.<sup>23</sup> First, the monomer **7a** dissolved in dry toluene was reacted with a pretreated mixture of Ni(cod)<sub>2</sub>, 2,2'-bipyridine, 1,5-cyclooctadiene, and dry DMF at 85 °C for 3 days under argon atmosphere, in the dark. Purification of the crude product gave a mixture of oligomers **8a** in 60% yield (Scheme 4). According to MALDI-TOF MS spectra the obtained mixture contained a series of

monobrominated and bromine-free linear and cyclic oligomers from two up to twelve repeat units (see Figs. 1S–3S in the Supplementary data). The almost exclusive presence of monobrominated and bromine-free oligomers revealed the occurrence of Ni-mediated hydrolysis of the bromines<sup>37</sup> during the

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