A Diaminoterephthalate-C_{60}-Retinoic Acid Triad as Material for Optoelectronic Applications

Anka Schubert and Jens Christoffers*

Institut für Chemie, Universität Oldenburg, Carl von Ossietzky-Str. 9–11, D-26111 Oldenburg

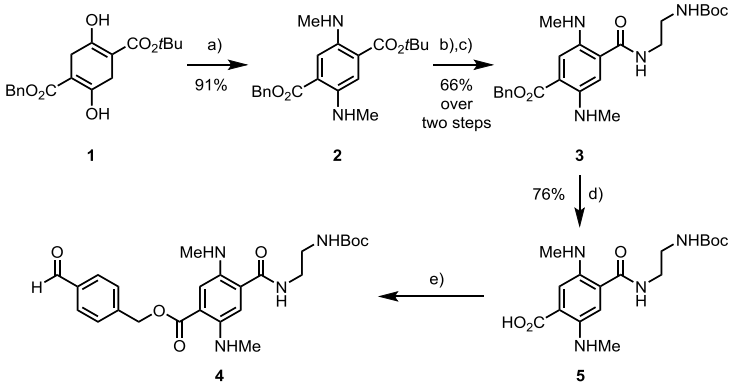
Herein we report a synthesis of a diaminoterephthalate triad functionalized with retinoic acid as well as fullerene C_{60}. This triad should be used as material for optoelectronic applications for example to investigate electron transfer processes by ultrafast laser spectroscopy. Precursor compounds are synthesized by the conversion of succinyl succinate into the diaminoterephthalate by oxidative amination followed by the implementation of the linkers by amidation. To accomplish the synthesis towards the target compound **7** retinoic acid and C_{60} are introduced by amidation and a 1,3-dipolar cycloaddition, respectively.

Introduction

The field of application for diaminoterephthalates has been extended during the last years.[1] They have been previously used as chromophores in a dyad with [60]fullerene.[2] The aim of our current work is to extend the structure of the dyad towards triad **7** including retinoic acid by the substitution of both acid groups of the diaminoterephthalate.[3]

Preparation of Precursor Compounds

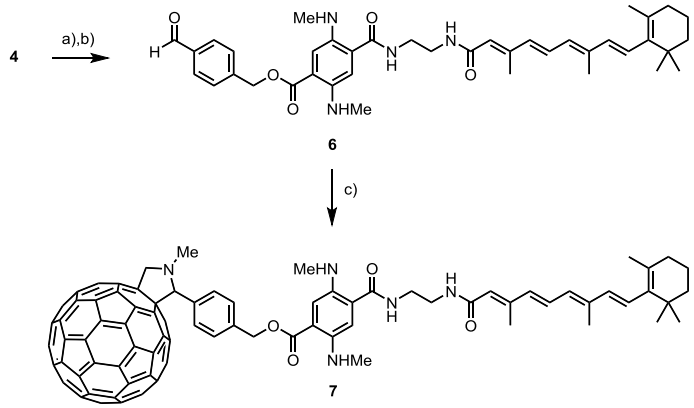
Succinyl succinate **1** is prepared by Dieckmann condensation of benzyl-*tert*-butyl succinate. The oxidative aminolysis is performed by the addition of a large excess of $MeNH_2$ and AcOH to obtain the red and crystalline compound **2**. After the cleavage of the *tert*-butyl ester group by TFA the first linker is implemented by amidation leading to product **3** (orange crystals). This can be converted into compound **5** by the hydrogenolysis of the benzyl ester. The implementation of the second linker group is performed by nucleophilic substitution with a benzaldehyde derivative leading to compound **4**.



Scheme 1. Preparation of the precursor compounds **1-5**.
a) $MeNH_2$, air, toluene, AcOH, reflux, 2 d; b) TFA, DCM, 45°C, 2 h; c) $NH_2(CH_2)_2NHBoc$, HATU, DIPEA, DCM, rt, 18 h; d) Pd/C, THF, H_2; e) *p*(CHO)$C_6H_4CH_2OH$, TBTU, Et_3N, DCM, rt, 18 h.

Preparation of the Target Compound

To prepare target compound **7** the amino group of **4** has to be deprotected first. In a reaction with TFA the TFA-salt of the amine should be obtained. The first effector group (retinoic acid) is introduced by a coupling reaction of the acid and the amine. In a further coupling step the fullerene should be implemented with sarcosine in a 1,3-dipolar cycloaddition.



Scheme 2. Plan for the preparation of target compound **7**. a) TFA / DCM (1:4), 0°C to rt, 16 h; b) retinoic acid, HATU, DIPEA, DCM, rt, 18 h; c) C_{60}, sarcosine, abs. toluene, N_2, reflux, 16 h.

Conclusion

Starting from succinyl succinate **2** with two cleavable ester functions a diaminoterephthalate with two methylamino groups has been prepared. Furthermore the implementation of two different linkers, a protected amine as well as an aldehyde, has been obtained. The final steps to receive the target compound are still ongoing but we are trying hard to accomplish this mission. When product **1** has finally been synthesized its properties should be investigated to find applications for example in the field of optoelectronics.

[1] a) S. Sulmann, M. Wallisch, A. Scholten, J. Christoffers, K.-W. Koch, *Biochemistry* **2016**, *55*, 2567-2577; b) L. Freimuth, J. Christoffers, *Chem. Eur. J.* **2015**, *21*, 8214-8221; c) N. Wache, A. Scholten, T. Klüner, K.-W. Koch, J. Christoffers, *Eur. J. Org. Chem.* **2012**, 5712-5722; d) N. Wache, C. Schröder, K.-W. Koch, J. Christoffers, *ChemBiochem.* **2012**, *13*, 993-998; e) R. Pflantz, J. Christoffers, *Chem. Eur. J.* **2009**, *15*, 2200-2209; f) Y. Zhang, P. Starynowicz, J. Christoffers, *Chem. Eur. J.* **2008**, 3488-3495.

[2] L. Freimuth, C. A. Rozzi, C. Lienau, J. Christoffers, *Synthesis* **2015**, *47*, 1325-1328.

[3] C. A. Rozzi, S. M. Falke, N. Spallanzani, A. Rubio, E. Molinari, D. Brida, M. Maiuri, G. Cerullo, H. Schramm, J. Christoffers, C. Lienau, *Nature Commun.* **2013**, *4*, 1602.