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Faculty of Material Science and Applied Chemistry
of Riga Technical University
Azenes Str. 14/24
LV-1048, Riga, Latvia
Phone: +371 7089249
Fax: +371 7615756
E-mail: ilze@ktf.rtu.lv

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Synthesis and Fluorescent Properties of New N(9) Substituted Push-pull Purines

Andrejs Šišuļins[1], Ērika Bizdēna[2], Ilze Neibolte[3], Māris Turks[4]
[1-4]*Riga Technical University*

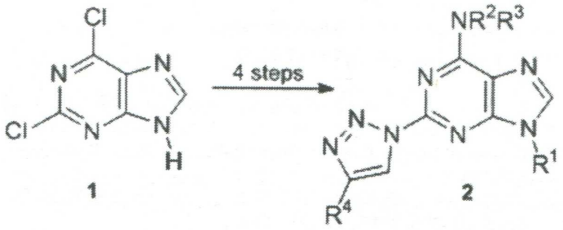
Keywords **– fluorescent purines, push-pull purines, *Click* reactions**

I. Introduction

Push-pull purine derivatives are attractive as sensors and reporters for biological applications. Recently the fluorescent purines as materials for electronic devices have also been developed.[1] We have reported that N6-substituted 2-triazolyl-adenine nucleosides exhibit strong fluorescence with emission maxima around 400 nm and quantum yields up to 53 %.[2]

II. General Conditions

The aim of this research was to synthesize N(9) alkylated purines with electron donor at C(6) and 4-substituted 1,2,3-triazol-1-yl group as acceptor at C(2) – so called push-pull purines – from 2,6-dichloro-*9H*-purine **1**. Target products **2** were obtained in four-step synthesis. Alkylation of 2,6-dichloro-*9H*-purine **1** with a long chain alkyl halogenide or tosyl ester in the presence of NaH provided 9-alkyl-2,6-dichloro-9H-purines. A nucleophilic substitution at C(2) and C(6) with NaN_3 gave 9-alkyl-2,6-diazidopurines. Further, two synthetic routs toward the main product **2** were developed: 1) nucleophilic substitution of azido group with amine at C(6), followed by a *click* reaction of 9-alkyl-6-amino-2-azido-*9H*-purine with terminal alkynes and 2) *click* reaction of 9-alkyl-2,6-diazido-*9H*-purine to afford 9-alkyl-2,6-(bis-triazolyl)-*9H*-purines, followed by S_NAr reaction on C(6)-triazolyl group with amine. *Click* reactions with terminal alkynes proceeded in DMF at 60–90 °C using $CuSO_4 \cdot 5H_2O$ and sodium ascorbate as catalyst generating system. The overall yields are 20–35 % in four steps.



1 **2**

2a: R^1=n-C_5H_{11}; NR^2R^3= —N⟨⟩; R^4= Ph

2b: R^1= ⟨⟩$(CH_2)_5$⟨⟩COOBn; NR^2R^3=—NH_2; R^4= Ph

2c: R^1= n-C_7H_{15}; NR^2R^3=—N⟨⟩; R^4= Ph

2d: R^1= n-C_7H_{15}; NR^2R^3=—N⟨⟩; R^4=n-C_5H_{11}

Scheme 1. Short scheme for synthesis of new N(9) substituted push-pull purines

TABLE 1
Fluorescent Properties of Products (2)

Resulting product 2	λ_{ex} (nm)	λ_{max} (Emis), (nm) in MeOH	Quantum yield (%)*
2a	350	457	43
2b	250	417	43
2c	250	423	52
2d	250	429	48

* Reference: quinine sulphate in 0.1 M H_2SO_4 with QY=53%

III. Summary

In summary, two new synthetic routs were developed for the preparation of N(9) substituted 6-amino-2-triazolylpurines. These compounds (**2**) exhibit bright blue fluorescence with emission maxima ar 417-457 nm and relative quantum yields around 50 %.

References

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