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V-SHAPED FLUOROPHORES - 2,3-BIS(ARYLTHIENYL)QUINOXALINE DERIVATIVES: SYNTHESIS AND PHOTOPHYSICAL PROPERTIES

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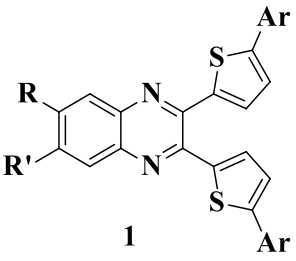
Abstract. Recently, interest in new organic photosensitive materials − derivatives of benzazines, which have found application as components of electronic and optoelectronic devices has increased.[1] V-shaped molecules based on 2,3-disubstituted quinoxalines possess intense fluorescence and are promising for use as luminescent materials.[2]

V-shaped push-pull 2,3-bis(arylthienyl)quinoxalines **1, 2** were obtained by Pd-catalyzed Suzuki cross-coupling reactions. Cyclocondensation of the corresponding diamines and 2,2'-thenil, followed by bromination of thiophene rings at positions 5' by the action of N-bromosuccinimide were carried out for the preparation of 2,3-bis(bromothienyl)derivatives, the key intermediates to quinoxalines **1**. 2,3-Bis(bromothienyl) derivatives of dibenzo and dipyrido annelated analogues, intermediates to derivatives **2**, were developed, for this purpose optimal conditions for the preparation of diamino derivatives and their cyclocondensation products with dibromothenil were found.



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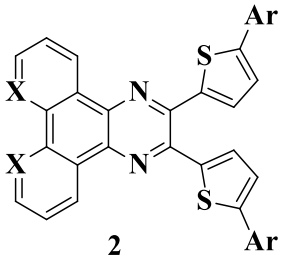

2

1: R = R' = F; R = R' = H; R = CN, R' = H; X = CH, N;

1, 2: Ar = 4-diethylaminophenyl, 4-diphenylaminophenyl, 4-(9*H*-carbazol-9-yl)phenyl, 9-ethyl-9*H*-carbazol-3-yl, 4-pyrene.

Derivatives **1** unsubstituted at positions 6 and 7 demonstrate emission maximum at 480–557 nm in toluene solutions.[3] The presence of substituents in the benzene ring of compounds **1** leads to long-wave shift of emission maximum (λ_{em} = 536–686 nm in DCM) and a decrease in quantum yield. Annelation of benzene rings leads to short-wave shift of emission maximum (λ_{em} = 503–597 nm in DCM for compounds **2** (X = CH)) and a slight increase in quantum yield.[4] Incorporation of strong electron donating aryl substituents into the thiophene ring leads to a significant long-wave shift of the absorption (by 20–70 nm) and emission (by 100–170 nm) maximum. Solvatochromism and protonation effect were studied, the ability of some derivatives to act as colorimetric and luminescent pH sensors was shown. Photophysical properties at two-photon excitation for quinoxaline/phenanthroline V-shaped luminophores were studied, we concluded that studied compounds are promising for 3D microscopy, photodynamic therapy and bioimaging.

References

1. Functionalized benzazines as luminescent materials and components for optoelectronics / E. V. Nosova, S. Achelle, G. N. Lipunova [et al.] // Russ. Chem. Rev. – 2019. – Vol. 88. – P. 1128–1178.

2. Y-shaped novel AIEE active push-pull quinoxaline derivatives displaying acidochromism and use towards white light emission by controlled protonation / S. Gupta, M.D. Milton // Dyes and Pigments. – 2021. – Vol. 195. – Art. 109690.

3. New 2,3-bis(5-arylthiophen-2-yl)quinoxaline derivatives: synthesis and photophysical properties / T. N. Moshkina, E. V. Nosova, G. N. Lipunova [et al.] // Asian J. Org. Chem. – 2018. – Vol. 7. – P. 1080–1084.

4. Synthesis and Photophysical Studies of Novel V-Shaped 2,3-Bis{5-aryl-2-thienyl}(dibenzo[*f*,*h*])quinoxalines / T. N. Moshkina, E. V. Nosova, A. E. Kopotilova [et al.] // Asian J. Org. Chem. – 2020. – Vol. 9. – P. 673–681.

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