

The Synthesis and Evaluation of Squarylium Dyes Based On the NIR Spectra Region

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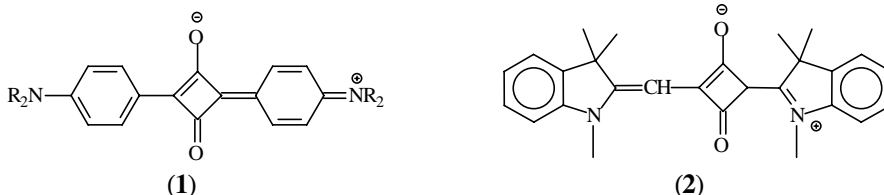
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Abstract

Several squarylium dyes, derived from benzothiazole and indoles, were synthesized as a potential NIR dyes with absorption in the 700-900 nm region. These chromophores were induced much more bathochromic shift in the absorption maximum of the compound relative to the neutral parent squarylium dyes which we were described before. The squaryliums offer a convenient way of linking the dye to functional substrates and may be an advantage to be potential chromophores for NIR-absorbing, NIR-Cut-off filter, PDT(Photo Dynamic Therapy) materials.

1. Introduction

Thus one can consider the 1,3-squarylium dyes to be formed by linking two donor acceptor-chromophores in a cross-conjugated manner by sharing the same electron acceptor unit. The most important 1,3-squarylium dyes are those with electron donor end groups based on heterocyclic residues [e.g. (2)], or arylamines [e.g. (1)], and both types may be symmetrical or unsymmetrical, depending on whether or not the two end groups are the same. These systems give absorption bands generally in the range ca. 650-800 nm, although examples are known which absorb as far as 900 nm, and with extinction coefficients ca. 100,000-300,000 $\text{l mol}^{-1}\text{cm}^{-1}$.

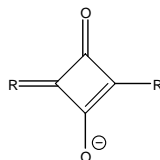


2. Experiment and Discussion

General procedure for the synthesis of symmetric 1,3-bis(heteroaryl)-squaraines:

Squaric acid was refluxed in a mixture of 1-butanol and toluene, removing the water formed azeotropically with

a Dean-Stark trap. After 1 hour, the appropriate heterocyclic compound was added and the reaction mixture was refluxed for 4 hrs and the reaction mixture was cooled to room temperature and the solvent removed on a rotary evaporator. The residue was recrystallized from 1-butanol and dried in an oven at 50C.



Compound (R)	λ_{\max} (nm) in Dichloromethane	Compound (R)	λ_{\max} (nm) in Dichloromethane
	660		640
	670/730		670/790
	666/700		650/800
	640		650/800

3. Conclusion

The several 1,3-bis(heteroaryl)-squaraines derived from indoline and benzothiazole derivatives were synthesized as potential near-infrared dyes with absorption in the 700-800 nm region. These dyes show interesting photophysical properties and may be used in bio-molecular probe and photosensitive sensor.

4. References

1. B. Patrick, M. V. George, P. V. Kamat, S. Das, and K. G. Thomas. *J. Chem. Soc. Faraday Trans.*, **88**, 671 (1992).
2. G. Dilek, E. U. Akkaya, *Tetrahedron Lett*, **41**, 3721-3724 (2000).
3. H. Nakazumi, C. L. Colyer, K. Kaihara, S. Yagi and Y. Hyodo, *Chem Lett*, **32**, 804-805 (2003).
4. S. H. Kim, S. H. Hwang, J. J. Kim, C. M. Yoon, S. R. Keum, *Dyes Pigments*, **37**, 145 (1998).
5. G. L. Ingig, *Recent Res. Dev., Pure Appl. Chem.*, **3**, 9, (1999).