

Bithiophene azo dyes bearing thiazole, benzothiazole and thiadiazole heterocycles: synthesis and comparative study of their photochromic properties

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Although a large variety of diarylazo compounds are used in the design of optical materials, only a few reports concerning the photoisomerization of heterocyclic azo dyes can be found in the literature. In the last years our group reported for the first time the synthesis and characterization of heterocyclic azo dyes bearing thiophene and pyrrole moieties as thermally stable conducting materials, solvatochromic probes and nonlinear optical systems. The E/Z isomerizable N=N double bond within a conducting chain can work as molecular switch, making these (hetero)aryl azo systems promising candidates as photochromic materials [1-6]. As part of our continuing interest in heterocyclic azo dyes for optical applications we report here the synthesis of dithiazole azo dyes **4** using as coupling components bithiophene and thiadiazolyldiazonium salts and the comparative study of the photochromic properties of 4 classes of bithiophene azo dyes **1-4**. This study reveals that the kinetics of the E-Z transformation of these systems is strongly influenced by the electronic nature of the heterocyclic diazene moiety as well as its position on the bithiophene system. Moreover, for benzothiazole **3** and thiadiazole **4** azo dyes the switching between the two photoisomers can be performed in 3 seconds with a significant conversion of the *trans*-isomer to the thermal unstable *cis*-isomer (19-21%) showing that they could be used as efficient photochromic materials.

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- [1] Coelho, P. J.; Castro, M. C. R.; Fonseca, A. M. C.; Raposo, M.M.M. *Dyes Pigments* **2012**, *92*, 745.
- [2] Raposo, M. M. M.; Castro, M. C. R.; Schellenberg, P.; Fonseca, A. M. C.; Belsley, M. *Tetrahedron* **2011**, *67*, 5189.
- [3] Raposo, M. M. M.; Fonseca, A. M. C.; Castro, M. C. R.; Belsley, M.; Cardoso, M. F. S.; Carvalho, L. M.; Coelho, P. J. *Dyes Pigments* **2011**, *91*, 62.
- [4] Raposo, M. M. M.; Castro, M. C. R.; Belsley, M.; Fonseca, A. M. C. *Dyes Pigments* **2011**, *91*, 454.
- [5] Coelho, P. J.; Carvalho, L. M.; Moura, J. C. V. P.; Raposo, M. M. M. *Dyes Pigments* **2009**, *82*, 130.
- [6] Coelho, P. J.; Carvalho, L. M.; Fonseca, A. M. C.; Raposo, M. M. M. *Tetrahedron Lett* **2006**, *47*, 3711.