

Synthesis and characterization of four novel 1,3-azole based push-pull heterocyclic systems

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Abstract:

Benz[X]azole derivatives are interesting compounds due to their diverse biological activities¹ and interesting optical properties.² The benzothiazole, benzimidazole and benzoxazole heterocycles are heteroaromatic electron deficient moieties that act as both acceptor groups and π -conjugated spacers with auxiliary electron withdrawing ability.^{2,3} Moreover, benzimidazole derivatives offers the possibility of substitution on the nitrogen atom for further tuning of their optical and electronic properties.

Recently we have reported the synthesis and evaluation of the electronic, thermal and optical properties of a large number of series of benz[X]azole derivatives functionalized with different π -spacers having in mind their application as optical chemosensors, nonlinear optical and photochromic materials, and emissive organic components for OLEDs.²

In continuation of the work developed in our research group, we report in this communication the synthesis, the characterization and the evaluation of the optical properties of four novel 1-(4-thiophene-2-yl)phenyl-1*H*-pyrrole derivatives functionalized with different benz[X]azole moieties (benzothiazole, benzimidazole and benzoxazole). The results showed that the optical properties could be readily tuned by changing the electronic nature of the azole ring, or even by introduction of a strong acceptor group.

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References

1. (a) Boiani, M.; Gonzalez, M., Imidazole and benzimidazole derivatives as chemotherapeutic agents.

Mini-Rev. Med. Chem. **2005**, 5 (4), 409-424; (b) Keri, R. S.; Patil, M. R.; Patil, S. A.; Budagumpi, S., A comprehensive review in current developments of benzothiazole-based molecules in medicinal chemistry. *Eur. J. Med. Chem.* **2015**, 89 (Supplement C), 207-251.

2. (a) Costa, S. P. G.; Batista, R. M. F.; Cardoso, P.; Belsley, M.; Raposo, M. M. M., 2-Arylthienyl-substituted 1,3-benzothiazoles as new nonlinear optical chromophores. *Eur. J. Org. Chem.* **2006**, 3938-3946; (b) Batista, R. M. F.; Costa, S. P. G.; Belsley, M.; Raposo, M. M. M., Synthesis and second-order nonlinear optical properties of new chromophores containing benzimidazole, thiophene, and pyrrole heterocycles. *Tetrahedron* **2007**, 63 (39), 9842-9849; (c) Batista, R. M. F.; Costa, S. P. G.; Malheiro, E. L.; Belsley, M.; Raposo, M. M. M., Synthesis and characterization of new thienylpyrrolyl-benzothiazoles as efficient and thermally stable nonlinear optical chromophores. *Tetrahedron* **2007**, 63 (20), 4258-4265; (d) Batista, R. M. F.; Ferreira, R. C. M.; Raposo, M. M. M.; Costa, S. P. G., Novel optical chemosensors for anions and cations based on an amino acid core functionalised with benzimidazoles. *Tetrahedron* **2012**, 68 (36), 7322-7330; (e) Pina, J.; Seixas de Melo J. S.; Batista, R. M. F.; Costa, S. P. G.; Raposo, M. M. M. Triphenylamine-benzimidazole derivatives: synthesis, excited-state characterization and DFT studies. *J. Org. Chem.* **2013**, 78 (22), 11389-11395; e) Castro, M. C. R.; Belsley, M.; Raposo, M. M. M., Push-pull second harmonic generation chromophores bearing pyrrole and thiazole heterocycles functionalized with several acceptor moieties: syntheses and characterization. *Dyes Pigments* **2016**, 128, 89-95; f) Garcia-Amorós, J.; Castro, M. C. R.; Coelho, P.; Raposo, M. M. M.; Velasco, D. Fastest non-ionic azo dyes and transfer of their thermal isomerisation kinetics into liquid-crystalline materials. *Chem. Commun.* **2016**, 52 (29), 5132-5135.
3. Revuelta, J.; Machetti, F.; Cicchi, S., Five-membered heterocycles: 1,3-azoles. In *Modern Heterocyclic Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA: 2011; pp 809-923.