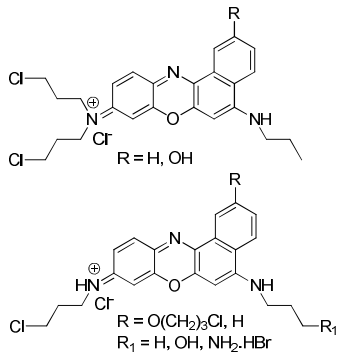
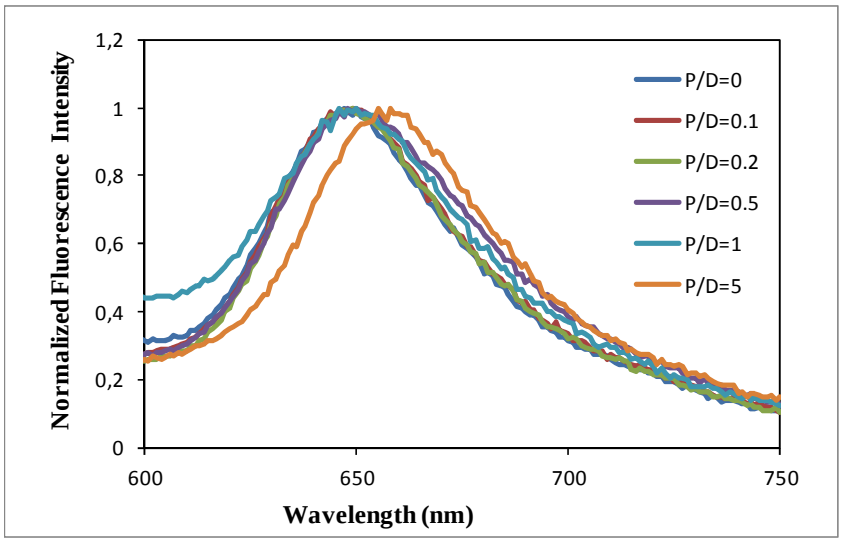
DNA fluorescence probes based on side-chain chlorinated benzo[*a*]phenoxazinium chlorides

B. R. Raju[a], A. D. G. Firmino[b], M. S. T. Gonçalves[b], P. J. G. Coutinho[a]
[a]*Centro de Física and* [b]*Centro de Química, Universidade do Minho,*
Campus de Gualtar, 4710-057 Braga, Portugal
ex2927@fisica.uminho.pt

Nile Blue, a benzo[*a*]phenoxazinium dye, has been reported as DNA probe,[1] and was considered a good intercalator of DNA double helix.[2] Mitra and collaborators clearly identified non-specific electrostatic and intercalative modes of interaction of the label with DNA at lower and higher DNA concentrations, respectively.[3]

Bearing in mind earlier observations combined with our current research interest on benzo[*a*]phenoxazinium dyes,[4] and following on from our previous evaluation of the potential of these family of fluorophores as DNA labels,[4c] we report the photophysical behaviour of several side chain chlorinated benzo[a]phenoxazinium chlorides functionalized with various types of terminals (hydroxyl, amino and methyl) at the 5- and 9-amino positions of the heteroaromatic ring. It was previously[4d], assigned a ~20nm red shift is observed upon intercalation with a previous quenching resulting from H-aggregate formation through electrostatic binding and/or a blue shift that was interpreted as basic form formation at the DNA grooves. In this work a big influence on the type and position of the terminal group is observed in the form of DNA interaction. An amino group at the 9-amino position greatly promotes intercalation that seems to be completed at a DNA phosphate to dye ratio (P/D) between 1 and 5.





Acknowledgments: Thanks are due to *Fundação para a Ciência e Tecnologia* (Portugal) for its financial support of a BPD to B. R. Raju (SFRH/BPD/62881/2009), CQUM and CFUM.

[1] Chen, Q.; Li, D.; Yang, H.; Zhu, Q.; Xu, J.; Zhao, Y. *Analyst* 1999, *124*, 901–907.
[2] Lakowicz, J. R.; Piszczek, G.; Kang, J. S. *Anal. Biochem.* 2001, *288*, 62–75.
[3] Mitra, R. K.; Sinha, S. S.; Pal, S. K. *J. Fluoresc.* 2008, *18*, 423–432.
[4] a) Frade, V. H. J.; Gonçalves, M. S. T.; Coutinho, P. J. G.; Moura, J. C. V. P. *J. Photochem. Photobiol., A* 2007, *185*, 220-230. b) Alves, C. M. A.; Naik, S.; Coutinho, P. J. G.; Gonçalves, M. S. T. *Tetrahedron Lett.* 2009, *50*, 4470–4474. c) C. M.A. Alves, Sarala Naik, P. J.G. Coutinho, M. Sameiro T. Gonçalves, *Tetrahedron* **65** (2009) 10441-10452. d) C. M.A. Alves, Sarala Naik, P. J. G. Coutinho, M. Sameiro T. Gonçalves, *Tetrahedron Lett*. **52** (2011) 112-116.