N,N-dimethyl-4-amino-2,1,3-benzothiadiazole: synthesis and luminescent solvatochromism

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2,1,3-benzothiadiazole (BTD) derivatives were widely applied as herbicides, fungicides and antibacterial agents. The strong withdrawing ability of BTD and its fluorescent properties make it appealing also for the preparation of luminescent materials. Polymers containing the BTD fragment were successfully exploited for advances applications such as organic light-emitting diodes (OLEDs), dyes, solar and photovoltaic cells, as recently reported by B.A.D. Neto *et al.* [*Eur. J. Org. Chem.* (2013) 228].

To the best of our knowledge, a complete synthetic procedure for *N*,*N*-dimethyl-4-amino-2,1,3benzothiadiazole (BTD^{NMe2}) from the commercially available 2,1,3-benzothiadiazole was never reported. The only reference available dates back to 1976 and describes the thermal decomposition of the corresponding ammonium salt [N.M. Slavachevskaja *et al.*, *Pharm. Chem. J.* **10** (1976) 327]. The synthetic route here proposed involves nitration of BTD in sulfonitric mixture, followed by reduction of the nitro-group and subsequent methylation with iodomethane. BTD^{NMe2} was isolated as dark red oil and it was fully characterized by means of nuclear magnetic resonance (NMR) and infrared spectroscopy. Solutions of BTD^{NMe2} in common organic solvents revealed to be appreciably luminescent in the visible range. The increase of dielectric constant caused a nonlinear red shift of the absorption and emission maxima, an increase of the Stokes shift and a reduction of the photoluminescence quantum yield. The electronic transitions related to the absorption and emission properties were associated to the HOMO-LUMO energy gap by means of electrochemical measurements and DFT calculations. Finally, BTD^{NMe2} was successfully used for the preparation of luminescent doped polymethylmethacrylate samples with intense orange emission.