2021 February 17-18 ONLINE

Small Chem International Online Conference

February 17-18, 2021

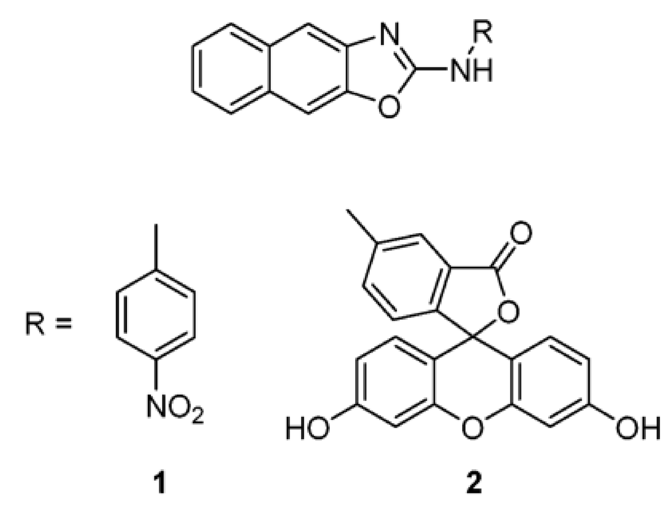
PROTECTION AGAINST CHEMICAL SUBMISSION: NAKED EYE DETECTION OF ϒ-HYDROXYBUTIRIC ACID IN SOFT DRINKS AND ALCOHOLIC BEVERAGES

Jose A. Sáez, Silvia Rodríguez-Nuévalos, Ana M. Costero, Pau Arroyo, Margarita Parra, Pablo Gaviña

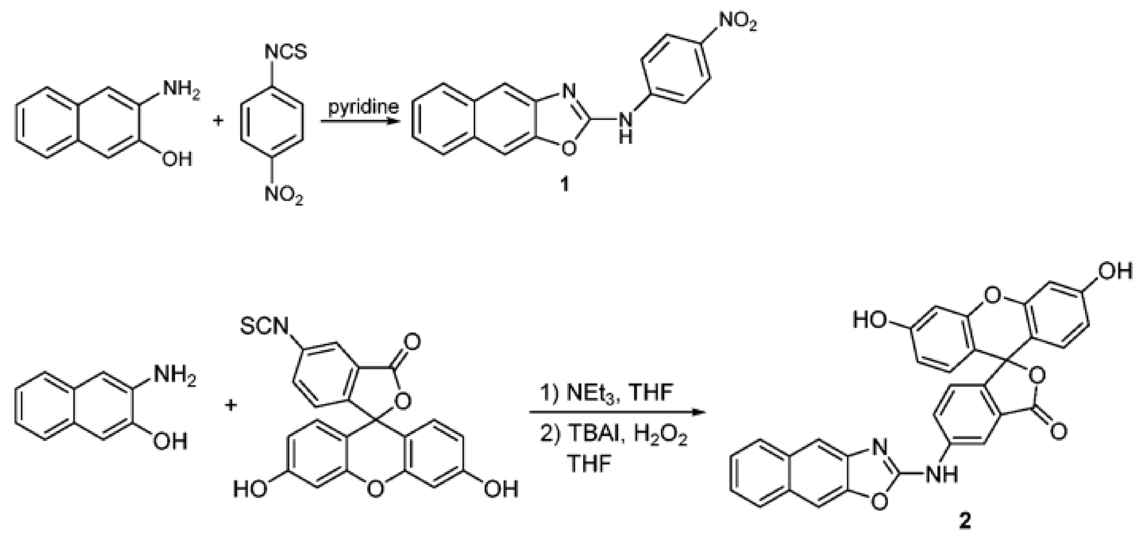
Keywords: GHB detection, chemical submission, sensors, chemical dosimeters, alcoholic beverages, organic synthesis

Introduction & synthesis

Chemical submission in an important social problem associated with sexual aggression. Among the compounds used by criminals to manipulate the will of a person is ϒ-hydroxybutyric acid (GHB) that can be introduced into the victim's drink without the victim being aware of it because it is a colorless, odourless and almost tasteless liquid. In addition, the effect after its intake is fast (15-30 min), lasts for periods of 6 to 8 hours and its detection is challenging because is quickly metabolized. Therefore, the preparation of colorimetric or fluorescent chemosensors to detect GHB is an active research field. Previous chromo-fluorogenic chemosensors able to detect GHB were either based on borodipyrromethene derivatives[1], enzymes coupled with a redox active dye[2] or cucurbiturils with fluorescent dyes[3]. In the present work, two new oxazole derivatives, **1** and **2** (see **Scheme 1**), able to detect ϒ-hydroxybutyric acid in soft drinks and alcoholic beverages are presented which were synthesized through the pathway depicted in **Scheme 2**.

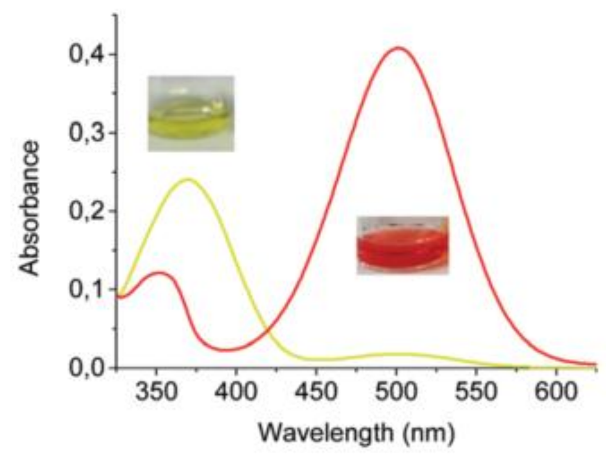


Scheme 1. Chemical structure of probes **1** and **2** for GHB detection.

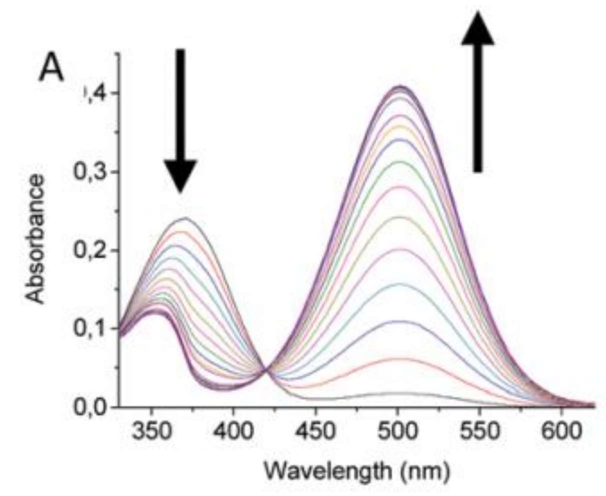


Scheme 2. Synthetic pathway to prepare probes **1** and **2**.

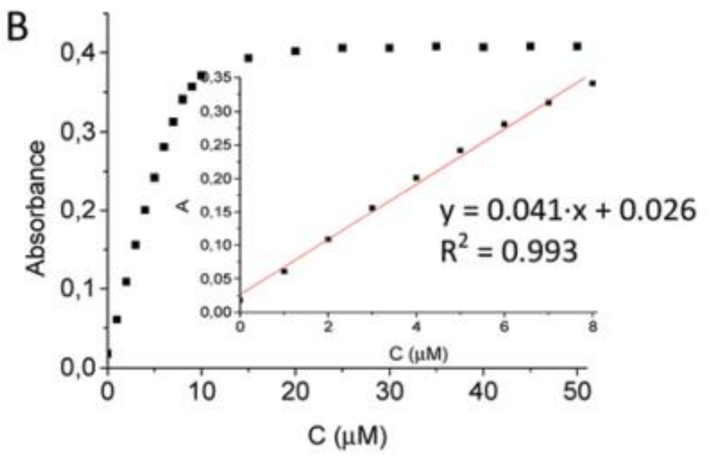
Detection & mechanism



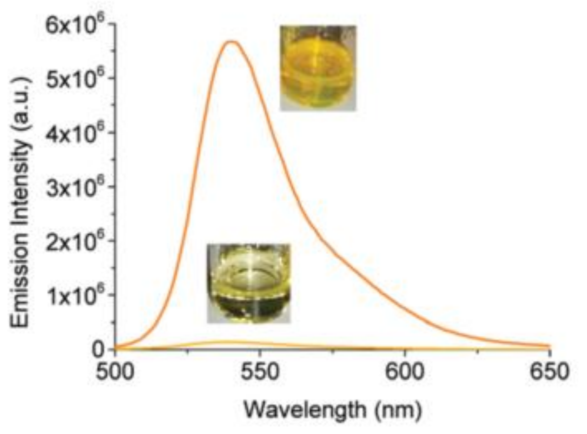
UV-Vis spectra of probe **1** alone (yellow curve) and in the presence of GHB 10 µM (red curve) in DMSO.



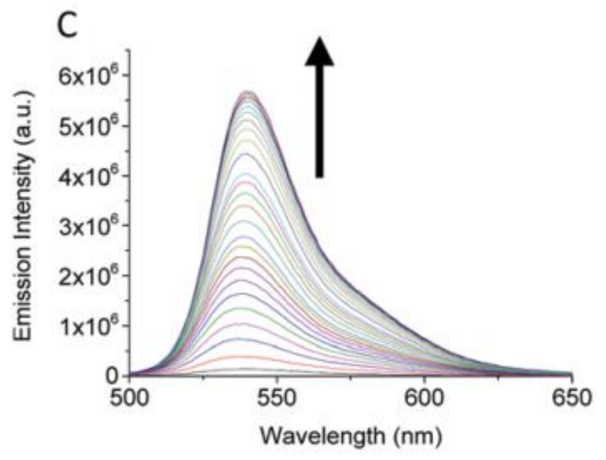
UV-Vis changes of probe **1** (10 µM in DMSO) with increasing amounts of GHB (0-5 eq).



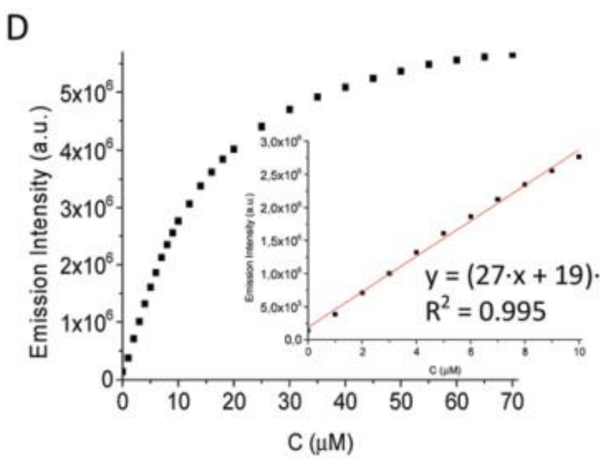
UV-Vis changes in the absorbance at 500 nm of DMSO solutions of probe **1** upon the addition of increasing amounts of GHB.



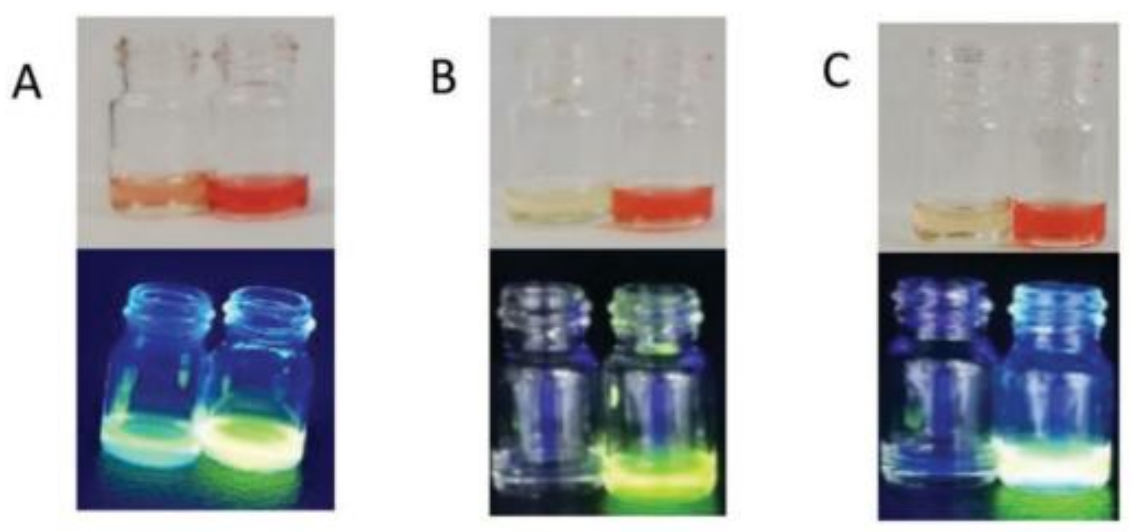
Fluorescence spectra of probe **2** alone (yellow curve) and in the presence of GHB 10 µM (orange curve)



Fluorescence changes of probe **2** (10 µM in DMSO) with increasing amounts of GHB (0-7 eq).



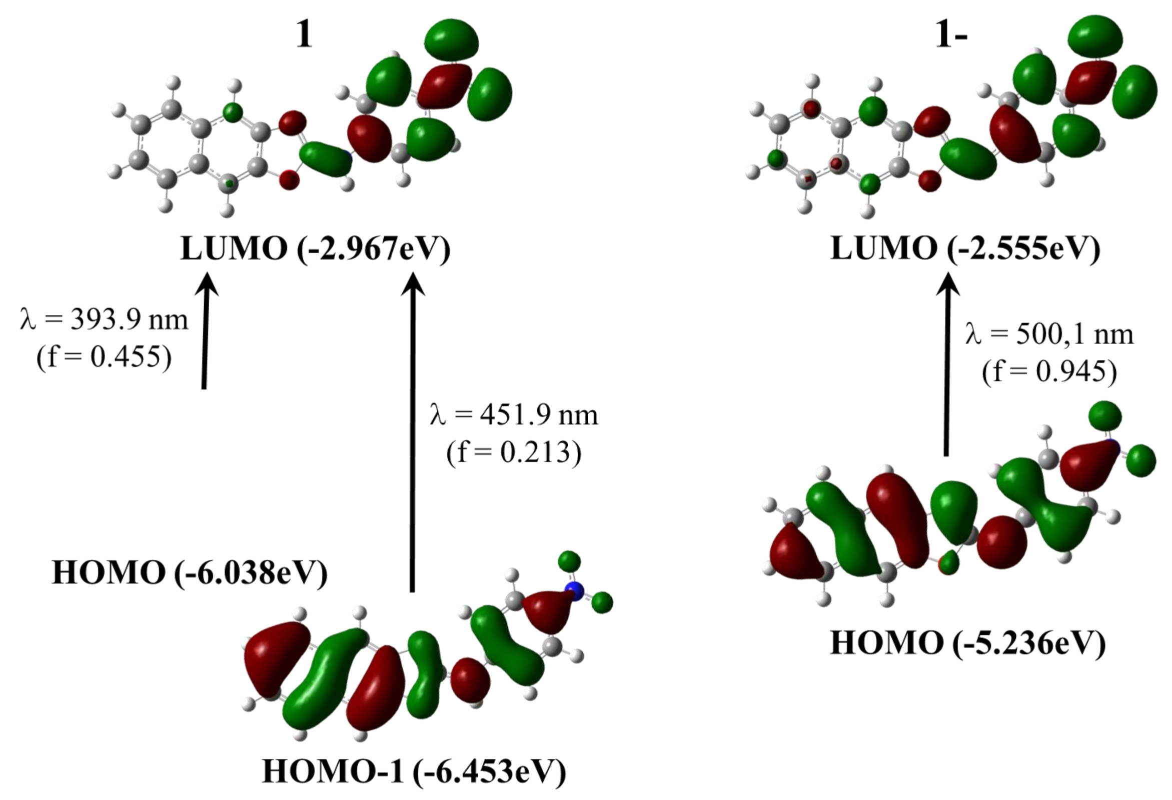
UV-Vis changes in the emission at 541 nm (excitation at 490 nm) of DMSO solutions of probe **2** upon the addition of increasing amounts of GHB.



Up: Color changes observed with probe **1** in the presence of (A) whisky, (B) cola, and (C) whisky/cola.

Down: Fluorescence changes observed with probe **1** in the presence of (A) whisky, (B) cola, and (C) whisky/cola.

In both cases the **left** vial contained the drink whereas the **right** vial contained the beverage spiked with GHB



The mechanism associated with the GHB detection of the probes was studied by UV-Vis titrations and ^{1}H NMR spectroscopy. The data obtained pointed to a single equilibrium between probe **1** and GHB linked to a upfield shift of all signals of the aromatic protons. This fact, consistent with an increase in the electron density of the probe as a consequence of the recognition process, was also supported by theoretical DFT calculations where the acidity of the amino group bearing the nitrophenol and fluorescein substituents was evaluated and the UV-Vis plots were predicted, pointing to the GHB-induced deprotonation of the probes as the reason of the chromo-fluorogenic response[4].

Jose A. Sáez Cases

Instituto Interuniversitario de Investigación de Reconocimiento Molecular y Desarrollo Tecnológico (IDM)
Universitat de València. Departament de Química Orgànica.
E-mail: josesaez@uv.es

[1] D. Zhai, Y. Qiao, E. Tan, W. Xu and Y.-T. Chang, Chem. Commun., 50 (2014) 2904.
[2] D. Bravo, D. Harris and S. Parsons, J. Forensic Sci., 49 (2004) 379.
[3] L. A. Baumes, M. B. Sogo, P. Montes-Navajas, A. Corma and H. García, Chem. – Eur. J., 16 (2010) 4489.
[4] S. Rodríguez-Nuévalos, A. M. Costero, P. Arroyo, J. A. Sáez, M. Parra, F. Sancenón and R. Martínez-Máñez, Chem. Commun., 56 (2020) 12600.

2021 February 17-18 ONLINE sC SmallChem