Sonophotoluminescence: pyranine emission induced by ultrasound

Muthupandian Ashokkumar and Franz Grieser*

Advanced Mineral Products Research Centre, School of Chemistry, University of Melbourne, Parkville, 3052, Australia

Sonoluminescence has been used to excite the water soluble acid–base fluorescent indicator trisodium 8-hydroxy-1,3,6-pyrenetrisulfonate, leading to light emission (sonophotoluminescence) from the dye.

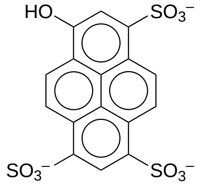
The acoustic driven collapse of microbubbles in solution results in a phenomenon referred to as sonoluminescence.[1] The emission spectrum obtained from multibubble sonoluminescence (SL) in water is quite broad, ranging from 200 to above 800 nm, with a maximum in the region of 250–350 nm.[1–3] In addition to SL, emission stemming from the ground state chemical reaction of ultrasonically generated oxidising radicals with luminol has also been observed.[4] In the latter case the spectrum obtained is similar to the chemiluminescence of luminol.

The broad band emission from SL raises the question of whether it can be conveniently used as an internal light source to excite other molecules in solution. To explore this possibility we have examined the 'trivial' excitation of trisodium 8-hydroxy-1,3,6-pyrenetrisulfonate (pyranine, POH), by SL, and the ensuing emission, which can be referred to as sonophotoluminescence (SPL).

Details of the experimental system used are given elsewhere.[5] Briefly, a modified Undatim D-Reactor (515 kHz) was fitted into the cavity of a spectrofluorimeter (Hitachi, F-4500) and spectra recorded directly. A full scan (200–800 nm) could be measured in *ca.* 2 min. The sonication of the aqueous solutions was carried out in pulsed mode using 4 ms pulses with a 1 : 3 duty cycle. The reactor was operated at *ca.* 15 W into 50 ml solutions. Under these conditions the temperature rise of the solutions sonicated was *ca.* 1° min^{-1}.

All solutions were made with Milli-Q water and used on the day of preparation. Pyranine was obtained from Molecular Probes Inc. and used as received. The UV-VIS spectrum of pyranine in water agreed with that reported by others.[6] The temperature of the solutions remained in the range of 20–25 °C while spectra were recorded.

Pyranine is a highly water soluble compound with well characterised photophysical properties.[6,7] Its chemical structure is shown below.



POH

Pyranine has a ground state pK_a = 7.2 but on excitation pK_a* = 0.5.[7] Its excited state lifetime is also sufficiently long (5 ns) such that deprotonation occurs over a wide pH range.[7] It is only when the pH is < *ca.* 2 that the emission from the POH* form begins to dominate. These photophysical properties of pyranine are evident in the absorption and fluorescence spectra (Fig. 1), at pH values above and below its ground state pK_a.

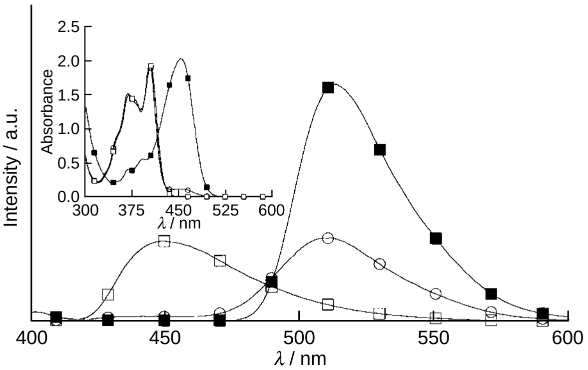


Fig. 1 Emission spectra (λ_{ex} = 350 nm) of 0.1 mM pyranine in water at various pH. Insert shows the absorption spectra obtained from the same solutions. Emission and absorption spectra were measured in standard 1 cm pathlength cuvettes. (Emission spectra are uncorrected.) pH = 10.7 (■), 6.4 (○), 0.7 (□).

Fig. 2 shows the emission observed when pyranine solutions (at several pH values) are sonicated. These spectra can be compared with the equivalent pH fluorescence spectra shown in Fig. 1. Close correspondence of the two sets of spectra is evident although there are some differences. Fig. 3 directly compares the standardised fluorescence and SPL from pyranine at pH = 6.4. Also shown is the SL signal obtained from water in the absence of pyranine. As can be seen, the SPL signal is slightly broader than the fluorescence band with a shoulder at 450 nm. The broadness and the shoulder are both due to the residual SL emission that has not been absorbed by ground state pyranine. It can be seen from Fig. 1 that at pH = 6.4 there is no substantial light absorption by ground state pyranine above *ca.* 440 nm.

At a pH of 10.7 all the pyranine exists in its ionised form, PO$^-$, and its absorption spectrum extends to *ca.* 500 nm (Fig. 1). Under these conditions all of the SL is absorbed at wavelengths below 500 nm and therefore the shoulder seen at 450 nm is no longer present.

At pH = 0.7 the reaction,

$$PO^{-*} + H^+ \longrightarrow POH^* \qquad (1)$$

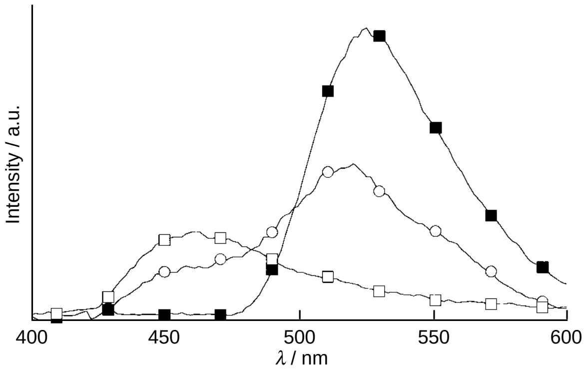


Fig. 2 Sonophotoluminescence of 0.1 mM pyranine in water at various pH. The emission is produced in a 4 cm diameter cell using a 3.5 cm diameter transducer plate. (Emission spectra are uncorrected.) pH = 10.7 (■), 6.4 (○), 0.7 (□).

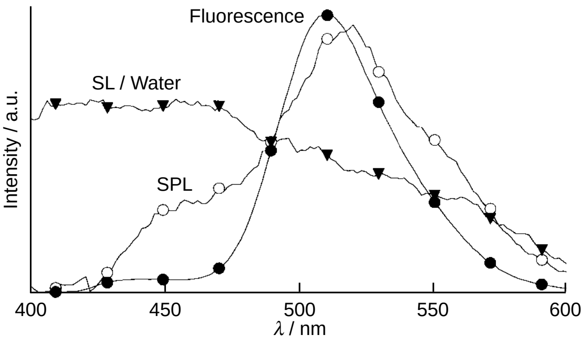


Fig. 3 A comparison of the fluorescence and SPL spectra of pyranine at pH = 6.4. The intensity maxima of the bands have been normalised to allow a better comparison. Under the quite different excitation conditions used the fluorescence intensity is *ca.* 600 times stronger than the SPL. Also shown is the SL from water. The intensity is on the same scale as that of the SPL. (Emission spectra are uncorrected.)

prevents emission from the PO^{-}* form and the emission recorded is a combination of SL and SPL from the POH* species.

In order to confirm that it is sonoluminescence that excites pyranine and not some thermal activation from heat leaking away from the acoustically collapsed bubble some experiments were carried out in the presence of butan-1-ol. Butanol has been found to quench the SL intensity from water[5] while enhancing sonochemical reactions in solution.[8,9] The latter indicates that bubble collapse in the presence of butanol still occurs and local heating still produces radicals that are responsible for the chemical reactions in solution.

Fig. 4 shows the effect that 0.1 M of butan-1-ol has on pyranine fluorescence and its SPL signal. It can be seen that butanol has a minimal effect on the fluorescence signal but almost completely quenches the SPL emission. This is consistent with butan-1-ol quenching the SL and hence eliminating photon excitation of pyranine.

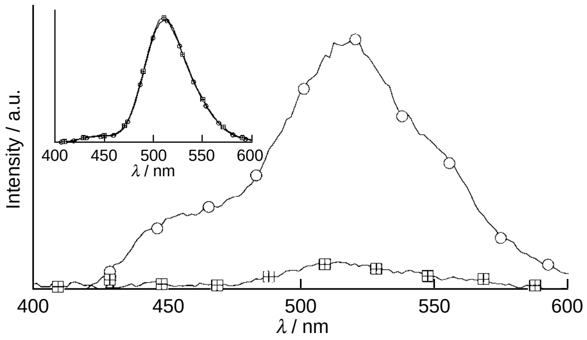


Fig. 4 Sonophotoluminescence spectra of 0.1 mM pyranine in water in the absence (○) and presence ⊞ of 0.1 M butan-1-ol at pH = 6.4. Insert shows the fluorescence spectra (λ_{ex} = 350 nm) of the same solutions. (Emission spectra are uncorrected.)

The results presented clearly show that SL can be used to excite solution solutes. One of the advantages offered by this method is that no external light source is required and photon excitation can, in principle, be achieved in optically opaque and remote sites. For example, photosensitizing drugs within a human body could be activated using SPL generated by an ultrasound source external to the body. We note also that since sonoluminescence is observed in a wide range of liquids[1,10,11] it should be possible to generate SPL in systems other than water.

Notes and References

* E-mail: f.grieser@chemistry.unimelb.edu.au

1 F. R. Young, *Cavitation*, McGraw-Hill Book Company, London, 1989.
2 T. G. Leighton, *The Acoustic Bubble*, Academic Press, London, 1994.
3 Y. T. Didenko and S. P. Pugach, *J. Phys. Chem.*, 1994, **98**, 9742.
4 E. N. Harvey, *J. Am. Chem. Soc.*, 1939, **61**, 2392; A. Henglein, R. Ulrich and J. Lilie, *J. Am. Chem. Soc.*, 1989, **111**, 1974.
5 M. Ashokkumar, R. Hall, P. Mulvaney and F. Grieser, *J. Phys. Chem. B*, 1997, **101**, 10 845.
6 O. S. Wolfbeis, E. Fürlinger, H. Kroneis and H. Marsoner, *Fresenius Z. Anal. Chem.*, 1983, **314**, 119.
7 M. J. Politi, O. Brandt and J. H. Fendler, *J. Phys. Chem.*, 1985, **89**, 2345.
8 J. Z. Sostaric, P. Mulvaney and F. Grieser, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 2843.
9 S. Au Yeung, R. A. Hobson, S. Biggs and F. Grieser, *J. Chem. Soc., Chem. Commun.*, 1993, 823.
10 E. B. Flint and K. S. Suslick, *J. Am. Chem. Soc.*, 1989, **111**, 6987.
11 R. D. Finch, *Ultrasonics*, 1963, **1**, 87.

Received in Cambridge, UK, 3rd December 1997; 7/08708J