A simple and smart oxygen sensor based on the intrazeolite reactions of a substituted anthraquinone†

Katherine L. McGilvray, Michelle N. Chrétien, Matthew Lukeman‡ and J. C. Scaiano*

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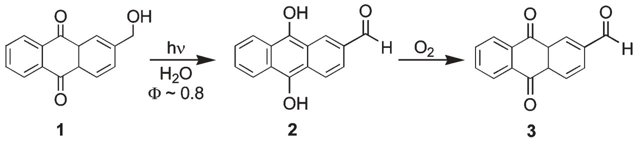
Inclusion of 2-(hydroxymethyl)anthraquinone in zeolite NaY leads to a solid, photoactivated, reusable oxygen sensor capable of reporting and memorizing oxygen contamination events by simple visual inspection.

The development of chemical sensors for molecular oxygen is a topic of considerable current interest, since they allow facile quality control in industrial processes, such as food packaging, where it is necessary to exclude oxygen.[1] In this communication, we report on the use of a recently studied photoisomerization as a colorimetric reporter for exposure to molecular oxygen. While the system we describe could be developed as a quantitative sensor for oxygen, we believe that its main value is derived from its simplicity, *i.e.*, an "instantaneous" reaction followed by a visually detected colour change. In addition, although the chemistry is sacrificial in nature, the sensor itself can be "recharged" and reused many times.

Lukeman *et al.* have recently described an efficient, excited state intramolecular redox reaction available to 2-(hydroxymethyl) anthraquinone (**1**).[2] The primary photochemical step is believed to be the deprotonation (by a protic solvent) of a benzylic C–H bond to generate a benzylic carbanion, which readily converts to give 2-formyl-9,10-dihydroxyanthracene (**2**) (Scheme 1). In an argon purged solution, the presence of, at most, 10^{-3} M of **2** was reported to impart on the solution a deep yellow-orange colour that was slowly bleached over the course of 1 h. Decolourization was greatly accelerated when oxygen was bubbled through the solution due to the oxidation of **2** to **3** (Scheme 1). A very high quantum yield of 0.8 was reported for the production of **3** from **1**. The oxygen-dependent decolourization of solutions of **2** suggested to us the possibility of employing this reaction for the qualitative (or quantitative) sensing of the presence of oxygen in gas streams, or for packaging applications involving oxygen (or air) sensitive materials.



Scheme 1

Liquid-based sensors offer a number of disadvantages, including the need for increased expertise in sample handling, as well as the dependence of the response on the diffusion and solubility of oxygen in the solvent. Specifically, in the case of **2**, its relatively short lifetime in solution (*ca.* 1 h) would make it impractical for most applications. We reasoned that the encapsulation of **1** in a suitable matrix could provide a more robust sensing material. The choice of an appropriate encapsulating matrix is critical; for example, solid polymers, while convenient in many respects, would limit oxygen diffusion and may not provide a sufficiently protic environment for the efficient phototautomerization of **1**.

Our laboratory has considerable experience in the use of zeolites for the encapsulation of organic molecules, and in particular on their application as hosts for photoinduced reactions.[3] The faujasite zeolite sodium Y (NaY) is a synthetic aluminosilicate of intermediate polarity, consisting of a tetrahedral arrangement of *ca.* 13 Å cavities interconnected by *ca.* 7.5 Å windows. 2-(Hydroxymethyl)anthraquinone (**1**) should penetrate easily into these cavities through the 7.5 Å apertures. Furthermore, zeolite inclusion is known to isolate molecules, reducing their reactivity. Compound **1** was incorporated into the zeolite from a dichloromethane solution to give a material with an occupancy of $\langle S \rangle = 0.4$ molecules per cavity. Briefly, the zeolite material was first dehydrated at 480 °C and then added to a dichloromethane solution of **1**. The slurry was stirred at room temperature for 3–4 h, and the resulting solid collected by filtration and dried under air, nitrogen or vacuum as desired. These experimental details have been provided in order to emphasize the ease with which this material can be prepared.

The diffuse reflectance spectrum of **1** in NaY (**1**@NaY) is consistent with absorption spectra reported for this compound in solution.[2] Exposure to UVA light (emission centered at 350 nm, *ca.* 50 W m^{-2}) led to the rapid (within seconds) development of a visible absorption, as shown in Fig. 1. It is clear that the zeolites (which are rarely truly 'dry') offer adequate polarity and protic availability for the photoredox reaction to occur efficiently.[4] Note that while the data shown in Fig. 1 corresponds to irradiation continued over 30 min (the powdered sample is shaken between exposure periods to ensure conversion to **2** throughout the sample, as indicated by the even colour distribution), the formation of the yellow intermediate was achieved in less than 25 min, while 50% of the visible colour change appeared quickly, within 8 min. However, adequate colour for sensing applications was developed within 10 s without shaking. Fig. 1 emphasizes that the preparation of the sensor **2**@NaY is a very forgiving process that does not

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Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Canada K1N 6N5. E-mail: tito@photo.chem.uottawa.ca; Fax: +1 (613) 562-5633; Tel: +1 (613) 562-5896

† Electronic supplementary information (ESI) available: Video clip showing "instantaneous" bleaching of **2**@NaY following exposure to air. See DOI: 10.1039/b610577g

‡ Current address: Department of Chemistry, Acadia University, 6 University Avenue, Wolfville, Nova Scotia, Canada, B4P 2R6. E-mail: mlukeman@acadiau.ca, Fax: (902) 585-1114; Tel. +1 (902) 585-1009

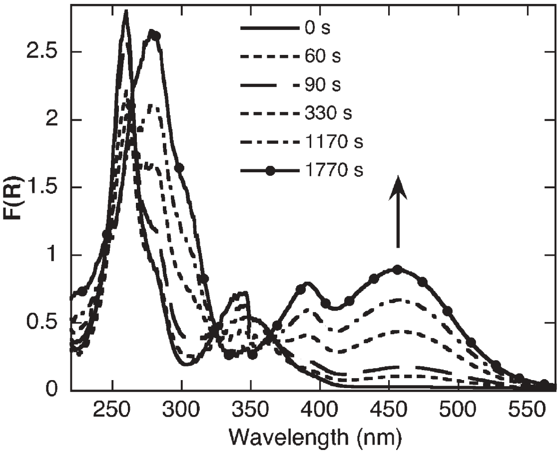

Fig. 1 Formation of **2** ($\lambda_{max} \sim 460$ nm) by UVA irradiation of **1** in zeolite NaY under nitrogen. The irregularity of traces at 350 nm is an instrumental artifact resulting from a lamp change in the spectrometer.

require a specific or rigorously controlled irradiation. The peaks in the diffuse reflectance spectrum are slightly red-shifted in relation to the data reported in aqueous acetonitrile solution; this is commonly observed for many aromatic species following zeolite inclusion.

Exposure of the solid material (stored under an inert atmosphere) to light gives it a striking yellow colour, as compared to the bright white colour of the solid prior to irradiation (Fig. 2) and following bleaching by oxygen. This yellow colour persists for extended periods of time, in comparison to the reported stability of *ca.* 1 h in solution. Furthermore, samples of **1**@NaY stored in the dark for more than 2 years still achieve the bright yellow colour following 10–30 s UVA irradiation under vacuum.

In contrast to the extensive colour change, the fluorescence spectra of the exposed and unexposed samples show very little difference. This is likely to be a result of the low conversion required for the formation of observable colour. This low conversion of the starting material allows the sample to be reused several times (*vide infra*).

When the seal of vials, such as those in Fig. 2, is broken and air is allowed into the sample, the material decolourizes instantaneously on the time scale of visual observation (less than 0.5 s); a consequence of the oxidation of the dihydroxy intermediate **2** to anthraquinone **3** (Scheme 1). Clearly, the reaction is facilitated by the structure of the zeolite, where each pore is identical and the network of cavities hosting the sensor is easily accessible to oxygen. The abundant sensitivity of this yellow material towards oxygen is observed by the conversion to **3** upon exposure to merely 0.1% oxygen. The instantaneous nature of the process under exposure to air is illustrated by a short video clip included as ESI.†

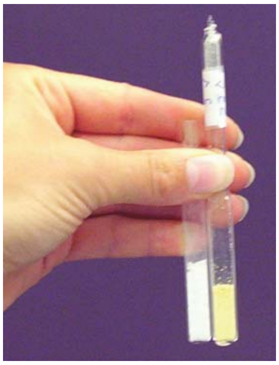

Fig. 2 Unexposed (left) and exposed (right) samples of **1**@NaY. The sample on the right has been sealed under vacuum and irradiated for ~10 s. On the CIE standard colour scale, the *b** parameter, measuring yellow tint, changes from 2.7 to 39 upon exposure.

As previously mentioned, this sensor can be reused several times. However, it is clear that only the colouration is reversed, the chemistry itself being irreversible in nature. Thus, the sacrificial nature of the sensor will limit its use to only a certain number of sensor events. In reality though, there are many applications (related to food packaging, for example) where a single-use, disposable sensor is required. In these cases, the simple preparation and low cost§ of this zeolite-based sensor are very attractive attributes.

In summary, zeolite inclusion greatly enhances the stability of photogenerated dihydroxyquinone (**2**) while simultaneously retaining its essentially instantaneous sensitivity to oxygen. The colour change is readily observable with effectively no equipment or operator training, although clearly the colourimetric nature of the sensor also lends itself to spectroscopic monitoring of a local or remote nature. Recharging requires only UVA light and could easily be performed with the same black lights that are widely used to verify the authenticity of currency or other security papers. The material is easily handled and prepared, stable prior to the photoisomerization event, and does not require protection from oxygen or visible light (again, prior to the formation of **2**). We envisage there being applications in gas streams, oxygen-free enclosures (such as glove-boxes) and air-tight or oxygen-free packaging. While we do not foresee the need for the zeolite-hosted sensor to come in contact with foodstuffs, it is worth noting that while the toxicity of **1** has not been fully studied, **1** is contained in herbal medicines that have been used for centuries. Furthermore, given its polarity, spontaneous release from the zeolite host is highly unlikely. The irreversible nature of the **2** → **3** transformation has the additional advantage of reporter memory, *i.e.*, if oxygen contamination were to occur in a gas flow, the sensor would bleach and remain in its decolourized state, even after an oxygen-free condition is restored. The operator would have control of reactivating the sensor once the oxygen contamination incident had been recorded.

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Notes and references

§ 1 g of this sensor could be prepared for approximately US $2.00 based on the retail prices of chemicals.

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3 For selected examples, see: (*a*) M. Alvaro, M. N. Chretien, V. Fornes, M. S. Galletero, H. Garcia and J. C. Scaiano, *J. Phys. Chem. B*, 2004, **108**, 16621; (*b*) A. Ricci, M. N. Chretien and J. C. Scaiano, *Chem. Mater.*, 2004, **16**, 2669; (*c*) M. N. Chretien, G. Cosa, H. Garcia and J. C. Scaiano, *Chem. Commun.*, 2002, 2154; (*d*) M. L. Cano, M. N. Chretien, H. Garcia and J. C. Scaiano, *Chem. Phys. Lett.*, 2001, **345**, 409; (*e*) S. Corrent, L. J. Martinez, J. C. Scaiano, H. Garcia and V. Fornes, *J. Phys. Chem. B*, 1999, **103**, 8097; (*f*) J. C. Scaiano and H. Garcia, *Acc. Chem. Res.*, 1999, **32**, 783.

4 This result suggests that zeolites of this type might be attractive host materials for other reactions of this type, *e.g.*: D. Mitchell, M. Lukeman, D. Lenherr and P. Wan, *Org. Lett.*, 2005, **7**, 3387.