

# SUPPORTING INFORMATION

## ***In Situ* Electrochemical-NMR Spectroscopy. The Reduction of Aromatic Halides.**

**Richard D. Webster**

*Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia.*

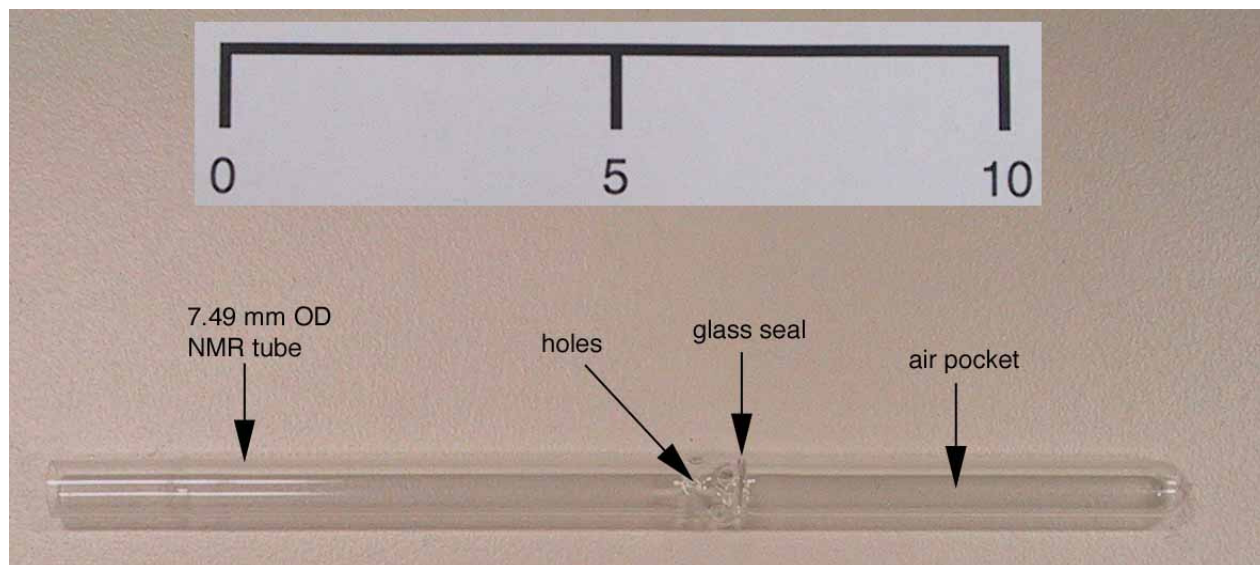
*E-mail: [webster@rsc.anu.edu.au](mailto:webster@rsc.anu.edu.au), Fax: + 61 2 6125 0750*

---

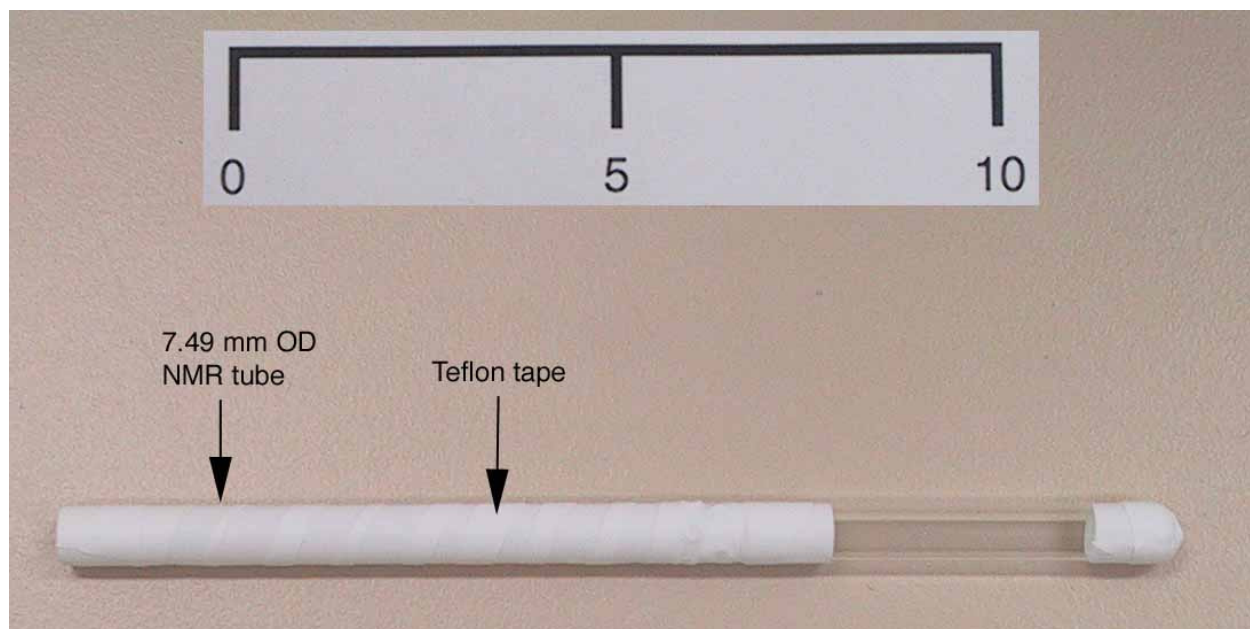
### CONTENTS

S-1.	Construction of Lower Section of Electrochemical-NMR Cell .....	2
S-2.	Construction of Upper Section of Electrochemical-NMR Cell .....	11
S-3.	Operation of Electrochemical-NMR Cell .....	12
S-4.	Voltammetric Behavior of Electrochemical-NMR Cell .....	15
S-5.	Additional Figures and Table .....	17
S-6.	Additional References .....	20

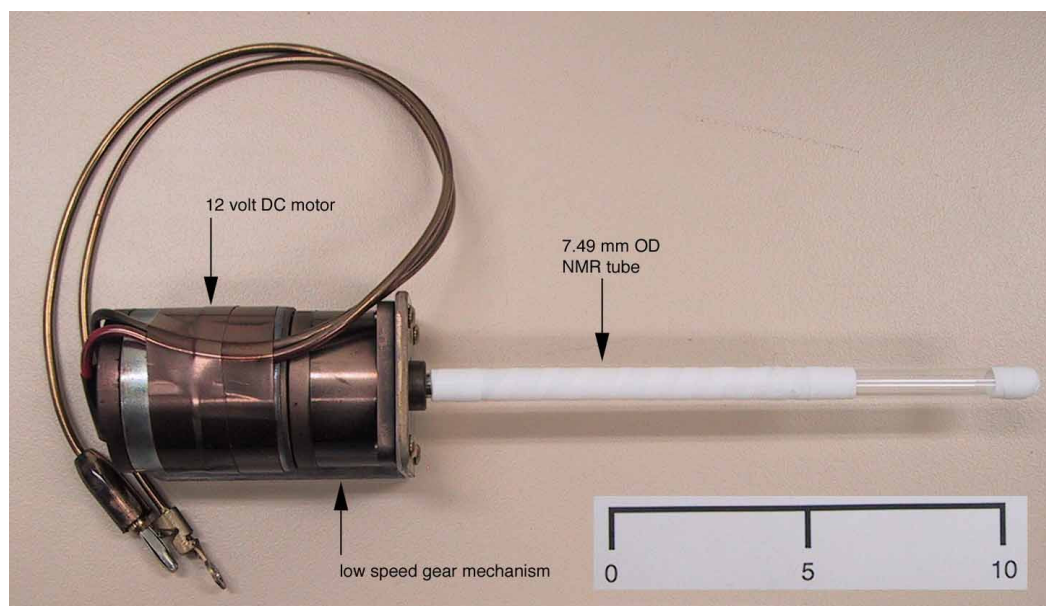
## S-1. Construction of Lower Section of Electrochemical-NMR cell. (Scale in cm.)



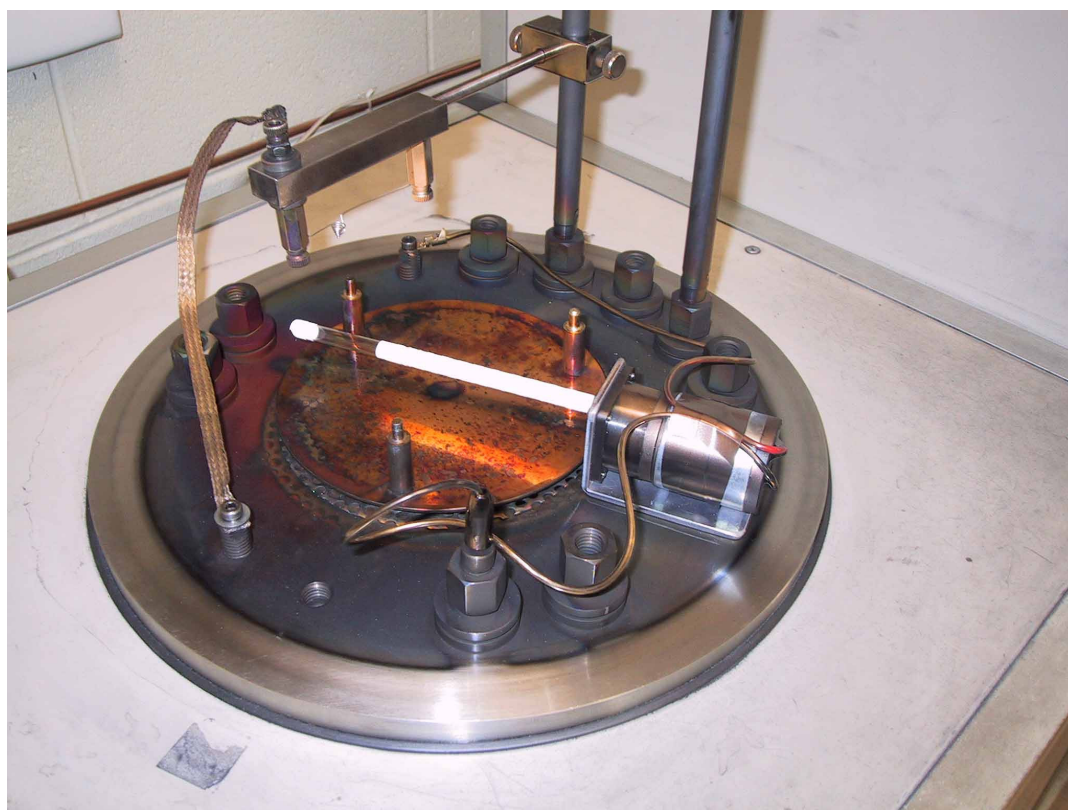
**S-1.1.** A 7.49 mm OD NMR tube (Wilmad, 513B-7PP) was modified so that it consisted of two segments. One segment was sealed at both ends to create an air pocket whilst the second segment remained open at one end. The open-ended segment served as the compartment to house the auxiliary electrode and contained several (ca. 1 mm) holes near the glass seal connecting the two segments. The holes provided solution contact between the auxiliary and gold film working electrode that was to be coated on the outer surface of the sealed segment of the NMR tube (above the area containing the air pocket).



**S-1.2.** The 7.49 mm OD NMR tube was cleaned in acid solution then rinsed in warm ethanol then water. The portions of the tube not requiring gold coating were masked with Teflon tape. The length of the gold coating was calculated to extend at least 5 mm above and below the position of the RF coils inside the 10 mm probe.

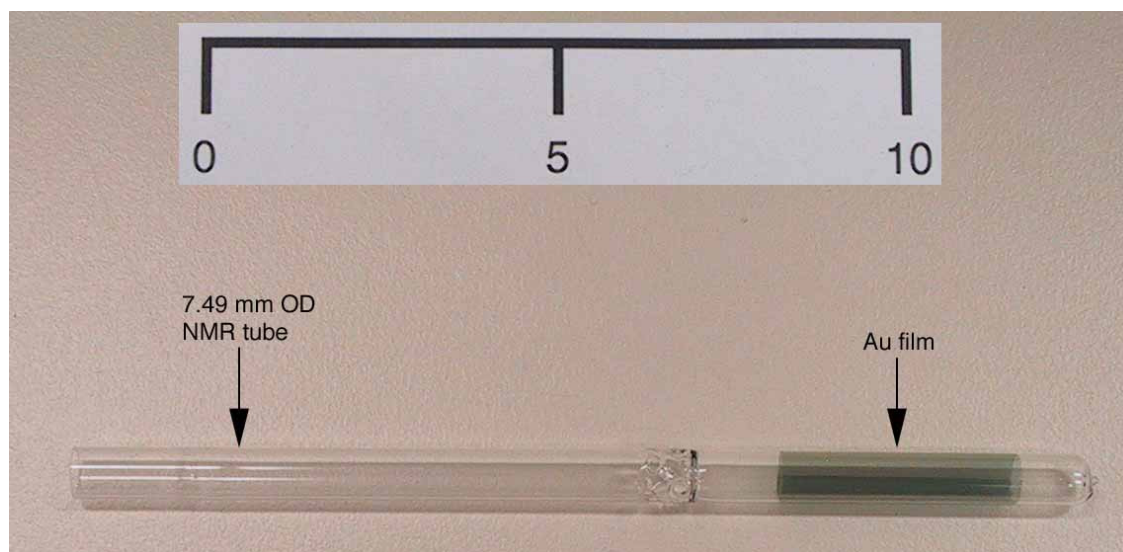


**S-1.3.** The Teflon masked NMR tube was connected to a 12 volt DC motor fitted with a low speed gearbox, so that the NMR tube rotated at ca. 1 revolution per second.

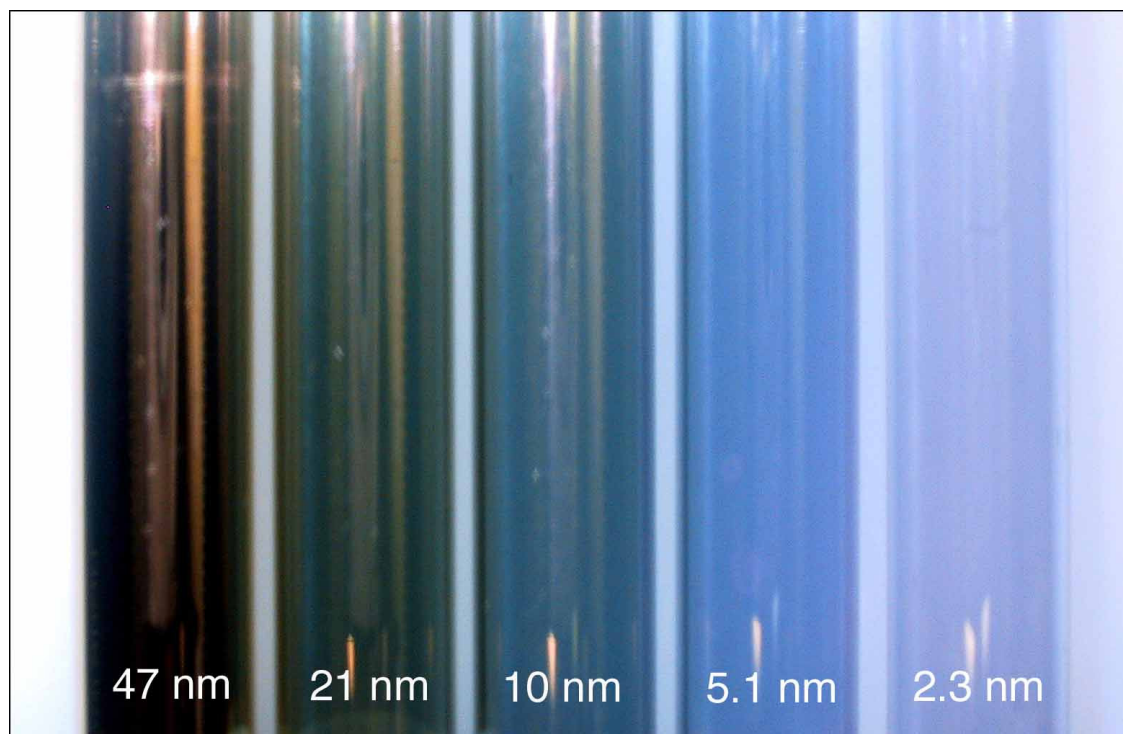


**S-1.4.** The motor/NMR tube was placed inside a vacuum evaporator that had built-in connections to a DC power supply. A weighed amount of gold was placed in the tungsten filament, which was positioned 5 cm from the surface of the middle of the NMR tube. Knowledge of the amount of gold (which was exhaustively heated) and the distance of the source to the NMR tube, allowed an *estimation* of the average thickness of the gold coating. Rotating the NMR tube during the coating process in the motor driven assembly helped to obtain a uniform gold coating on the glass, which was essential in aiding the shimming procedure (see below).

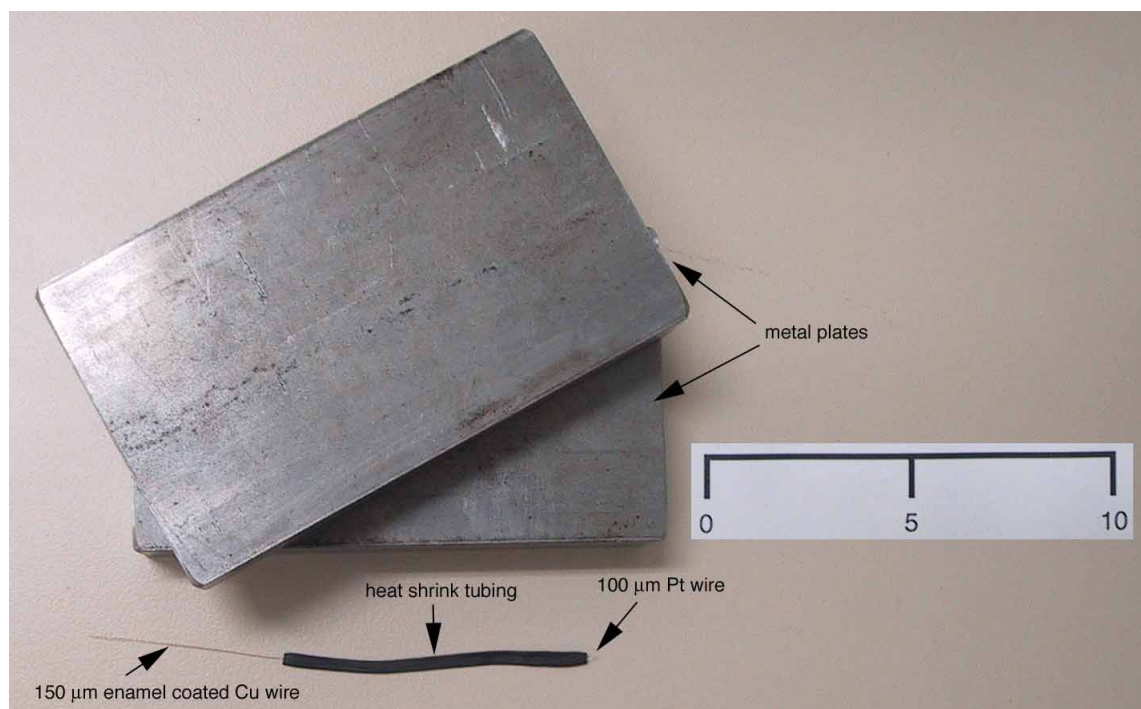




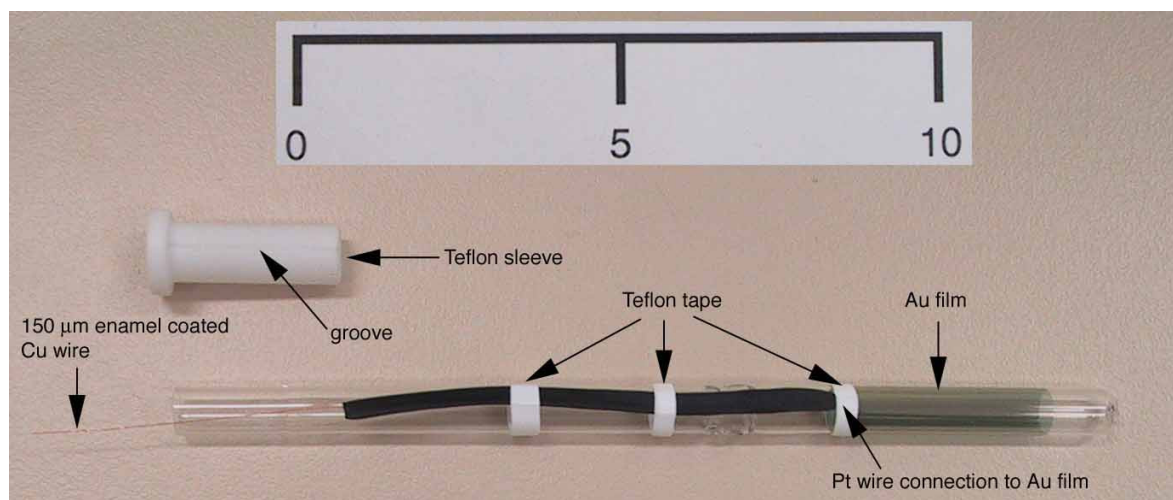
**S-1.5.** The thin gold films produced in the coating process were fragile and easily abraded (the films could be wiped off easily with a soft tissue), so care was taken in handling the tubes and removing the Teflon tape.



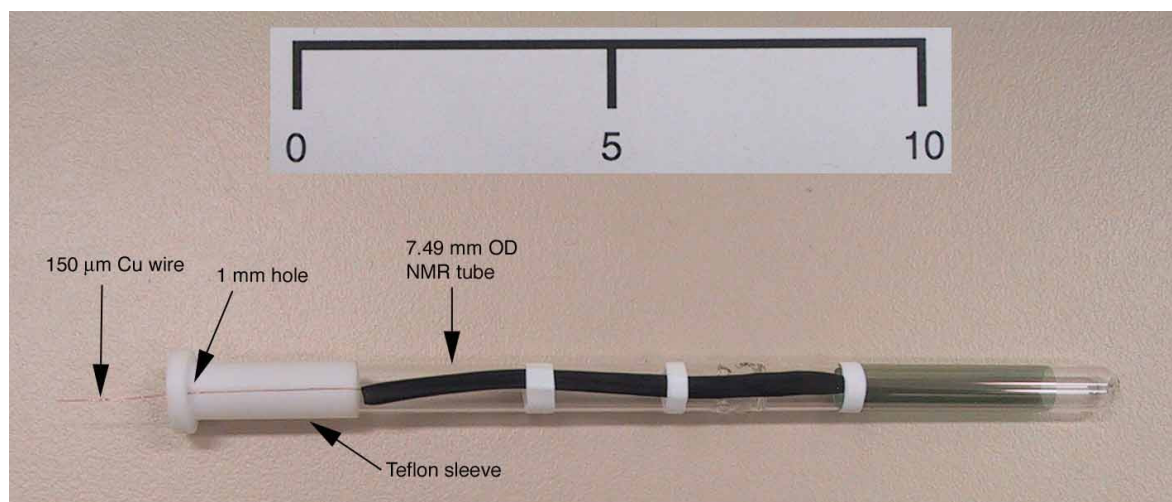
**S-1.6.** The above photograph shows gold films of variable thicknesses coated on 7.49 mm OD NMR tubes. Thin films of gold when viewed by reflected light exist in a range of colors depending on the thickness of the gold and the method of preparation of the films. The difference in color occurs as a result of rapid variation of the extinction coefficient with wavelength, with resultant rapid variation of reflectance.<sup>1</sup> Such behavior has been treated theoretically by assuming that the films exist as a collection of small spherical particles. The colors range from purple/blue, blue, blue-green, yellow-green through to a constant golden yellow after a minimum thickness is reached. The film thicknesses given above are only approximate (based on a simplified calculation using the distance of the gold source from the glass surface and the mass of gold), although the ratios are accurate. Using the scale above, it was found that film thicknesses around 10 nm (blue-green) gave a good compromise between electrochemical and NMR performance (see Results and Discussion).



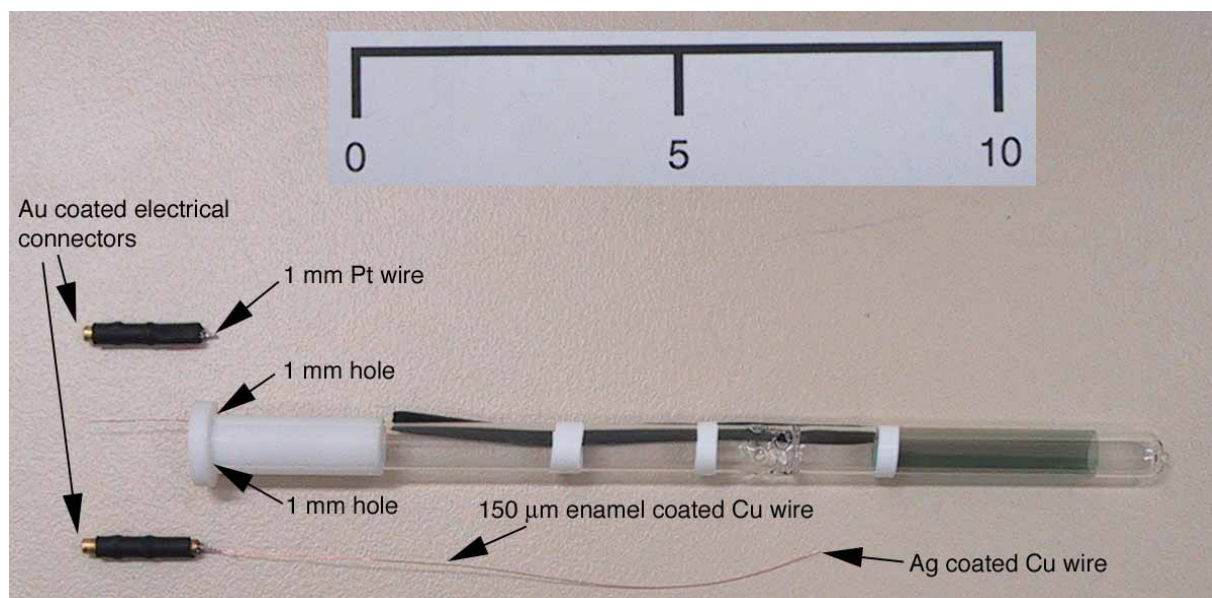
**S-1.7.** A 100  $\mu\text{m}$  diameter platinum wire was connected to a 150  $\mu\text{m}$  diameter enamel coated copper wire (the enamel was stripped from the portion of the copper connected to the platinum). The two wires were placed inside a piece of heat shrink tubing, heated with a hot-air gun and flattened in a vice between two metal plates. This ensured that the copper-platinum connection was insulated (when placed in solution). The platinum wire was trimmed so that a 3 mm length extended from the end of the flattened heat shrink tubing. The platinum-copper wire served as the electrical connection to the gold working electrode (thin platinum foil could also be used to make the connection to the working electrode).



**S-1.8.** The 3 mm length of platinum wire extending from the heat shrink tubing was connected to the 7.49 mm OD NMR tube by pressing it against the gold film and wrapping Teflon tape tightly around the tube. The heat shrink tubing was held in place against the NMR tube in several places in order to prevent the thin platinum wire connector from slipping free of the Teflon tape. Because the electrical resistance of the gold film was much greater than that of the platinum wire, it was preferable that the platinum wire had a small contact area with the solution to prevent the electrolysis occurring preferentially at the platinum wire.

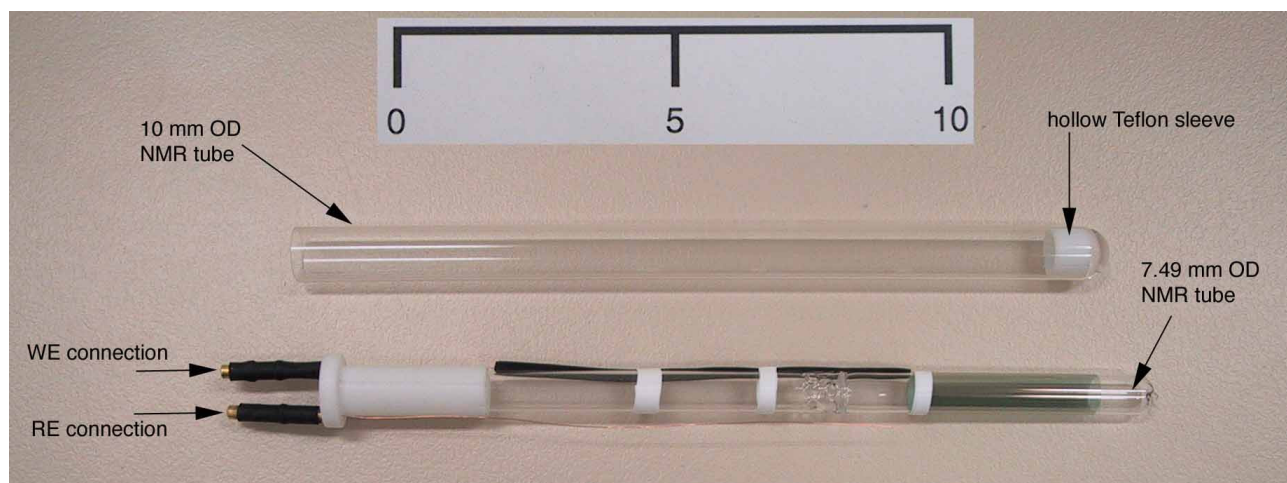


**S-1.9.** The 7.49 mm OD NMR tube was inserted into a hollow Teflon sleeve that was designed to hold an outer 10 mm OD NMR tube symmetrically around the inner (7.49 mm OD) tube and to support the connections to the working, auxiliary and reference electrodes. The 150  $\mu\text{m}$  copper wire that connected to the 100  $\mu\text{m}$  platinum wire was threaded through a hole in the top of the Teflon sleeve. A groove was machined lengthwise in the Teflon sleeve within which the copper wire rested (see S-1.8). The groove allowed the outer 10 mm OD NMR tube to slide over the sleeve without interfering with the 150  $\mu\text{m}$  copper wire.

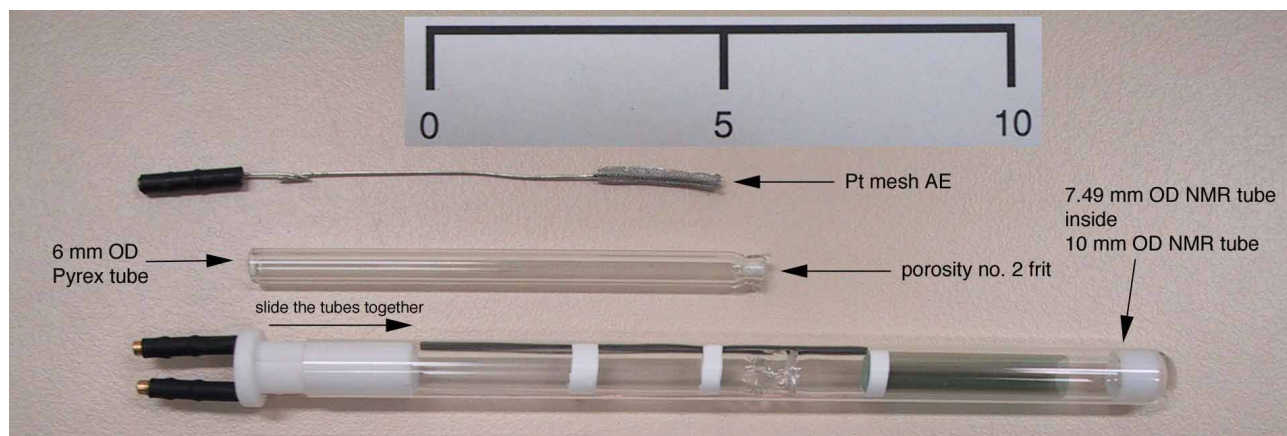


**S-1.10.** The reference electrode consisted of a 150  $\mu\text{m}$  enamel shielded copper wire, where the final 1 mm portion closest to the gold film working electrode was stripped of enamel and coated with silver, to produce a pseudo-silver reference electrode. The enamel on the 150  $\mu\text{m}$  copper wire was resistant to organic solvents such as acetonitrile and dimethylsulfoxide (and their deuterated analogues) but was not stable in chlorinated solvents used for electrochemistry, such as  $\text{CH}_2\text{Cl}_2$  and  $\text{CD}_2\text{Cl}_2$ . The reference electrode wire was threaded through a 1 mm hole in the top of the Teflon sleeve (in the same fashion as the copper wire connecting to the working electrode), run along a groove in the sleeve and positioned within 5 mm of the gold film working electrode. The connection to the reference electrode was made by a 1 mm platinum wire inserted into the end of a gold plated female electrical connector. The same type of connection was used for the working electrode wire. The 1 mm platinum wires (in the electrical connectors) were pressed into the 1 mm holes in the top of the Teflon sleeve. The "press-fit" provided sufficient electrical contact with the copper wires that joined to the gold and silver working and reference electrodes respectively.

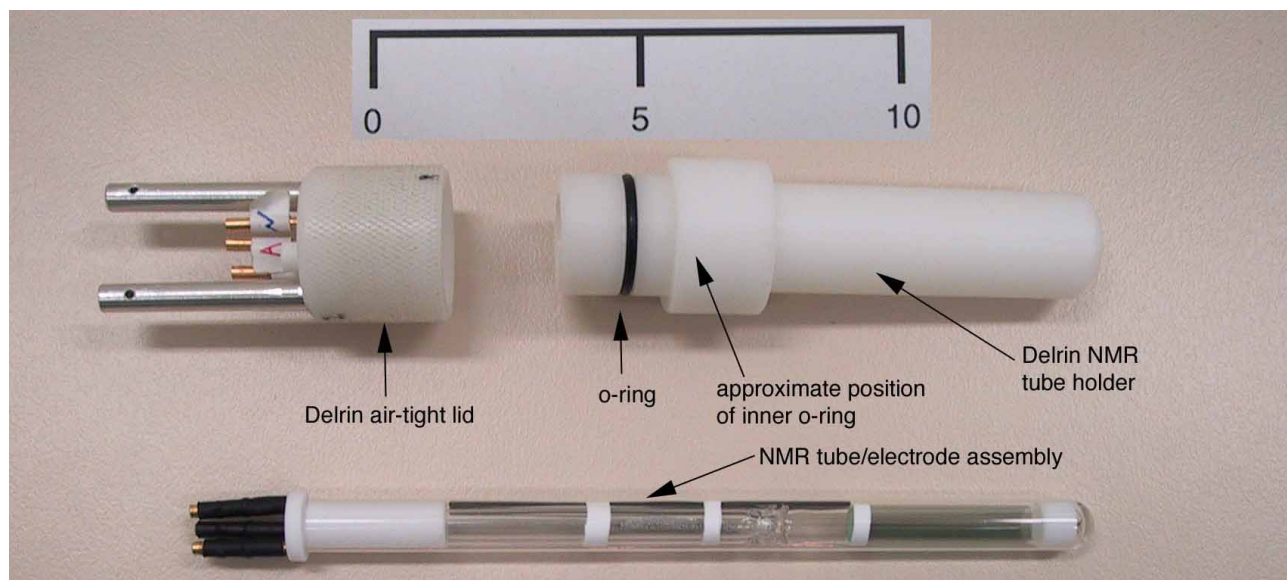
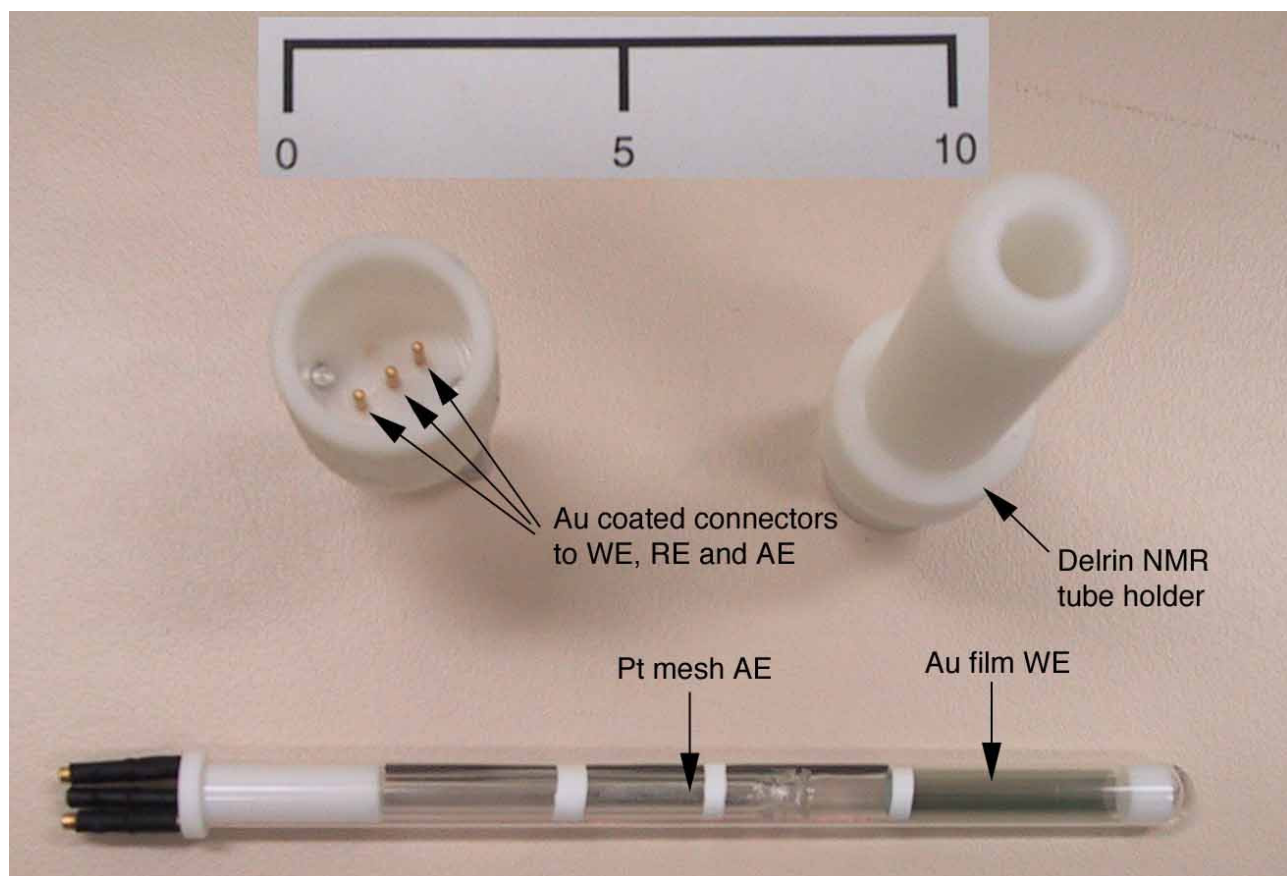




**S-1.11.** The 7.49 mm OD NMR tube was inserted into a 10 mm OD NMR tube (Wilmad, 513-7PP), with care being taken not to scrape the gold film. The 10 mm OD NMR tube had a hollow Teflon sleeve placed near its base, into which the 7.49 mm OD NMR tube slid. The purpose of the sleeves (top and bottom) was to keep the two tubes an equidistant apart so as to maintain a high symmetry in the portion of the tubes that resided within the RF coils. Prior to joining the tubes together, the connection between the gold film working electrode and gold-coated connector at the top of the upper Teflon sleeve was checked with a digital voltmeter (DVM). (AE = auxiliary electrode, RE = reference electrode, WE = working electrode).

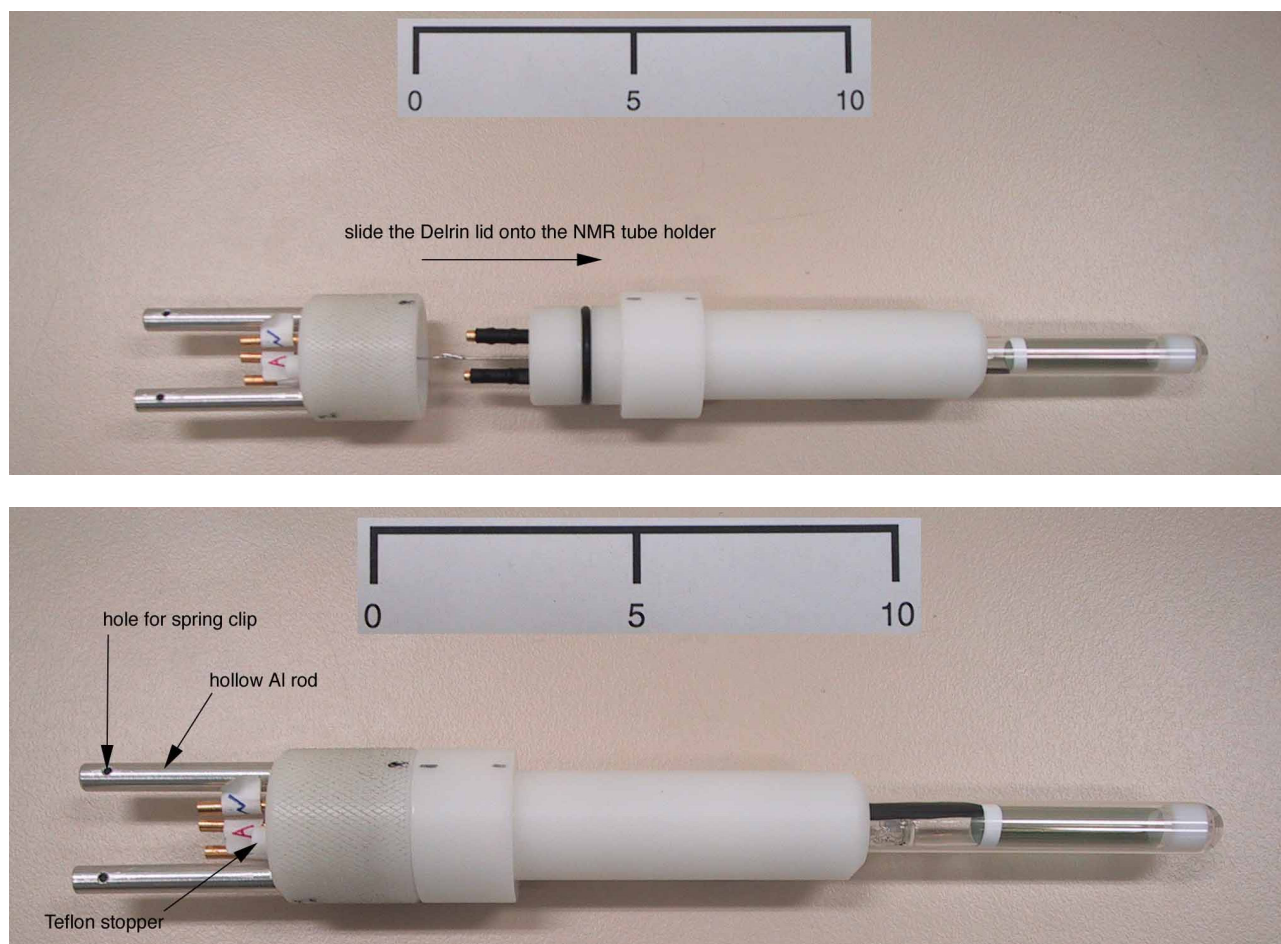


**S-1.12.** A separate additional compartment was made for the platinum mesh auxiliary electrode from a 6 mm OD Pyrex tube containing a porous frit in the base, which rested on two small glass legs. (The auxiliary electrode compartment resided well away from the region of the spectrometer housing the RF coils, so there was no need to construct it from a high precision NMR tube.) The 6 mm OD Pyrex tube was inserted inside the 7.49 mm OD NMR tube so that it rested on top of the glass seal above the segment containing the air pocket. Solution (and therefore, electrical) contact between the working and auxiliary electrodes was made through the frit at the base of the 6 mm OD Pyrex tube and through the holes in the middle of the 7.49 mm OD NMR tube.



**S-1.13.** The NMR tube/electrode assembly was inserted inside the Delrin NMR tube holder (that was manufactured in-house), which had an internal o-ring on the *inner* surface (not visible in the above diagrams, but shown in Figure 1 in the Experimental section of the paper). The connections to the three female connectors in the top of the Teflon sleeve were made by three male connectors glued into the Delrin lid (upper photograph).





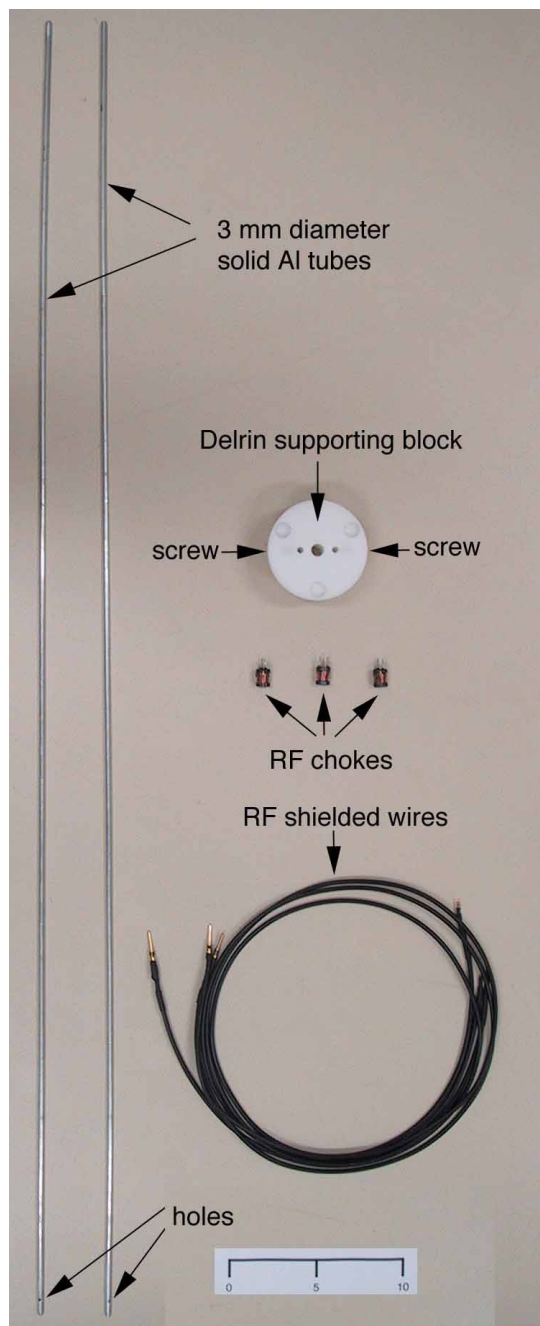
**S-1.14.** In practice, it was simplest to connect the auxiliary electrode to the Delrin lid first, then to slide the Delrin lid onto the Delrin NMR tube holder so that the connections to the working and auxiliary electrodes slotted into place (upper photograph). The lid could not be rotated around the tube holder without breaking the connections to the working and reference electrodes, so marks were placed on the Delrin lid and Delrin NMR tube holder as indicators of accidental movement.

The lower section of the electrochemical-NMR cell shown in S-1.14 was designed so that it could be fully disassembled after each experiment, with the 7.49 mm OD NMR tube cleaned and recoated with a fresh gold film. (In actuality, there existed several modified 7.49 mm OD NMR tubes that were cleaned and recoated with gold in batches.) The assembly procedure shown in S-1.7 through S-1.14 could be performed in < 1 hour.



**S-1.15.** The assembled cell had a 3 mm diameter hole drilled in the Delrin lid that allowed it to be deoxygenated under vacuum in a Schlenk tube type apparatus and purged in a nitrogen atmosphere. The cell was filled with a deoxygenated solution *via* an airtight syringe through the 3 mm hole, which was sealed with a Teflon stopper. The filling solution passed through the frit at the base of the auxiliary electrode compartment before filling up the area surrounding the working electrode, with the process taking around 4-5 minutes. The total solution volume of the cell was *ca.* 2 mL. The volume of solution that resided between the 10 mm OD (9.07 mm ID) and 7.49 mm OD NMR tubes and within the RF coils inside the magnet was 0.33 cm<sup>3</sup>.

## S-2. Construction of Upper Section of Electrochemical-NMR cell. (Scale in cm.)



**S-2.1.** The upper section of the electrochemical cell was constructed from two 3 mm diameter aluminum rods, shielded copper wires, RF chokes, and a Delrin block that held the aluminum rods in place and supported the RF chokes.



**S-2.2.** The aluminum rods were slid into holes in the Delrin block and held in place with screws in the side of the Delrin. The RF shielded wires were taped to the side of the aluminum rods, passed through a hole in the centre of the Delrin block and connected to the RF chokes. The RF chokes had two connections (going into and coming out of the coils), which allowed a convenient location to attach the wires from the potentiostat (see S-3.4).



### S-3. Operation of Electrochemical-NMR cell.



**S-3.1.** The aluminum rods in the upper section were inserted into the hollow aluminum rods in the lid of the lower section and held together with a stainless steel spring clip. The shielded wires taped to the aluminum rods were connected to the gold fittings in the lid of the electrolysis cell. The cell was now fully assembled and ready to be placed in the NMR magnet.



**S-3.2.** The height of the glass tubes inside the lower section of the electrolysis cell were checked using a NMR tube height controller to verify that the tube would be correctly positioned inside the probe. The photograph above shows the position of the gold film in relation to the RF coils inside the magnet (the gold film extended 5-7 mm above and below the position of the RF coils).

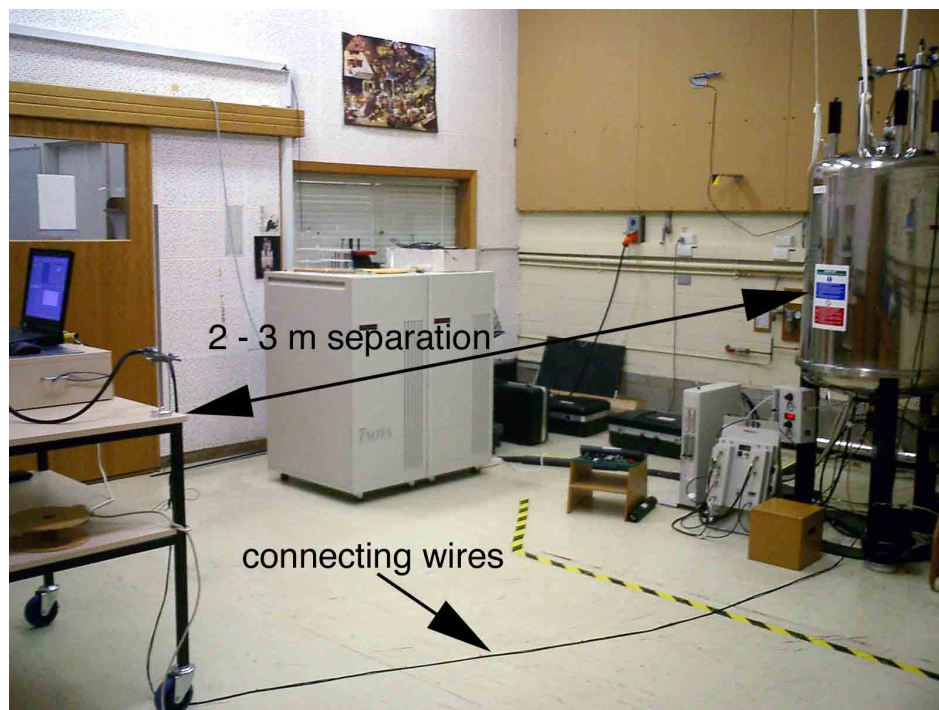
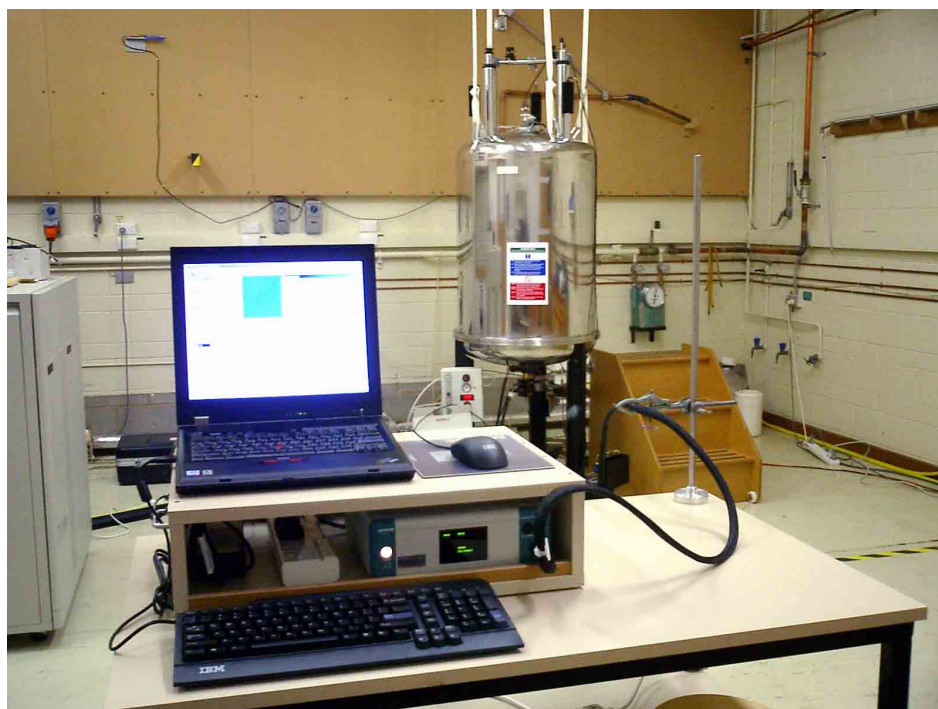


**S-3.3.** The air turbine spinning system was turned off at the NMR computer console. The electrochemical-NMR cell was lowered into the magnet so that the lower Delrin NMR tube holder rested in the correct position within the probe. The height of the upper Delrin block (containing the RF chokes) was adjusted about the aluminum rods so that it rested in the correct position on the upper entrance to the NMR magnet. The screws holding the aluminum rods to the Delrin upper block were tightened so that the Delrin block would be in the correct position for all future measurements. The 10 mm probe was tuned to optimize the sensitivity.



**S-3.4.** The RF shielded wires that connected to the potentiostat were clipped onto the RF chokes on top of the cell. The magnetic field gradients were minimized by manually adjusting the shim coils. The shimming procedure took 2-3 hours to perform the first time the electrochemical cell was placed inside the NMR magnet. However, the highly symmetrical design of the segment of the electrochemical cell that resided within the RF coils meant that the original shim set could be saved and recalled for later use, so that subsequent shimming took only a few minutes. Using accurate and reproducible gold film thicknesses also aided the shimming.





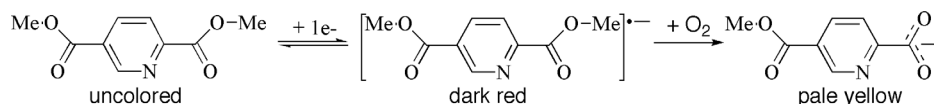
**S-3.5.** The computer-controlled potentiostat was placed at least 2-3 m from the NMR magnet to minimize the interference caused by the strong magnetic field. Having relatively long (5-6 m) RF shielded wires connecting the potentiostat to an electrochemical-NMR cell is not usually desirable from an electrochemical perspective, but in this instance did not significantly interfere with the potential control or current measurement of the cell, since the measured currents were generally quite large ( $\geq 50 \mu\text{A}$ ).



## S-4. Voltammetric Behavior of Electrochemical-NMR Cell.



**S-4.1.** The photographs above show the constant potential one-electron reduction of 40 mM dimethyl pyridine-2,5-dicarboxylate in  $\text{CH}_3\text{CN}$  with 0.25 M  $\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte (Scheme 1).<sup>2</sup>



**Scheme 1**

Dimethyl pyridine-2,5-dicarboxylate was chosen for electrolysis because it is uncolored in its neutral state, while the associated anion radical is red with a very high molar absorptivity, which enables the progress of the reaction to be visually monitored. Furthermore, since the anion radical is formed by applying a high negative potential (-1.9 V vs  $\text{Fc}/\text{Fc}^+$ ), it reacts immediately with molecular oxygen (if present) to form a weakly colored carboxylate anion product. Therefore, the continuance of the dark red color as the electrolysis progresses is a good indication that the cell remains airtight.

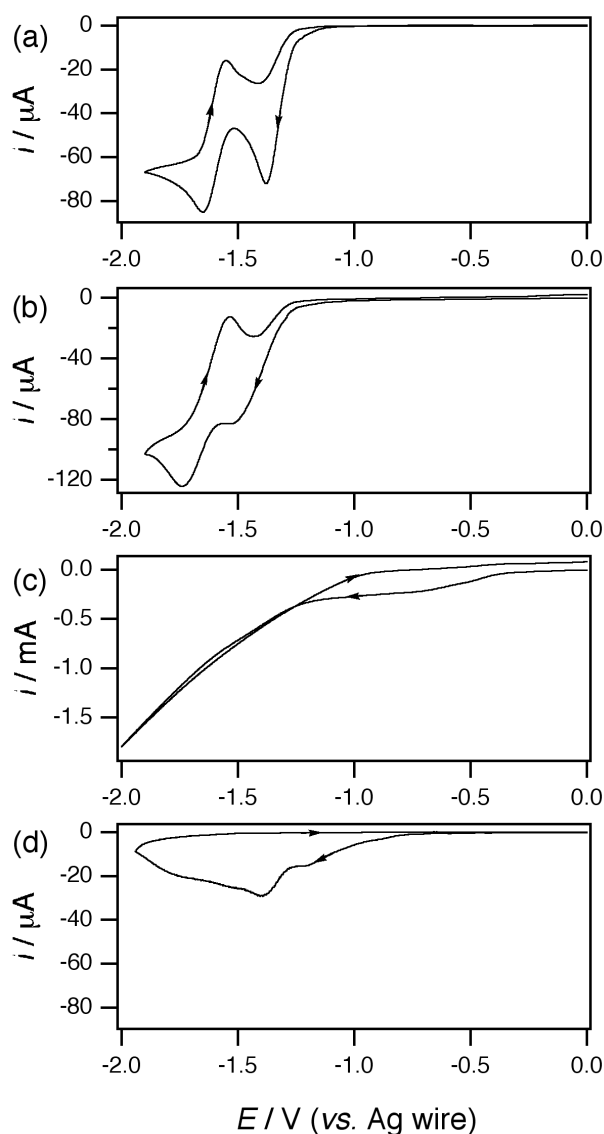
Several factors that impacted on the performance of the electrochemical-NMR cell could be ascertained by visually observing the electrolysis reaction shown above.

In the early stages of the controlled potential electrolysis ( $t < 10$  minutes), the anion radical was observed to move from the top of the gold working electrode towards the auxiliary electrode compartment (S-4.1). The rate of movement of the anion radical was considerably faster than what was expected solely by diffusion control ( $D = 2.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ), and instead is likely to be caused by migration effects due to the high concentration of analyte (0.04 M) in relation to the supporting electrolyte concentration (0.25 M). The reduction of aromatic halides (described in the Results and Discussion section of this paper) leads to the hydrogenated neutral compound (ArH) in high yield as the principal product that is detectable by *in situ* NMR spectroscopy. Since ArH forms very rapidly, its distribution within the NMR cell is unlikely to be as affected by migration compared to the other stable charged species that are produced (such as  $X^-$ ). This is supported by the observation that the signal intensity of the product (ArH) appeared close to that of the starting material (ArX). Thus, the performance of the electrochemical-NMR cell in situations where less than electrochemically optimal concentrations of supporting electrolyte are used, will likely vary depending on the charge on the final products.

The red radical anion was observed to initially form at the upper portion of the gold electrode (closest to the auxiliary electrode) and then with increasing time ( $t > 5$  minutes) significant electrolysis also occurred at the middle and lower portions (S-4.1). This effect is most likely caused by the unsymmetrical position of the auxiliary electrode in relation to the working electrode and the relatively high resistance over the length of the gold (*ca.* 200-400  $\Omega$  for a 10 nm film) that results in uneven current distribution over the working electrode surface. Having a second auxiliary electrode below the gold film working electrode would assist the current distribution, but would greatly complicate the overall cell design. The connection to a second auxiliary electrode would need to be made from the bottom of the cell to avoid having a connecting wire running through the sensitive region of the spectrometer that contains the RF coils.

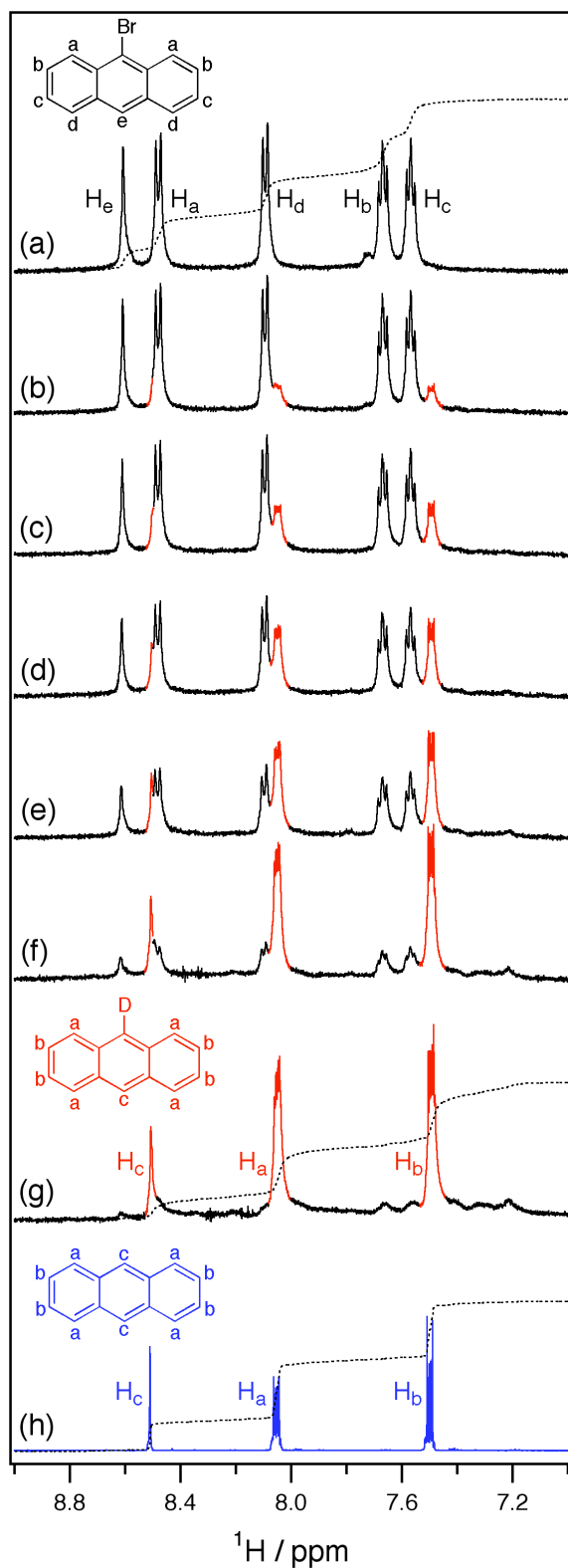
Bulk electrolysis cells that rely on diffusion or convection to supply fresh material to the working (and auxiliary) electrodes are less efficient than those where the solutions are stirred. Attempts were made to increase the flux of material to the working electrode by modifying the cell so that argon gas was bubbled through a thin glass tube than ran directly through the centre of the cell. Surprisingly, the bubbles that ran up the flat walls of the cell between the 10 and 7.49 mm OD NMR tubes introduced very little mixing and only a small increase (10 - 20 %) in electrolysis current was detected (it appeared that the volume of solution that the bubble displaced was largely replaced by the same volume of solution as the bubble moved up the tube). Furthermore, spectra could not be collected while gas bubbles were passed through the solution since the magnetic field gradients within the cell were disturbed resulting in a very broad and distorted NMR line shape.

## S-5. Additional Figures and Table.



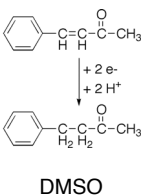
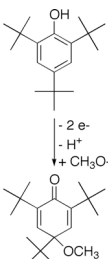
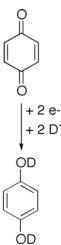
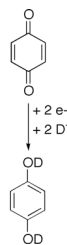
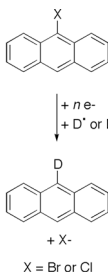
**S-5.1.** Cyclic voltammograms of 25 mM 9-chloroanthracene obtained in  $\text{CD}_3\text{CN}$  at a scan rate of  $50 \text{ mV s}^{-1}$ . (a) 1 mm diameter planar Au working electrode with 0.25 M  $\text{Bu}_4\text{NPF}_6$ . (b) 3 mm length of 100  $\mu\text{m}$  diameter Pt wire as the working electrode inside the electrochemical-NMR cell with 0.25 M  $\text{Bu}_4\text{NPF}_6$ . (c) 10 nm thick Au coated 7.49 mm OD NMR tube as the working electrode with 0.25 M  $\text{Bu}_4\text{NPF}_6$ . (d) 1 mm diameter planar Au working electrode with 0.5 M  $\text{LiClO}_4$  as the supporting electrolyte and with the reference electrode isolated in a salt bridge containing 0.25 M  $\text{Bu}_4\text{NPF}_6$ .





**S-5.2.** 500 MHz  $^1\text{H}$  NMR spectra (a-g) obtained in the *in situ* electrochemical-NMR cell during the electrochemical reduction of 25 mM 9-bromoanthracene in  $\text{CD}_3\text{CN}$  containing 0.25 M  $\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte. (a) Prior to electrolysis. (b) 7-12 minutes. (c) 17-22 minutes. (d) 25-30 minutes. (e) 40-45 minutes. (f) 47-52 minutes. (g) 60-65 minutes. (h) 25 mM anthracene in  $\text{CD}_3\text{CN}$  obtained in a 5 mm OD NMR tube.

**S-5.3.** Summary of information relating to the design of the electrochemical cells, NMR instrumentation and the experimental conditions that were used in papers reporting *in situ* electrochemical-NMR spectroscopy of solution phase reactions.

Parameter	Reference (see main text)						
	(1)	<sup>a</sup> (2)	(3)	(4)	(5)	(6)	This work
NMR Probe Size / mm	5	Not stated	10	5	5	16 (Used 10 mm NMR tube)	10
<sup>1</sup> H NMR Frequency / MHz	60	60 and 80	90 (Static cell); 400 (Hydrodynamic cell)	60	400	300	500
NMR Tube Rotating / Yes or No	Yes	Yes	Yes (Static cell); Not stated (Hydrodynamic cell)		No	Yes	No
Nucleus	<sup>1</sup> H	<sup>1</sup> H	<sup>13</sup> C	<sup>1</sup> H	<sup>1</sup> H	<sup>1</sup> H	<sup>1</sup> H
Hydrodynamic or Static Electrochemical Cell	Hydrodynamic	Not stated	Hydrodynamic and static	Static	Static	Static	Static
Electrode Positioned Within RF Coils / Yes or No	No	Not stated	Not stated	Yes	Yes	Yes	Yes
Compounds Studied	 <p>DMSO</p>	$M^- + M \leftrightarrow M + M^-$ (M = <i>p</i> -benzoquinone, ubiquinone, nitrobenzene, 3-nitroorthoxylene, <i>p</i> -nitrotoluene, 4-nitroorthoxylene, <i>p</i> -toluenenitrile, anthracene, naphthalene, chlorobenzene)  Vitamin A + e <sup>-</sup> → products			$[Fe(CN)_6]^{4-} + e^- \rightleftharpoons [Fe(CN)_6]^{3-}$  H <sub>2</sub> O		 <p>X = Br or Cl</p>
Solvents and Electrolytes	Methanol/water (1:1) pH 10 carbonate buffer	DMF/C <sub>6</sub> D <sub>6</sub> (1:1) Bu <sub>4</sub> NClO <sub>4</sub> , Bu <sub>4</sub> NI, Et <sub>4</sub> NI	CH <sub>3</sub> OH/CD <sub>3</sub> OD NaClO <sub>4</sub>	D <sub>2</sub> O KCl, DCl	D <sub>2</sub> O K <sub>2</sub> SO <sub>4</sub>	D <sub>2</sub> O KCl, DCl	CD <sub>3</sub> CN Bu <sub>4</sub> NPF <sub>6</sub> , Et <sub>4</sub> NPF <sub>6</sub>
Information Obtained	Monitoring reactions	Electron exchange kinetics and monitoring reactions	Monitoring reactions	Monitoring reactions	Frequency shift of H <sub>2</sub> O in the presence of paramagnetic species	Monitoring reactions	Monitoring reactions

<sup>a</sup> Few experimental details were given regarding the design of the electrochemical cell.

## S-6. Additional References.

- (1) Heavens, O. S. *Optical Properties of Thin Solid Films*; Butterworths: London, 1955.
- (2) Webster, R. D.; Bond, A. M.; Compton, R. G. *J. Phys. Chem.* **1996**, *100*, 10288-10297. Webster, R. D.; Bond, A. M. *J. Chem. Soc., Perkin. Trans.2*, **1997**, 1075-1079. Webster, R. D.; Bond A. M.; Coomber, D. C. *J. Electroanal. Chem.* **1998**, *442*, 217-227. Webster, R. D. *J. Chem. Soc., Perkin Trans. 2*, **2002**, 1882-1888.