

Supporting Information for

Study of the spontaneous attachment of polycyclic aryldiazonium salts onto amorphous carbon substrates

Deirdre M. Murphy,^a Ronan J. Cullen,^a Dilushan R. Jayasundara,^a Eoin M. Scanlan,^a

*and Paula E. Colavita.^{a, *}*

a - School of Chemistry, University of Dublin Trinity College, College Green, Dublin 2, Ireland

* Corresponding author. E-mail: colavitp@tcd.ie.

Determination of the relative absorption cross section of the $\nu_s(\text{NO}_2)$ mode of 4NBD, 4NND and 5NND

In order to normalise in situ monitoring data to reflect the surface density of absorbed molecules at the carbon surface as a function of time, we used an internal standard for determining relative absorption cross sections for 4NBD, 4NND and 5NND. Potassium ferricyanide was chosen as the internal standard as it displays a single strong absorbance at 2115 cm^{-1} that does not interfere with infrared peaks of the three compounds. The IR absorption of $\text{K}_3[\text{FeCN}_6]$ is shown in Figure SI.1

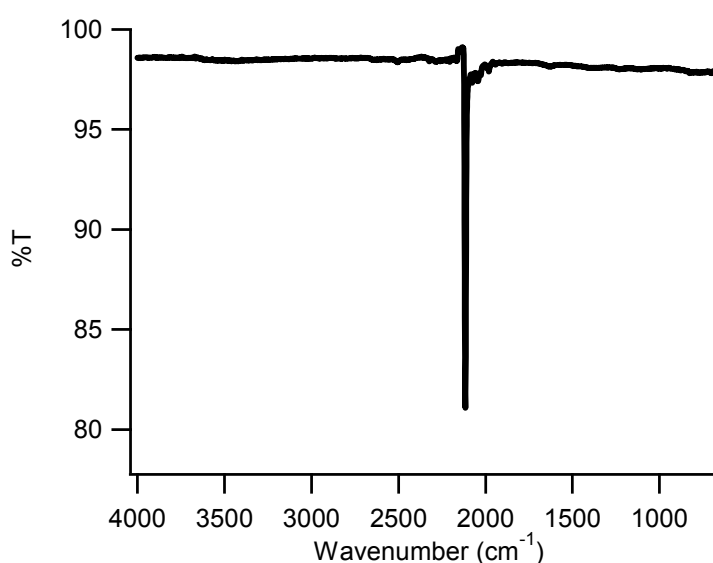


Figure SI.1: IR spectrum of $\text{K}_3[\text{FeCN}_6]$

A known percentage (per weight) of internal standard and compound were combined and their absorption spectra measured using ATR spectroscopy. Examples of the spectra obtained for 4NBD, 4NND and 5NND are shown in Figure SI.2, Figure SI.3 and Figure SI.4, with the internal standard (IS) peak labelled. Experiments were carried out three times and the average ratio of the internal standard to symmetric N—O stretching peaks were used to normalise for differences in cross section among 4NBD, 4NND and 5NND.

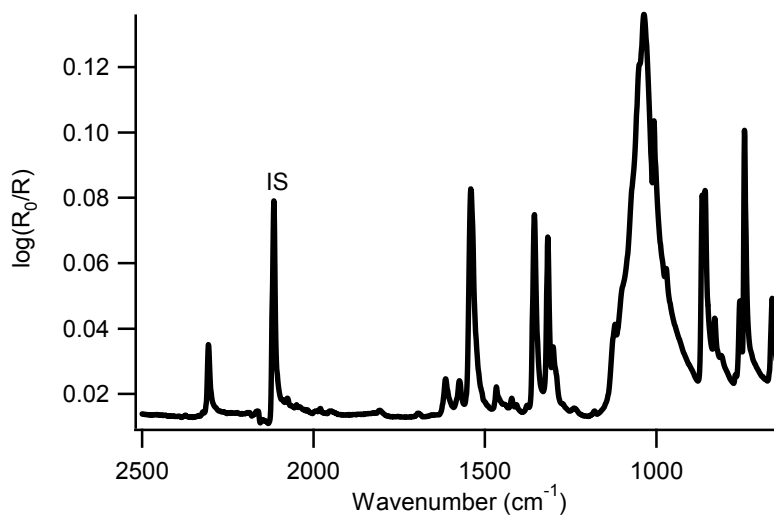


Figure SI.2: IR spectrum of 4NBD

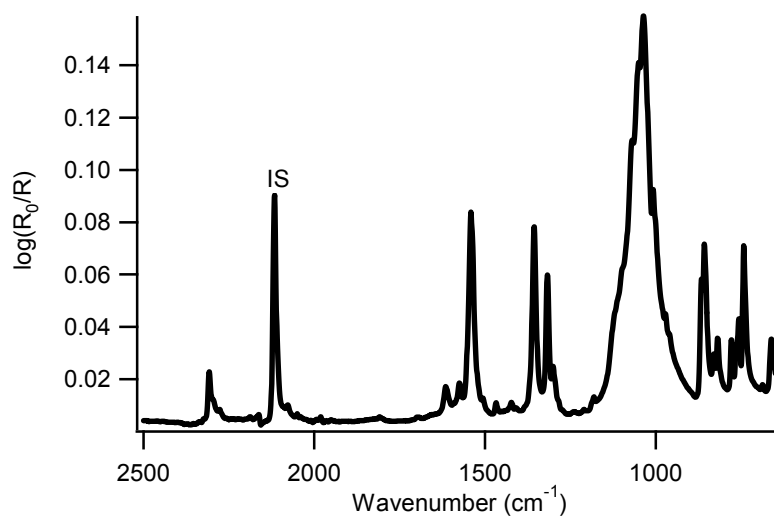


Figure SI.3: IR spectrum of 4NND

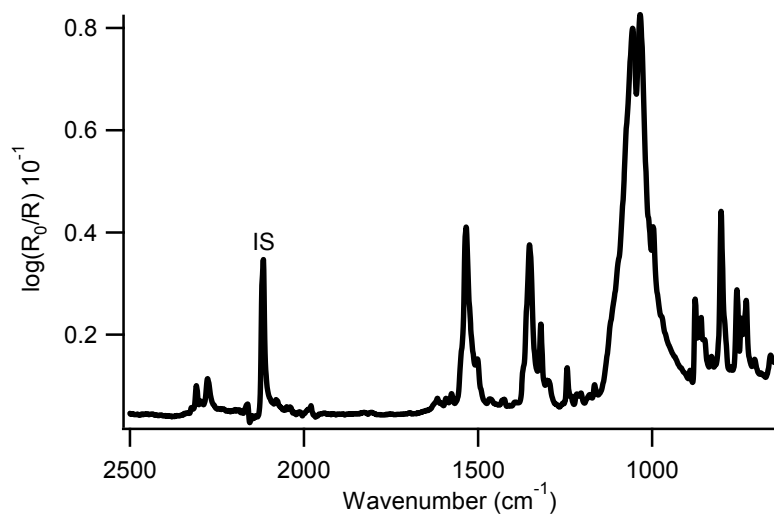


Figure SI.4: IR spectrum of 5NND

Reduction potentials of the diazonium group in 4NND and 5NND

In order to determine the reduction potential of the aryldiazonium moiety we carried out cyclic voltammetry experiments in 7×10^{-4} M anhydrous acetonitrile solutions of 4NND and 5NND, containing also 0.1 M tetrabutylammonium perchlorate as supporting electrolyte.

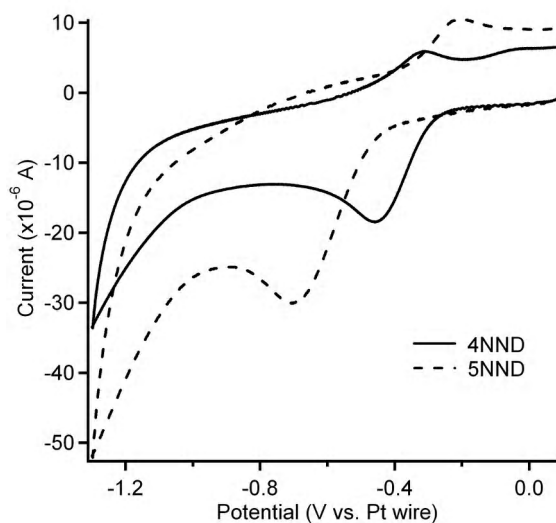


Figure SI.5: Cyclic voltammetry at 0.2 V s^{-1} , showing reduction peaks of diazonium ($-\text{N}_2^+$) groups of 4NND and 5NND in acetonitrile solution.

Infrared surface spectra in the 2600-1600 cm^{-1} region

Infrared surface spectra of 4NND and 5NND films at carbon surfaces showing details in the region 2600-1600 cm^{-1} where $-\text{N}_2^+$ stretching modes would be expected. The large peak (negative or positive) at 2350 cm^{-1} is due to atmospheric carbon dioxide.

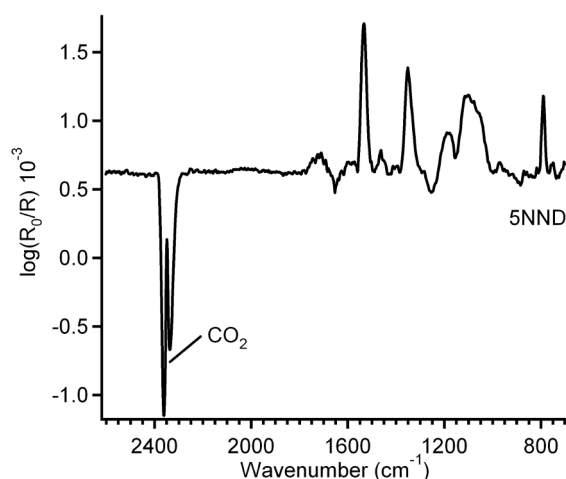


Figure SI.6: IRRAS spectra of a-C substrates following immersion in 1×10^{-3} M 5NND aqueous solution for 1 h.

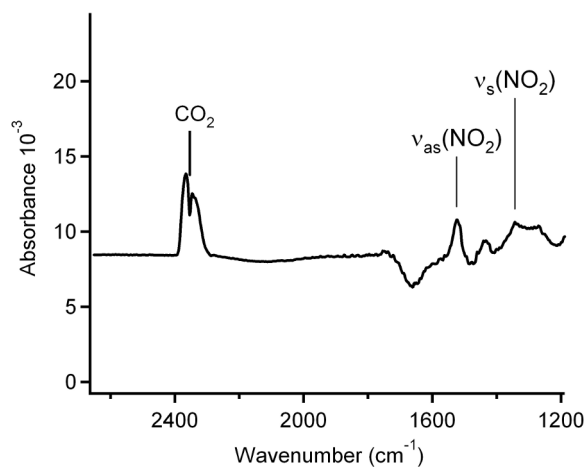


Figure SI.7: ATR-FTIR spectra collected at 5.3 h following injection of a 1×10^{-4} M 4NND aqueous solution