

Naphthalene Diimides – A Prodigy for Molecular Devices

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N,N-Dipentyl-naphthalene diimide ((pent)₂NDI) undergoes a single reduction process either chemically or electrochemically to yield the corresponding radical anion in high yield. The reduction is characterised by dramatic changes in the absorption, emission and EPR spectra of (pent)₂NDI. These changes in spectroscopic output upon an electronic input can be described as a simple "ON/OFF" switching mechanism with which to apply a "bottom-up" approach to molecular device manufacture.

1. Introduction

The design and realisation of a set of molecules capable of performing functions that mimic those executed by macroscopic electronic devices is of great scientific interest.[1] This area of science, broadly termed molecular electronics, employs either single molecules or sets of complex molecular assemblies specifically designed for applications as switches, wires, shuttles, rectifiers and logic gates.[2] One of the driving forces behind this so-called "bottom-up" approach to device manufacture is that the complexities arising from the traditional "top-down" approach to miniaturization, in which elemental arrays are dismantled atom-by-atom, leads to complications e.g. quantum tunnelling effects, the localisation of charge, and fabrication issues.[2,3] The "bottom-up" approach to molecular devices is far more advantageous as it employs a discrete number of molecules designed to achieve a specific function, either on their own, or as components of a more complex supramolecular assembly.

[4,5] Obviously, for device manufacture, the active component(s) must display a number of important features such as long-term stability, ease of fabrication, have an addressable response, have fast response times, a high sensitivity of detection, and may provide attachments to conventional electrodes and semiconductors. Electrochemical and photochemical inputs and outputs are among the easiest to interface to macroscopic systems, making them amenable to the multi-scale engineering required for the eventual creation of pragmatic devices. This view is strongly supported by theoretical calculations that suggest reversible electron transfer can serve as the basis for a molecular switch.[6] Hence, components that have the ability to act as an efficient electron acceptor, and that can be functionalised easily so as to interface with electrodes show promise as molecular electronic components. Looking for a simple and effective system working at the molecular level, we turned our attention to the naphthalene diimides (NDI). Here we describe how a molecule can be used to perform simple logic operations^{1,2} through spectroscopic addressable outputs, such as EPR spectroscopy, fluorimetry and UV-Vis spectroscopy (Fig. 1). The inputs necessary to invoke the addressable output can be electronic or chemical - bridging the transition period between nanometer scale devices and those used in the macroscopic world.

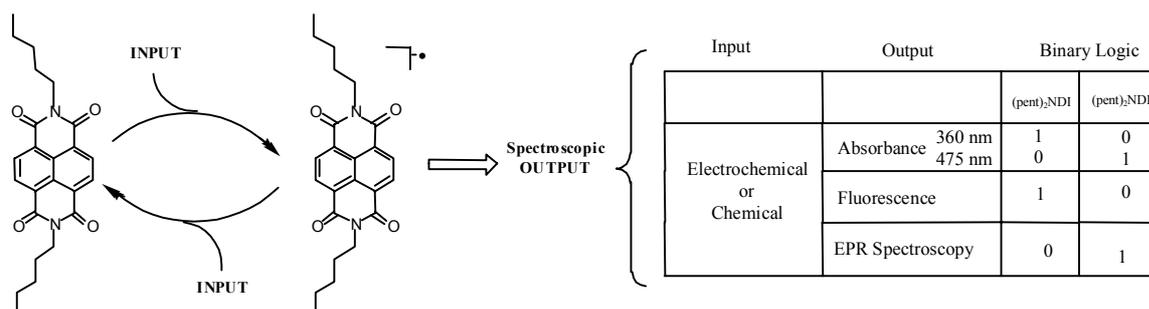


Fig 1. Electrochemical or chemical reduction of (pent)₂NDI leads to dramatic changes in a range of spectroscopic outputs which can be interpreted as simple binary logic operations.

2. Methods

Cyclic voltammetry was performed on a Bioanalytical System BAS model 100W at 20±2°C using tetrabutylammonium hexafluorophosphate as supporting electrolyte. All potentials are estimated against potentials of the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. The analyzed solutions were purged with solvent saturated nitrogen prior to experiments and blanketed with nitrogen during the experiments. Optically transparent thin-layer electrolysis (OTTLE) experiments were conducted on Varian Cary 5 UV-VIS-NIR spectrophotometer (Varian OS2 software) supported with a Bioanalytical System (BAS). The experiments were performed in a 1 mm quartz cuvette at a platinum gauze electrode. Platinum wire was used as the auxiliary electrode and Ag/AgCl in 3 M KCl as the reference electrode. Electron paramagnetic resonance measurements were performed at X-band frequencies with either a Varian E-12 spectrometer (~ 9.1 GHz) or a Bruker ESP380 spectrometer (~ 9.7 GHz). Fluorescence spectra were obtained on Perkin Elmer Luminescence Spectrometer LS50B supported with FLWinLab 3.0 software package.

3. Results

Electrochemical reduction of a DMF solution of (pent)₂NDI ($E_{1/2} = -1.0$ V vs Fc/Fc⁺) led to the formation of strong electronic transitions in the visible spectrum at 476 nm ($\epsilon = 30000$ dm³mol⁻¹cm⁻¹), 608 nm ($\epsilon = 7800$ dm³mol⁻¹cm⁻¹), 683 ($\epsilon = 3500$ dm³mol⁻¹cm⁻¹) and 763 nm ($\epsilon = 6000$ dm³mol⁻¹cm⁻¹) attributed to the formation of (pent)₂NDI⁻ (Fig. 1). The high stability of the radical anion generated can be adjudged by the intense purple colour of the resulting solution, which persists for hours under aerobic conditions. Oxidation of the radical anion, either through aerial oxidation or electrochemically leads to the regeneration of the starting (pent)₂NDI without a significant yield loss, as indicated by OTTL experiments or from the values of the limiting current before and after electrolysis.

Despite recent developments in the complexity of logic operations exhibited by molecular devices, by far the most common of the spectroscopic outputs utilised are absorbance and emission spectroscopy. Absorbance output is less sensitive than fluorescence as a means of detection but allows for multi-operations to occur. For example, absorbance shows regions where some wavelengths are switched "off-on" (e.g. 476 nm) and some when it is switched "on-off" (e.g. 360 nm) at the same time (Fig. 2). Thus opposite switching actions can be displayed by one molecular system.

In terms of molecular logic utilising one input and either transmission or absorbance as an output, YES (PASS) and NOT logic can be demonstrated by monitoring the appropriate wavelengths. YES is obtained at 480 nm, when a high input gives a high output; and a low input gives a low output. NOT logic corresponds to an inversion of YES logic and is exhibited at 380 nm. Monitoring the isobestic points (417 nm) gives a low value irrespective

of input and thus corresponds to PASS 0. NOT logic can also be expressed through the change in fluorescence output ($\lambda_{em} = 565 \text{ nm}$) of $(\text{pent})_2\text{NDI}$, which is reduced in intensity upon its conversion to $(\text{pent})_2\text{NDI}^-$ using either electrochemical or chemical means using cobaltacene ($E_{1/2} = -1.3 \text{ V vs Fc/Fc}^+$) as the chemical reductant.

EPR as a technique has not previously been explored in any great detail as an output, although its high sensitivity and fast timescale of resolution (GHz) make it an appropriate technique. Samples of $(\text{pent})_2\text{NDI}^-$ were prepared by bulk electrolysis of a solution of $(\text{pent})_2\text{NDI}$ in DMF. In frozen solution (glass) at 150 K a single strong line devoid of any hyperfine structure was observed at $g \sim 2.003$. The complexity of the signal changed in the liquid phase at 295 K, where anisotropic g and nuclear hyperfine interactions are averaged to zero. The multi-line spectrum shown in Figure 3 was observed for a 0.1 mM solution of $(\text{pent})_2\text{NDI}$ in *N,N*-dimethylformamide. This is centered around $g \sim 2.004$ and exhibits 13 groups of 5 lines each. Spectrum simulations using the Bruker SOPHE software [7] showed uniquely that the 13 groups arise from the isotropic hyperfine interaction of the unpaired electron with 2 equivalent nitrogen nuclei ($A_N(\text{iso}) = 0.9 \times 10^{-4} \text{ cm}^{-1}$) and 4 equivalent protons ($A_{H1}(\text{iso}) = 1.8 \times 10^{-4} \text{ cm}^{-1}$) of the naphthalene diimide unit. The splitting of each group into a further 5 lines arises from a smaller interaction with four external NCH_2 protons ($A_{H2}(\text{iso}) = 0.2 \times 10^{-4} \text{ cm}^{-1}$). Similar 13 line spectra are also obtained upon the addition of cobaltacene to $(\text{pent})_2\text{NDI}$ in DMF. In each case, the strong signal generated upon reduction of the EPR silent $(\text{pent})_2\text{NDI}$ can be applied as a YES operation.

In conclusion, we have shown that the reversible conversion of $(\text{pent})_2\text{NDI}$ to $(\text{pent})_2\text{NDI}^-$ can be monitored by a number of spectroscopic techniques and that these changes

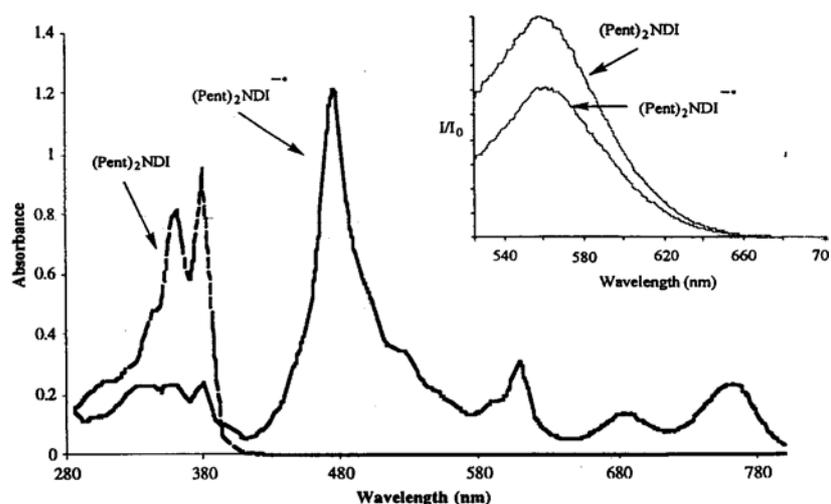


Fig. 2. Electronic spectrum, reduction of 0.4 mM $(\text{pent})_2\text{NDI}$ to $(\text{pent})_2\text{NDI}^-$, $E = -500 \text{ mV vs Ag/AgCl}$, DMF + 0.1 M Bu_4NPF_6 , 293 K. Inset: Emission spectrum ($\lambda_{ex} = 488 \text{ nm}$) of 0.1 mM $(\text{pent})_2\text{NDI}$ in DMF chemically reduced using cobaltacene.

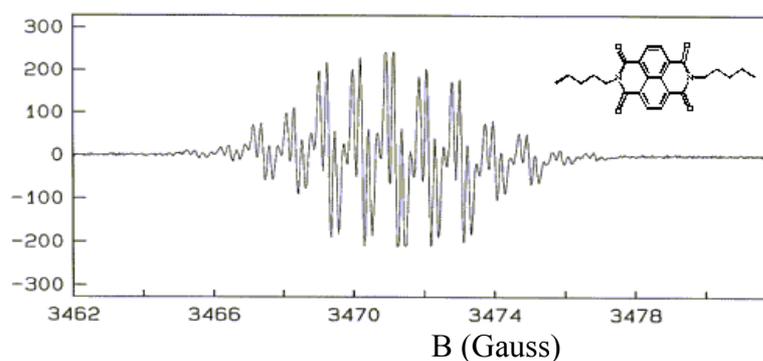


Fig. 3. First derivative EPR spectrum of a 0.1 mM solution of $(\text{pent})_2\text{NDI}$ in *N,N*-dimethylformamide at 295 K. Microwave frequency 9.748 GHz, field correction of + 4.3 G not applied, microwave power 0.05 mW, 50 kHz modulation amplitude 0.1 G.

can be rationalized as very simple molecular logic operations. The power of the naphthalene diimides such as (pent)₂NDI to act as components to more complex molecular electronic devices lies not only in the breadth of spectroscopy offered, their stability and ease of fabrication but in their ability to interact favourably with known supramolecular components.[8] We are also developing the sensory capability of these units.

Acknowledgments

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References

- [1] P. Vettiger and G. Binnig, *Scientific American* **288**, 35 (2002).
- [2] *Molecular Electronics*, J. Jortner and M. Ratner (Eds), Blackwell Science Ltd, Oxford, 1997.
- [3] The first time the concept of the “bottom-up” approach was seriously contemplated was by the Nobel Laureate R.P. Feynman in his historic address “There is Plenty of Room at the Bottom”: R.P. Feynman, *Eng. Sci.* **23**, 22 (1960).
- [4] V. Balzani, A. Credi, S.J. Langford, and J.F. Stoddart, *J. Am. Chem. Soc.*, **119**, 2679 (1997).
- [5] F. Raymo and S. Giordani, *Proc. Natl. Acad. Sci.* **99**, 4941 (2002).
- [6] J.J. Hopfield, J.N. Onuchic, D.N. Beratan, *Science*, **241**, 817 (1988).
- [7] M. Griffin, A. Muys, C. Noble, D. Wang, C. Eldershaw, K. Gates, K. Burrage and G. Hanson, *Mol. Phys. Repts.* **26**, 60 (1999).
- [8] G.D. Fallon, S.J. Langford and M.A.P. Lee, *Chemistry Letters*, 578 (2001).