Downloaded from rsif.royalsocietypublishing.org

JOURNAL OF THE ROYAL SOCIETY Interface

Use of the electrochromic behaviour of lanthanide phthalocyanine films for nicotinamide adenine dinucleotide detection

T Basova, I Jushina, A.G Gürek, V Ahsen and A.K Ray

J. R. Soc. Interface 2008 **5**, 801-806
doi: 10.1098/rsif.2007.1241

References This article cites 24 articles
http://rsif.royalsocietypublishing.org/content/5/24/801.full.html#ref-list-1

Email alerting service Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click here

To subscribe to *J. R. Soc. Interface* go to: http://rsif.royalsocietypublishing.org/subscriptions

This journal is © 2008 The Royal Society

Downloaded from rsif.royalsocietypublishing.org

JOURNAL OF THE ROYAL SOCIETY Interface

J. R. Soc. Interface (2008) **5**, 801–806
doi:10.1098/rsif.2007.1241
Published online 30 October 2007

Use of the electrochromic behaviour of lanthanide phthalocyanine films for nicotinamide adenine dinucleotide detection

T. Basova[1,*], I. Jushina[1], A. G. Gürek[2], V. Ahsen[2,3] and A. K. Ray[4]

[1] *Institute of Inorganic Chemistry, Lavrentiev Prospect 3, Novosibirsk 630090, Russia*
[2] *Department of Chemistry, Gebze Institute of Technology,*
PO Box 141, 41400 Gebze-Kocaeli, Turkey
[3] *TUBITAK-Marmara Research Center, Materials Institute, PO Box 21,*
41470 Gebze-Kocaeli, Turkey
[4] *Department of Materials, Queen Mary, University of London,*
Mile End Road, London E1 4NS, UK

Electrochromic properties of spun films of bis[octakis(hexylthio)phthalocyaninato] dysprosium(III) were investigated for determining nicotinamide adenine dinucleotide hydride (NADH) in water solutions. A spin-coated film deposited on indium tin oxide electrode displays only one redox couple (at $E_{1/2}=0.78$ V). The films of $[(C_6H_{13}S)_8Pc]_2Dy$ were modified chemically or electrochemically for the detection of reduced NADH in water solution. The modified film in the oxidized $([(C_6H_{13}S)_8Pc]_2Dy)^+$ form is believed to be reduced to its neutral form on interaction with NADH.

Keywords: phthalocyanines; bisphthalocyanines; chemical sensors; electrochromic properties

1. INTRODUCTION

Among the variety of phthalocyanine families, intensive research interest has recently been shown in double-decker lanthanide derivatives ($LnPc_2$) for potential device applications due to their high intrinsic conductivity and physically interesting electrochemical and electrochromic properties (Weiss & Fischer 2003). These compounds possess a π-conjugated macrocycle-centred radical as demonstrated by electron spin resonance studies (Chang & Marchon 1981; Bouvet 2003). All lanthanide bis(phthalocyanines) and related double-deckers normally undergo multiple reversible reductions of the π-orbitals of the conjugated macrocycle and a single reversible oxidation when dissolved in non-aqueous media (Buchler & Ng 2000; Kadish *et al.* 2001). Their interesting electronic properties are due to their neutral radical state and the strong interaction between two tightly bound phthalocyanine rings. For example, an increase in the on-state current by three orders of magnitude was achieved by employing lutetium bisphthalocyanine as a buffer layer in the fabrication of organic thin-film transistors due to its high carrier density (Wang *et al.* 2005).

When substituents are placed on the Pc ring, not only is enhanced solubility of the compound observed, but also a supramolecular organization in thin films can be achieved (Sheng *et al.* 2006). The most common substituents are alkyl, alkoxy or alkoxymethyl chains (Wang *et al.* 2006). Some examples of octakis(alkylthio)-substituted bisphthalocyanines are also available in the literature (Gürek *et al.* 2001). The synthesis of double-decker phthalocyanines with the ability to be deposited in thin films has stimulated the development of novel sensing device structures by exploiting the changes in physicochemical properties of bisphthalocyanines caused by their ambient environment (de Saja & Rodriguez-Mendez 2005). UV–visible spectra of thin films of bisphthalocyanines are susceptible to the exposure of electron donor and electron acceptor gases. Langmuir–Blodgett films of erbium bis[octakis(octyloxy)phthalocyaninato] complex were exploited for use in different types of room temperature conductometric NO_2 sensors (Xie *et al.* 2001, 2003). The exposure of $LuPc_2$ to NO_x caused the shift of the Q-band to a higher wavelength, leading a change in the film colour from green to red. The exposure to ammonia, an electron donor gas, produced a shift of the Q-band to a lower wavelength and films became blue. Colours and UV–visible spectra of oxidized and reduced forms of bisphthalocyanines were found to depend upon different types of substituents (Gorbunova *et al.* 2001). The Elovich-type desorption of the electron acceptor NO_2 gas on Langmuir–Blodgett films of alkylthio-substituted bis(naphthalocyaninato) rare earth complexes was identified from absorption spectroscopic studies (Chen *et al.* 2004). A voltammetric sensor array was fabricated using lutetium, gadolinium and

---

[*] Author for correspondence (tbasova@mail.ru).

Received 28 September 2007
Accepted 8 October 2007

This journal is © 2007 The Royal Society

Downloaded from rsif.royalsocietypublishing.org

praseodymium bisphthalocyaninates and was found to be capable of discriminating between different types of wines with a good-quality performance of an electronic tongue (Parra *et al.* 2004). Using tert-butylcalix[4]arene bridged bis double-decker lutetium(III) phthalocyanines as sensing membrane, AT-cut quartz crystal resonator sensors exhibited a fast and reversible response to the presence of solvent vapours in the particle per million range (Ceyhan *et al.* 2007).

This article presents the results of an experimental investigation of the electrochromic properties of spun films of bis[octakis(hexylthio)phthalocyaninato] dysprosium(III) and application of these properties for the detection of nicotinamide adenine dinucleotide hydride (NADH) in water solutions. This bisphthalocyanine molecule with long alkyl substituents is soluble in common organic solvents and exhibits liquid crystalline properties. The oriented films of these molecules may, therefore, be easily deposited by the spin-coating technique while thin film formation of unsubstituted bisphthalocyanine films is achieved only by thermal vacuum deposition. The thermally induced molecular reorganization within spin-coated films of $[(C_6H_{13}S)_8Pc]_2Dy$ has already been reported (Gürek *et al.* 2006).

Nicotinamide adenine dinucleotide (NAD^+) is found in all living systems and takes part in many oxido-reductase reactions. In its reduced and enzymatically active form, the NADH molecule transfers two electrons and a proton to a substrate in the presence of a suitable enzyme, resulting in the oxidation of NADH to NAD^+. The ratio of NAD^+ to NADH may often indicate the metabolic state associated with several age-related diseases such as diabetes, cancers and neurodegenerative diseases (Lin & Guarente 2003). The complex redox behaviour exhibited by the NAD^+/NADH couple under physiological conditions has prompted extensive electrochemical studies of the reaction. By using concentrations up to 8 mM, the electrochemical oxidation of NADH was investigated on different types of modified electrodes for enzyme-based electrocatalytic systems (Rao *et al.* 1999; Bartlett & Simon 2003; Banks & Compton 2005; Deore & Freund 2005). The detection limit was found to be as small as 0.3 μM using the conductometric technique. Exploitation of electrochromic properties of $[(C_6H_{13}S)_8Pc]_2Dy$ films for the determination of NADH in phosphate buffer water solution is, therefore, of practical importance.

2. MATERIAL AND METHODS

The material used for the characterization of spin-coated films is bis[4,5,4′,5′,4″,5″,4‴,5‴-(octakis(hexylthio) phthalocyanine)] of dysprosium(III) $[(C_6H_{13}S)_8Pc]_2Dy$ (figure 1), the synthesis of which was reported earlier (Gürek *et al.* 2006). β-nicotinamide adenine dinucleotide, reduced disodium salt hydrate (NADH>98%), was obtained from Sigma. The films of dysprosium phthalocyanine were deposited by spin-coating the spreading solution of phthalocyanine molecules in chloroform (5 mg ml^{-1}). The speed of substrate rotation was 3000 rotations per minute (rpm). Spinning was continued for 30 s during which time the solvent had evaporated to generate a film of the phthalocyanine derivative. The indium tin oxide (ITO)-coated slides were used as substrates.

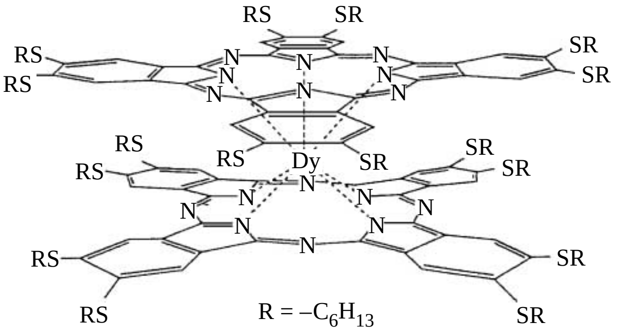

Figure 1. Chemical structure of bis[4,5,4′,5′,4″,5″,4‴,5‴-octakis(hexylthio)phthalocyanine] of dysprosium(III) $[(C_6H_{13}S)_8Pc]_2Dy$.

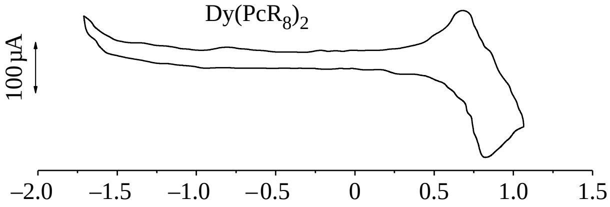

Figure 2. Cyclic voltammograms of in a spin-coated $[(C_6H_{13}S)_8Pc]_2Dy$ film on ITO electrode in phosphate buffer at 25°C. Scan rate, 0.1 V s^{-1}.

The films were modified either chemically (exposing the films in HNO_3 vapours) or electrochemically. The electrochemical oxidation behaviour was investigated in a three-electrode cell with 0.05 M phosphate buffer KH_2PO_4+0.05 M K_2HPO_4 (KH_2PO_4/K_2HPO_4, pH=7.1±0.05) aqueous solution as an electrolyte. The working electrode was an ITO plate on which the $[(C_6H_{13}S)_8Pc]_2Dy$ was deposited. A saturated calomel electrode (SCE) and a platinum sheet were used as the reference electrode and counter electrode, respectively. Electrochromical spectral changes were monitored using a UV–VIS spectrophotometer (Shimadzu UV–VIS-3101PC) scanning in the range of 400 to 900 nm along with a standard 1 cm quartz cell and the same electrodes and electrolytes with ITO electrode held perpendicular to the light beam. Polarized Raman spectra were recorded with a Triplemate, SPEX spectrometer equipped with a multichannel detector, LN-1340PB, Princeton Instruments in back-scattering geometry. The spectral resolution was 5 cm^{-1}. The 488 nm line of a 50 mW Ar-laser was used for spectral excitation.

3. RESULTS AND DISCUSSION

In this work, the electrochemical properties were measured for the films of $[(C_6H_{13}S)_8Pc]_2Dy$ spin coated on ITO slides. Spin-coated films displayed only one redox couple (at $E_{1/2}=0.78$ V versus SCE; figure 2). Lutetium phthalocyanine with the same type of substituents exhibited a transition to the oxidized form at $E_{1/2}=0.88$ V (Yilmaz *et al.* 2003). No

Downloaded from rsif.royalsocietypublishing.org

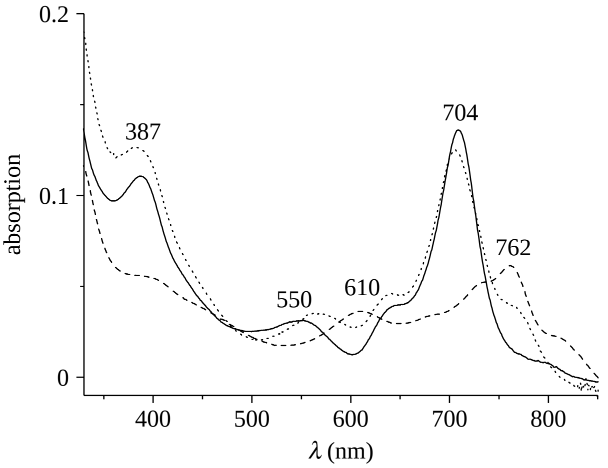

Figure 3. Electronic absorption spectra of a spin coated $[(C_6H_{13}S)_8Pc]_2Dy$ film on ITO electrode in phosphate buffer at 25°C: neutral form (solid line), electrochemically oxidized form (dashed line) and film after the addition of NADH solution (5×10^{-3} M) to the phosphate buffer (dotted line). The spectra of the electrochemically oxidized form and the film after the addition of the NADH solution to the phosphate buffer have been recorded at an applied potential of +0.85 V versus SCE.

reductions were observed under the experimental conditions. This observation was similar to the behaviour reported by Toupance *et al.* (1999) for $Lu[(C_nH_{2n+1}OCH_2)_8Pc]_2$, where it was difficult to obtain a well-defined first reduction peak in a LB film of the compound. The redox potentials of the double-decker lutetium(III) phthalocyanines was found to depend greatly upon the type of supporting electrolyte used. The reduced anionic forms of double-decker lutetium(III) phthalocyanines are believed to be associated with mono- and divalent alkali metal cations and this association also occurred with the cations in our $4C_8P^+Br^-$ matrix, thus leading to a larger stabilization of the electroreduced forms of phthalocyanine in the film. A similar result was also obtained for the lutetium(III) analogue of $[(C_6H_{13}S)_8Pc]_2Dy$ investigated in this work (Yilmaz *et al.* 2003).

For the detection of NADH in water solution, the films of $[(C_6H_{13}S)_8Pc]_2Dy$ were modified chemically or electrochemically. By applying a potential of +0.85 V the oxidized form was obtained. The UV–visible spectra of $[(C_6H_{13}S)_8Pc]_2Dy$ films in neutral and oxidized forms are presented in figure 3. The evolution of the spectral change upon the first oxidation is similar to that for the $[(C_6H_{13}S)_8Pc]_2Lu$ analogue (Yilmaz *et al.* 2003). The colour of the film was observed to change from brown (neutral form) to green.

The chemical oxidation was achieved by exposing the films to HNO_3 vapours for approximately 2 min in a closed cell. The films were taken out of the cell, washed with water and dried with argon. The conversion to the oxidized form was controlled by recording the UV–visible spectra of the films. The spectrum of the chemically oxidized form is presented in figure 4. The difference between the absorption spectra of the electrochemically and chemically oxidized films may be attributed to the combination of structural changes associated with redox processes and an effect of protons due to the oxidation by NO_2 vapours from HNO_3 solution.

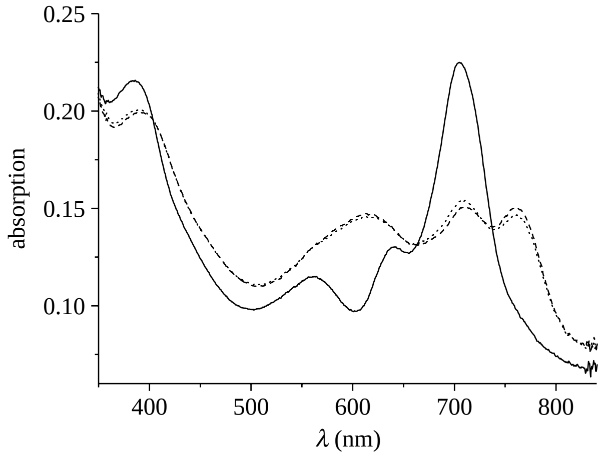

Figure 4. Electronic absorption spectra of $[(C_6H_{13}S)_8Pc]_2Dy$ in a spin-coated film: neutral form (solid line), chemically oxidized form (dashed line), and chemically oxidized form (dotted line) after 2 h.

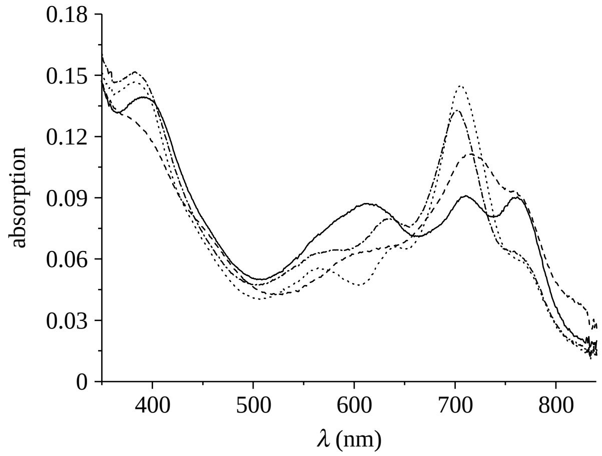

Figure 5. Electronic absorption spectra of $[(C_6H_{13}S)_8Pc]_2Dy$ in a spin-coated film: chemically oxidized form in phosphate buffer (solid line), after interaction with NADH (10^{-4} M) in phosphate buffer solution (dashed line), after interaction with NADH in phosphate buffer (10^{-3} M; dot-dashed line), and after interaction with NADH (5×10^{-3} M) in phosphate buffer (dotted line).

The oxidized form is stable in open air for at least 2 h and the spectra of the mixture of oxidized and neutral forms were observed after this period of time. The spectrum of the film with the oxidized form immersed in the buffer solution is not significantly different from the one recorded in open air (figure 5, solid line). The modified films were then immersed into the cell with NADH in phosphate buffer solution and the spectra were recorded again. The spectra of $[(C_6H_{13}S)_8Pc]_2Dy$ films after the interaction with NADH solutions of three different concentrations are shown in figure 5. The intensity of the original Q-band at 762 nm corresponding to the oxidized form decreases while the intensity of the band at approximately 708 nm increases, corresponding to the neutralization of the oxidized phthalocyanine. The dependence of the optical density of these bands on the NADH concentration is presented in table 1. The rise

Downloaded from rsif.royalsocietypublishing.org

Table 1. Dependence of optical density (D) on the NADH concentrations (figure 5).

NADH concentration (mol l^{-1})	D at 708 nm	D at 762 nm
10^{-4}	0.110	0.092
10^{-3}	0.128	0.063
5×10^{-3}	0.144	0.060

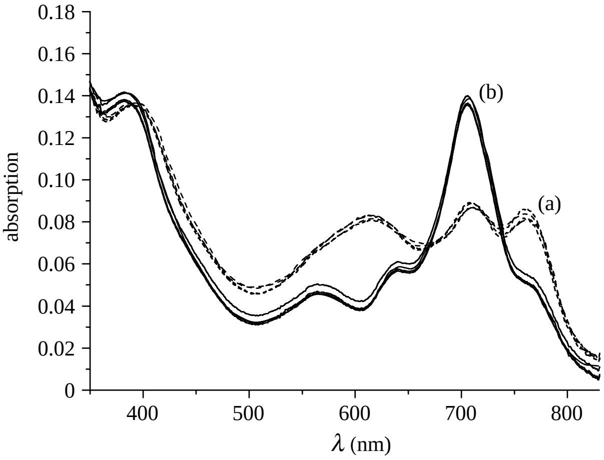

Figure 6. Electronic absorption spectra of $[(C_6H_{13}S)_8Pc]_2Dy$ in a spin-coated film after 1st, 5th, 15th and 20th cycles of oxidation by HNO_3 vapour (a) and subsequent interaction with NADH (5×10^{-3} M) in phosphate buffer solution (b).

in peak intensity at 708 nm, together with a small diminishing peak at 762 nm with the increase in concentrations of NADH from 10^{-4} to 5×10^{-3} M, points to an increase in the proportion of the neutral form. It should also be pointed out at this stage that the change in the film colour from green (in oxidized form) to brown was observed.

The chemical forms in NADH solution were not specially investigated in this work. However, on the basis of the absorption spectroscopy data, the following scheme of interaction of bis[octakis(hexylthio)phthalocyaninato] dysprosium(III) films with NADH may be proposed.

The processes of reduction and oxidation of $[(C_6H_{13}S)_8Pc]_2Dy$ films were found to be reversible. After reduction, the films were oxidized with HNO_3 vapours or electrochemically again and the procedure was repeated 20 times over 2 days to confirm the reproducibility. The spectra after some cycles of the film interaction with NADH and subsequent film oxidation by HNO_3 vapours are presented in figure 6. It can be seen that both spectra retained their characteristic features after repeated oxidation and reduction processes. As shown in figure 7, the neutral and electrochemically oxidized forms of $[(C_6H_{13}S)_8Pc]_2Dy$ can be clearly identified using Raman spectra owing to the changes observed in the relative intensities of the determined vibrations. Vibrational characterization of neutral, oxidized and reduced forms of differently substituted bisphthalocyanine was performed including surface-enhanced resonant Raman scattering and infrared techniques (Aroca *et al.* 1992; Faulques *et al.* 2000; Bao *et al.* 2006). The qualitative assignment of the vibrations of $[(C_6H_{13}S)_8Pc]_2Dy$ was carried out on the basis of a comparison with Raman spectra of different bisphthalocyanine derivatives and the results are summarized in table 2. The change in the relative intensities occurred for molecular vibrations associated with the central phthalocyanine macrocycle. In fact, macrocycle breathing at 686 and 752 cm^{-1} and pyrrole and isoindole stretching vibrations in the range

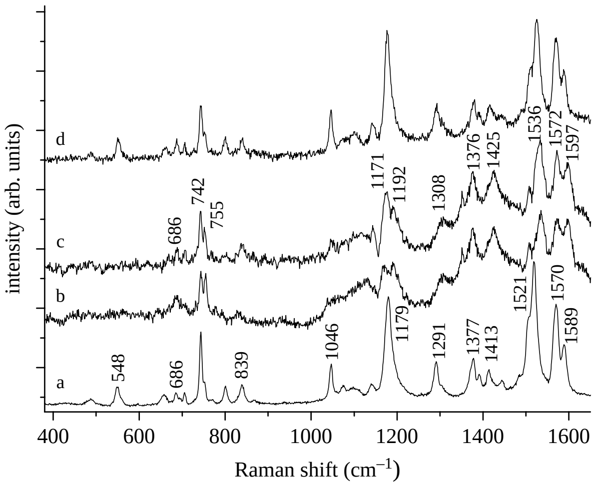

Figure 7. Raman spectra of a spin-coated $[(C_6H_{13}S)_8Pc]_2Dy$ film on ITO electrode in phosphate buffer at 25°C: (a) neutral form, (b) electrochemically oxidized form, (c) chemically oxidized form and (d) film after the addition of NADH solution.

Table 2. Characteristic Raman band (cm^{-1}) of neutral and oxidized form of $[(C_6H_{13}S)_8Pc]_2Dy$.

neutral form	oxidized form	assignment
487	483	Pc breathing
548		Pc breathing
658	644	Pc breathing
686	686	Pc breathing
706		
742	742	C–H bending
752	755	Pc breathing
771	778	C=N stretching
801		
839	832	Pc breathing
1046	1041	C–H bending
1074		C–H bending
1142	1130	pyrrole breathing
1179	1171	C–H bending
1192	1192	C–H bending
1291	1308	C–H bending
	1352	pyrrole stretching
1377	1376	isoindole stretching
1391		isoindole stretching
1413	1425	isoindole stretching
1443		isoindole stretching
1506	1507	coupling of pyrrole and aza stretching
1521	1536	aza stretching
1570	1572	benzene stretching
1589	1597	benzene stretching

Downloaded from rsif.royalsocietypublishing.org

1300–1530 cm^{-1} are believed to be strongly affected by the change in electronic distribution due to oxidation of the phthalocyanine molecule. The Raman spectra shown in figure 7*d* obtained after the addition of NADH solution are believed to be characteristic of the neutral form since it is similar to the spectrum of the initial form before chemical or electrochemical oxidation (figure 7*a*). Spectroelectrochemical data indicate the reduction of $([(C_6H_{13}S)_8Pc]_2Dy)^+$ form to the neutral form associated with the interaction with NADH.

4. CONCLUSION

Films of bis[octakis(hexylthio)phthalocyaninato] dysprosium(III) $[(C_6H_{13}S)_8Pc]_2Dy$ were deposited on an ITO electrode, and cyclic voltammogramic measurements showed the presence of only one redox couple at $E_{1/2}=0.78$ V. For the detection of NADH in water solution, the films of $[(C_6H_{13}S)_8Pc]_2Dy$ were modified chemically or electrochemically. UV–visible spectra for both chemically and electrochemically modified films were investigated and the reduction and oxidation processes were found to be reversible. Neutral and electrochemically oxidized forms of $[(C_6H_{13}S)_8Pc]_2Dy$ were identified using Raman spectra. The reduction of $([(C_6H_{13}S)_8Pc]_2Dy)^+$ to $[(C_6H_{13}S)_8Pc]_2Dy$ form was associated with the interaction with NADH. The change in the film colour from green (in oxidized form) to brown was visually observed.

This work was supported by the Royal Society funding for the International Joint Project.

REFERENCES

Aroca, R., Battisti, D., Luk'yanetz, E. A. & Tomilova, L. G. 1992 Surface enhanced Raman-scattering of green and blue lutetium diphthalocyanine. *J. Mol. Liquids* **53**, 147–153. (doi:10.1016/0167-7322(92)80056-N)

Banks, C. E. & Compton, R. G. 2005 Exploring the electrocatalytic sites of carbon nanotubes for NADH detection: an edge plane pyrolytic graphite electrode study. *Analyst* **130**, 1232–1239. (doi:10.1039/b508702c)

Bao, M., Wang, R. M., Rintoul, L., Liu, Q. Y., Arnold, D. P., Ma, C. Q. & Jiang, J. Z. 2006 Vibrational spectroscopy of phthalocyanine and naphthalocyanine in sandwich-type (na)phthalocyaninato and porphyrinato rare earth complexes—part 14. The infrared and Raman characteristics of phthalocyanine in "pinwheel-like" homoleptic bis[1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninato] rare earth(III) double-decker complexes. *Vib. Spectrosc.* **40**, 47–54. (doi:10.1016/j.vibspec.2005.07.001)

Bartlett, P. N. & Simon, E. 2003 Measurement of the kinetic isotope effect for the oxidation of NADH at a poly(aniline)-modified electrode. *J. Am. Chem. Soc.* **125**, 4014–4015. (doi:10.1021/ja028943e)

Bouvet, M. 2003 Radical phthalocyanines and intrinsic semiconduction. In *Porphyrin handbook*, vol. 19 (eds K. M. Kadish, K. M. Smith & R. Guilard), pp. 37–104. New York, NY: Academic Press.

Buchler, J. W. & Ng, D. K. P. 2000 Metal tetrapyrrole double- and triple-deckers with special emphasis on porphyrin systems. In *Porphyrin handbook*, vol. 3 (eds K. M. Kadish, K. M. Smith & R. Guilard), pp. 245–294. New York, NY; Burlington MA: Academic Press.

Ceyhan, T., Altindal, A., Ozkaya, A. R., Erbil, M. K. & Bekaroglu, O. 2007 Synthesis, characterization, and electrochemical, electrical and gas sensing properties of a novel tert-butylcalix[4]arene bridged bis double-decker lutetium(III) phthalocyanine. *Polyhedron* **26**, 73–84. (doi:10.1016/j.poly.2006.07.035)

Chang, A. T. & Marchon, J. C. 1981 Preparation and characterization of oxidized and reduced forms of lutetium diphthalocyanine. *Inorg. Chim. Acta* **53**, L241–L243. (doi:10.1016/S0020-1693(00)84810-0)

Chen, Y. L., Liu, H. G., Pan, N. & Jiang, J. Z. 2004 Langmuir–Blodgett films of substituted bis(naphthalocyaninato) rare earth complexes: structure and interaction with nitrogen dioxide. *Thin Solid Films* **460**, 279–285. (doi:10.1016/j.tsf.2004.02.003)

Deore, B. A. & Freund, M. S. 2005 Reactivity of poly (anilineboronic acid) with NAD(+) and NADH. *Chem. Mater.* **17**, 2918–2923. (doi:10.1021/cm050647o)

de Saja, J. A. & Rodriguez-Mendez, M. L. 2005 Sensors based on double-decker rare earth phthalocyanines. *Adv. Colloid Interface Sci.* **116**, 1–11. (doi:10.1016/j.cis.2005.03.004)

Faulques, E., Baibarac, M., Galmiche, L., L'Her, M., Pondaven, A. & Baltog, I. 2000 SERS spectra of mono and bisphthalocyanine complexes deposited on Ag and Au supports. *Spectrosc. Lett.* **33**, 625–631.

Gorbunova, Y., Rodriguez-Mendez, M. L., Kalashnikova, I. P., Tomilova, L. & de Saja, J. A. 2001 Langmuir–Blodgett films of bis(octakispropyloxy) samarium bisphthalocyanine. Spectroscopic and gas-sensing properties. *Langmuir* **17**, 5004–5010. (doi:10.1021/la0102760)

Gürek, A. G., Ahsen, V., Luneau, D. & Pècaut, J. 2001 Synthesis, structure, spectroscopic properties, and magnetic properties of an octakis(alkylthio)-substituted lutetium(III) bisphthalocyanine. *Inorg. Chem.* **40**, 4793–4797. (doi:10.1021/ic010240v)

Gürek, A. G., Basova, T., Luneau, D., Lebrun, C., Kol'tsov, E., Hassan, A. & Ahsen, V. 2006 Synthesis, structure, and spectroscopic and magnetic properties of mesomorphic octakis(hexylthio)-substituted phthalocyanine rare-earth metal sandwich complexes. *Inorg. Chem.* **45**, 1667–1676. (doi:10.1021/ic051754n)

Kadish, K. M., Nakanishi, T., Gurek, A. G., Ahsen, V. & Yilmaz, I. 2001 Electrochemistry of a double-decker lutetium(III) phthalocyanine in aqueous media. The first evidence for five reductions. *J. Phys. Chem. B* **105**, 9817–9821. (doi:10.1021/jp012636y)

Lin, S. J. & Guarente, L. 2003 Nicotinamide adenine dinucleotide, a metabolic regulator of transcription, longevity and disease. *Curr. Opin. Cell Biol.* **15**, 241–246. (doi:10.1016/S0955-0674(03)00006-1)

Parra, V., Hernando, T., Rodriguez-Mendez, M. L. & de Saja, J. A. 2004 Electrochemical sensor array made from bisphthalocyanine modified carbon paste electrodes for discrimination of red wines. *Electrochim. Acta* **49**, 5177–5185. (doi:10.1016/j.electacta.2004.06.031)

Rao, T. N., Yagi, I., Miwa, T., Tryk, D. A. & Fujishima, A. 1999 Electrochemical oxidation of NADH at highly boron-doped diamond electrodes. *Anal. Chem.* **71**, 2506–2511. (doi:10.1021/ac981376m)

Sheng, N., Li, R. J., Choi, C. F., Su, W., Ng, D. K. P., Cui, X. G., Yoshida, K., Kobayashi, N. & Jiang, J. Z. 2006 Heteroleptic bis(phthalocyaninato) europium(III) complexes fused with different numbers of 15-crown-5 moieties. Synthesis, spectroscopy, electrochemistry, and supramolecular structure. *Inorg. Chem.* **45**, 3794–3802. (doi:10.1021/ic0600937)

Toupance, T., Plichon, V. & Simon, J. 1999 Substituted bis(phthalocyanines): electrochemical properties and probe beam deflection (mirage) studies. *New J. Chem.* **23**, 1001–1006. (doi:10.1039/a905248h)

Downloaded from rsif.royalsocietypublishing.org

Wang, J., Wang, H., Zhang, J., Yan, X. & Yan, D. 2005 Organic thin-film transistors with improved characteristics using lutetium bisphthalocyanine as a buffer layer. *J. Appl. Phys.* **97**, 026 106. (doi:10.1063/1.1840093)

Wang, X. Y., Chen, Y. L., Liu, H. G. & Jiang, J. Z. 2006 Spectroscopic and structural characteristics of Langmuir–Blodgett films of bis[2,3,9,10,16,17,24,25-octakis(octyloxy) phthalocyaninato] rare earth complexes. *Thin Solid Films* **496**, 619–625. (doi:10.1016/j.tsf.2005.09.131)

Weiss, R. & Fischer, J. 2003 Lanthanide phthalocyanine complexes. In *The porphyrin handbook*, vol. 16 (eds K. M. Kadish, K. M. Smith & R. Guilard), pp. 171–246, NewYork, NY: Academic Press.

Xie, D., Jiang, Y., Jiang, J., Wu, Z., Li, Y. & Liang, B. J. 2001 Gas sensitive Langmuir–Blodgett films based on erbium bis[octakis(octyloxy)phthalocyaninato] complex. *Sensor Actuat. B Chem.* **77**, 260–263. (doi:10.1016/S0925-4005(01)00743-2)

Xie, D., Jiang, Y. D., Ren, T. L. & Liu, L. T. 2003 A novel NO_2 gas sensor based on bis[phthalocyaninato] samarium complex/silicon hybrid charge-flow transistor. *IEEE Sensors J.* **3**, 796–800. (doi:10.1109/JSEN.2003.820363)

Yilmaz, I., Nakanishi, T., Gurek, A. G. & Kadish, K. M. 2003 Electrochemical and spectroscopic investigation of neutral, oxidized and reduced double-decker lutetium(III) phthalocyanines. *J. Porphyr. Phthalocya.* **7**, 227–238.