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Stabilization of naphthalene-1,8:4,5-dicarboximide radicals in zirconium phosphonate solid materials and thin films

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Solid zirconium phosphonate (ZP) materials were prepared by direct precipitation of *N*,*N*′-bis(2-phosphonoethyl)naphthalene-1,8:4,5-dicarboximide (NDI-BP) from aqueous solution by addition of a $ZrOCl_2$ solution. Slow precipitation in the presence of HF gave crystalline NDI-BP/ZP materials with a layered structure, whereas rapid precipitation in the absence of HF gave mainly amorphous materials. When $ZrOCl_2$ solutions were added to photolyzed NDI-BP solutions, radical-doped solid materials with intense EPR response were obtained. Multilayer thin films of NDI-BP/ZP were grown on gold substrates in a layer-by-layer fashion, by exposing the phosphonate-rich modified surface to solutions of $ZrOCl_2$ and NDI-BP, alternately. Electrochemical reduction of 20-layer films resulted in the formation of stable NDI-BP radical anions and dianions.

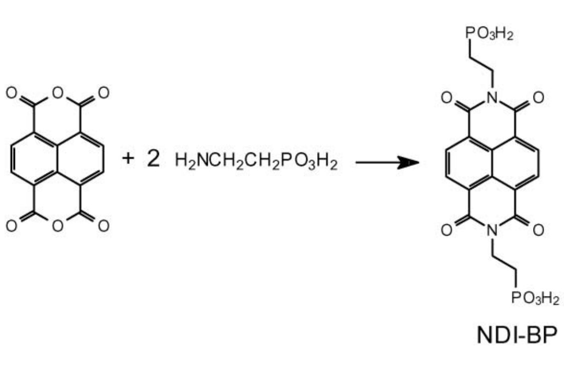
Introduction

Naphthalene-1,8:4,5-dicarboximides (NDIs) constitute a class of compounds of great current interest, mainly because of their remarkable electrochemical[1–3] and photochemical[4–6] properties. The most important feature of NDIs is their facile reduction to give stable radical anions. NDI radical anions have been generated by either chemical,[7] electrochemical[1–3] and photochemical[4–6] means. Due to these properties, NDIs have potential usefulness in a series of applications, such as laser dyes in the NIR spectral region,[7] organic conducting materials[8] and in photoinduced intramolecular charge-transfer.[4,9–13] Radical formation is also behind the biological effects of NDIs, like the oxidative photocleavage of DNA,[14–16] which makes NDIs potential candidates in photodynamic therapy for the treatment of cancer.

In order to fully exploit the potential of NDIs, however, it is highly desirable to incorporate the molecules into organized materials, particularly those in which the aromatic rings are held in a π-stacked arrangement,[7] thus favoring radical stabilization, since the lone electron can be delocalized over several aromatic rings. A promising way to achieve π-stacking is to incorporate the organic molecules in zirconium phosphonate (ZP) layered materials.[17–19] ZP materials are usually prepared by mixing aqueous solutions of a zirconium salt and an organic bisphosphonate, resulting in the precipitation of solids with a layered structure, analogous to that of inorganic α-zirconium phosphate. Most organic compounds with two phosphonate groups on opposite sides can be incorporated into ZP materials (as long as the cross section of the molecule does not exceed 25 Å^2).[18,19]

We describe here the preparation and properties of layered NDI-containing zirconium phosphonate solid materials (NDI-BP/ZP). For this purpose, we synthesized *N*,*N*′-bis(2-phosphonoethyl)naphthalene-1,8:4,5-dicarboximide (NDI-BP) [eqn. (1)], an NDI-bisphosphonate designed specially to be incorporated into ZP compounds. The NDI-BP/ZP materials studied here were capable of stabilizing photogenerated imide radicals for periods as long as seven days, and are therefore potential candidates for light harvesting devices.

In addition to the solid materials, we also describe here the construction of self-assembled multilayer thin films of NDI-BP/ZP, grown on gold surfaces in a layer-by-layer fashion, according to the method developed by Mallouk *et al.*[19–21] Stable imide radicals were produced in the films by electrochemical reduction. These films are analogous to the NDI-BP/ZP thin films grown on quartz and silicon substrates, recently reported by our group.[22] Other authors have used Langmuir–Blodgett (LB)[23–25] or spin-coating[26] methods to prepare NDI-containing thin films. These methods, however, are based on weak interactions between the layers, resulting in films that are both thermally and solvolytically unstable, in contrast to the highly stable films obtained by the zirconium phosphonate method. Monolayers of NDIs covalently attached to gold surfaces have also been reported in the literature, but the technique employed in that case did not allow the assembly of multiple layers.[27]



NDI-BP

(1)

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Experimental

Synthesis of *N*,*N*′-bis(2-phosphonoethyl)naphthalene-1,8:4,5-dicarboximide (NDI-BP)

NDI-BP was synthesized by an adaptation of the previously reported method.[28] A mixture of naphthalene-1,8:4,5-tetracarboxylic dianhydride (Aldrich) (1.04 g, 3.9 mmol) and 2-aminoethylphosphonic acid (Aldrich) (0.97 g, 7.8 mmol) was refluxed in dry *N*,*N*′-dimethylformamide (80 mL) for 20 hours. The mixture was allowed to cool, and the solid formed was filtered off, washed with cold ethanol and dried under vacuum, giving 1.13 g of crude NDI-BP. The product was purified by suspending it in water (150 mL) and slowly adding, under stirring, 6 mL of a 0.2 M NaOH solution (to give pH ∼4), leading to the dissolution of the solid. The resulting solution was filtered and kept for 15 hours in a closed vessel saturated with HCl, causing the precipitation of a slightly yellow solid. The solid was filtered off and washed with 20 mL portions of cold H_2O, followed by cold H_2O–EtOH (1 : 1) and finally cold EtOH. Vacuum drying gave 0.58 g of analytically pure NDI-BP (1.2 mmol, 31% yield). Elemental analysis, infrared and ^{1}H-NMR data were all in agreement with the previously reported data.[28]

Preparation of solid ZP materials

(a) Rapid precipitation method. The neutral NDI-BP/ZP material was prepared by mixing equal volumes of 7 mM aqueous solutions of NDI-BP and $ZrOCl_2$. The precipitated solid was filtered off, washed with water and dried, giving a white powder. Elemental analysis (CHN), calculated (for NDI-BP : Zr 1 : 1): 38.0% C; 2.11% H; 4.92% N. Found: 40.8% C; 4.14% H; 5.31% N. Infrared (cm^{-1}): 1254, 1395, 1802, 1890, 2459, 2593, 2773, 3780. For the preparation of the radical-doped solid, the same procedure was used, but the NDI-BP solution was irradiated for 5 min with a high pressure Hg lamp prior to the addition of the zirconium solution, giving a brown solid. The elemental analysis and infrared spectrum of this solid were very similar to those found for the neutral sample described above. EPR spectra of the solids were registered with a Bruker ER 200D-SRC spectrometer. Powder X-ray diffraction patterns were obtained with a Miniflex Rigaku Diffractometer (CuKα radiation). Conductivity measurements were made with the powders compressed in a glass capillary, as described in the literature.[29]

(b) Slow precipitation method. Hydrofluoric acid (40 μL of a 40% aqueous solution) was added to a solution of $ZrOCl_2$ (10 mg, 0.056 mmol) in 10 mL of water. A solution of NDI-BP (28.6 mg, 0.059 mmol) in water (40 mL) was added to the Zr^{4+} solution. The resulting clear solution was left standing in a closed vessel for seven days, keeping a slow flow of N_2 over the surface. The precipitated white solid was then filtered off, washed with water and dried, giving 31 mg of the NDI-BP/ZP material. Elemental analysis (CHN), calculated: 38.0% C; 2.11% H; 4.92% N. Found: 32.3% C; 2.85% H; 4.86% N. The lower than expected carbon content has been found for other organic ZP materials,[30] and can be attributed to incomplete combustion.

Irradiation experiments

NDI-BP solutions were irradiated with a high pressure Hg lamp (Bausch & Lomb, 200 W). The absorption spectra of the irradiated samples were recorded after selected time intervals.

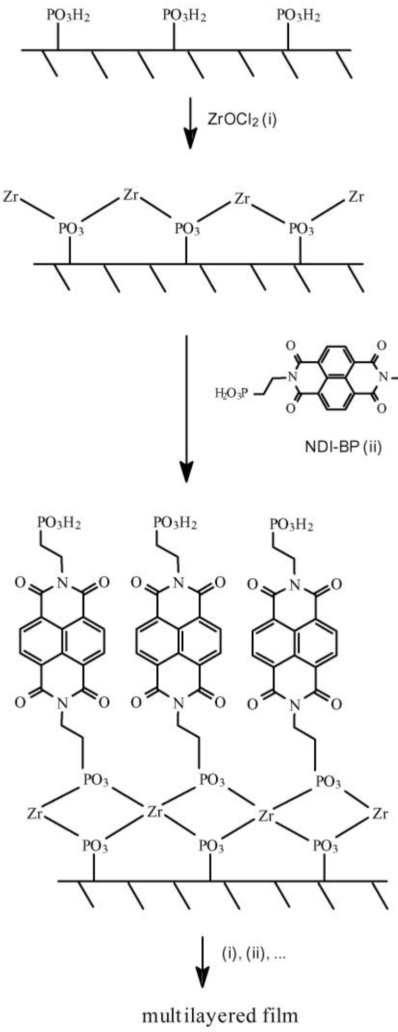
Thin film construction

Gold coated slides were prepared by sputtering gold vapor on borosilicate glass slides, giving a 50 nm thick layer. The gold surfaces were then washed with acetone, then primed by exposure to a 1 M ethanolic solution of 2-mercaptoethanol (48 hours, room temperature), followed by $POCl_3$ in acetonitrile (0.2 M $POCl_3$ + 0.2 M collidine, 15 min, room temperature), giving a surface rich in phosphonate groups. NDI-BP/ZP multilayer films were then grown on this surface by sequential exposure to aqueous solutions of $ZrOCl_2$ (1 mM, 10 min, room temperature) and NDI-BP (0.54 mM, 10 min, room temperature), as shown in Scheme 1. The samples were washed copiously with water between each deposition step.

Cyclic voltammetry

Electrochemical measurements on the modified working gold electrodes were carried out with a Princeton Applied Research model 283 potentiostat, using a $Ag/AgNO_3$ (0.1 M in acetonitrile) reference electrode ($E_0 = 0.261$ V *versus* SCE) in a Luggin compartment and a platinum wire auxiliary electrode. The experiments were performed in acetonitrile containing 0.1 M $LiClO_4$, under an argon atmosphere.

Cyclic voltammograms of NDI-BP in solution were obtained in water containing 0.1 M NaCl and 0.01 M phosphate buffer (pH = 7), using a saturated Ag/AgCl reference electrode in 1 M KCl solution ($E_0 = -0.020$ V *versus* SCE) and a platinum disk working electrode, under an argon atmosphere.



Scheme 1 Layer-by-layer growth of NDI-BP/ZP thin films on gold electrodes.

Results and discussion

Preparation of solid NDI-BP/ZP materials

The materials were prepared by the direct precipitation method, which consists in mixing NDI-BP and $ZrOCl_2$ aqueous solutions, either in the presence or in the absence of HF.[17] Powder X-ray diffraction patterns of the NDI-BP/ZP solids obtained are shown in Fig. 1. Samples prepared by rapidly mixing NDI-BP and Zr(IV) solutions produced mainly amorphous materials, with only small amounts of a crystalline phase (Fig. 1a), in contrast to the crystalline materials obtained when the precipitation was performed slowly in the presence of HF (Fig. 1b). Hydrofluoric acid is known to form strong complexes with zirconium cations, thus preventing the rapid precipitation of the ZP solids.[17–19] When the HF is removed slowly with a stream of inert gas, precipitation occurs, resulting in the formation of crystalline materials, as observed with other organic phosphonates.[18,30]

The X-ray diffraction pattern of the crystalline sample shows the first peak at d = 12.6 Å, with a second order of this reflection at d = 6.3 Å (Fig. 1b). The presence of these peaks is strong evidence for a layered structure in the case of the slowly precipitated NDI-BP/ZP solids, with an interlayer distance of 12.6 Å, as shown schematically in Fig. 2. This structure is in agreement with literature data, since it is known that most organic phosphates and phosphonates form layered compounds with zirconium, with segregated organic and inorganic lamellae.[18,19] Furthermore, the interlayer distance of 12.6 Å in crystalline NDI-BP/ZP is in reasonable agreement with the ellipsometric thickness of 10.2 Å per layer, found for NDI-BP/ZP thin films grown on silicon wafers in a layer-by-layer fashion.[22]

If the NDI-BP molecules were perpendicular to the plane of the inorganic layer in the crystalline materials, the expected interlayer distance would be *ca.* 18.9 Å, which is the sum of the thickness of the inorganic layer (taken as 6.8 Å),[18] and the length of the NDI-BP molecule, measured between the carbons adjacent to the phosphorus atoms [12.1 Å, calculated with the program WebLab ViewerLite (distributed free of charge by Accelrys Inc., http://www.accelrys.com/viewer/viewerlite/index.html)]. The experimental value of d = 12.6 Å, nevertheless, indicates that the NDI-BP molecules are actually lying down relative to the inorganic sheet, with an estimated tilt angle of 60°. A similar tilt angle was found by Kwan and co-workers for oligoimide monolayers self-assembled on gold.[27] Fig. 2 depicts an idealized structure for the NDI-BP/ZP crystalline materials.

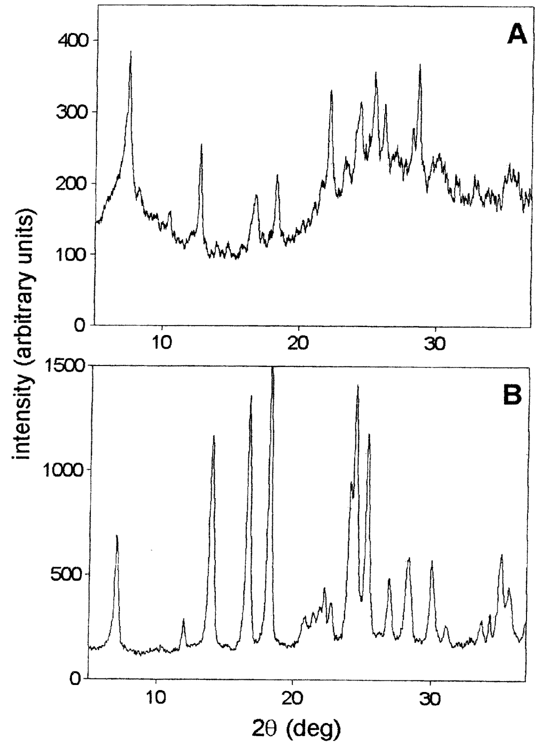


Fig. 1 Powder X-ray diffraction patterns for NDI-BP/ZP solid materials prepared by rapidly mixing NDI-BP and $ZrOCl_2$ solutions (**A**) or by the slow precipitation method over seven days with added HF (**B**).

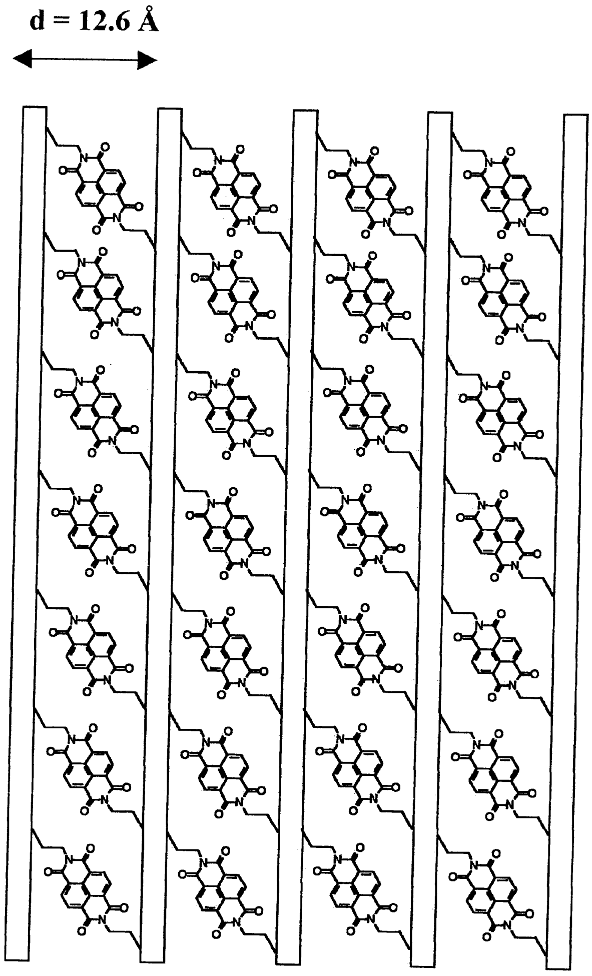


Fig. 2 Idealized layered structure proposed for NDI-BP/ZP crystalline materials.

Most organic bis-phosphonates form layered ZP compounds with structures analogous to inorganic α-zirconium phosphate (α-ZP), but with the organic groups acting as pillars, keeping apart the inorganic layers.[18,19] In these materials, the binding sites are apart from each other by 5.3 Å. In order to be accommodated within the α-ZP framework, the van der Waals cross section of the organic portion of the molecule should not exceed 25 Å^2. It has been shown that larger organic molecules also form layered ZP compounds, but with structures distinct from the usual α-ZP type found for smaller molecules.[31,32] For NDI-BP/ZP materials, the van der Waals cross section of the aromatic molecule in its bulkier portion (the naphthalene ring) was estimated as *ca.* 18 Å^2 (using WebLab ViewerLite), showing that an α-ZP structure is possible in this case. A definite assignment of the structure, however, is not possible with the present data.

Preparation of radical doped NDI-BP/ZP materials

When a concentrated, air-equilibrated aqueous solution of NDI-BP was irradiated, the initially colorless solution turned purple within a few seconds, indicating the presence of imide

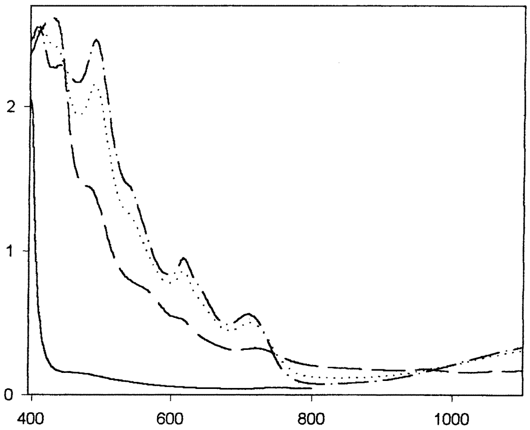


Fig. 3 (A) Absorption spectra of a 7 mM aqueous NDI-BP solution after irradiation with a high pressure Hg lamp. Irradiation time: 0 min (—); 2 min (–·–·–); 4 min (···); 12 min (– – –).

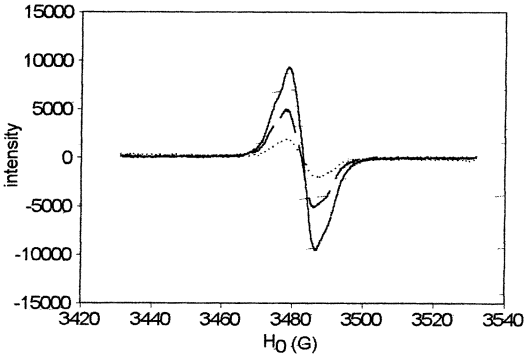


Fig. 4 EPR spectra of a radical-containing NDI-BP/ZP material prepared by direct precipitation of an irradiated NDI-BP solution with a $ZrOCl_2$ solution, registered at different times after the precipitation. Time: 4 hours (—); 72 hours (– – –); 168 hours (···). Frequency: 9.97 GHz; amplitude modulation: 1.0 G; frequency modulation: 100 kHz.

radicals. The absorption spectrum of a 7 mM NDI-BP solution irradiated for 2 min (Fig. 3) shows clearly the peaks at 490, 617 and 713 nm attributable to imide anion radicals[7,33] (the spectral region below 400 nm, not shown, is completely obscured due to the high concentration). In addition, a broad absorption band appears in the NIR region (*ca.* 1100 nm), which can be attributed to radical π-dimers.[7] Radical concentration in the irradiated solutions can be estimated from the spectra using the literature value of $\varepsilon = 6400\ M^{-1}\ cm^{-1}$ for the maximum near 610 nm.[33] The radical concentration obtained after 2 min of irradiation was 0.14 mM, corresponding to 2% of the total amount of NDI-BP present. Further irradiation resulted in a decrease in the concentration of the radical (Fig. 3), with the appearance of a band with $\lambda_{max} = 425$ nm, probably due to dianion formation.

It is remarkable that imide radicals were formed by irradiation of a NDI-BP aqueous solution without any added electron donor, and without any precautions to exclude atmospheric oxygen. Photoreduction of NDIs has been more often carried out by irradiation in the presence of an electron donor, such as 1,4-diazabicyclo[2.2.2]octane (DABCO).[5] This phenomenon has been attributed to the electron transfer from the donor to NDI triplet state, which is efficiently formed upon irradiation.[5,9] In some cases, however, photoreduction without any added reducing agent (self-quenching) has been observed.[5,15] In those cases, the electron donor is presumably a neutral NDI molecule, generating a pair of anion radical–cation radical species.

Radical-containing NDI-BP/ZP solids were prepared by adding at once $ZrOCl_2$ aqueous solutions (7 mM) to equal volumes of irradiated NDI-BP aqueous solutions (7 mM). This procedure resulted in the precipitation of dark brown NDI-BP/ZP solids, in contrast to the white solids obtained when non-irradiated NDI-BP solutions were precipitated with Zr. The brown materials remained unbleached for several days, even when exposed to atmospheric oxygen, and the presence of imide radicals was confirmed by EPR spectroscopy (Fig. 4). The radical-doped materials showed an intense EPR signal, characteristic of imide radicals ($g = 2.0452$), which was not present in the white solids precipitated without irradiation. The signal decayed rather slowly, and even after seven days there were still detectable amounts of radical, although the sample was kept exposed to air. The EPR signal in Fig. 4 apparently has two components, which can be attributed to imide radicals either in an amorphous or in a crystalline environment, since these materials must be similar to the rapidly precipitated sample from Fig. 1a.

The great stabilization of imide radicals within the NDI-BP/ZP solids is remarkable, and can be attributed mainly to two factors: delocalization of the lone electron of the radical over several stacked aromatic rings and shielding against atmospheric oxygen by the solid framework. The broad EPR signal observed in Fig. 4 is a strong evidence for the delocalization effect, since NDI-BP radicals in solution show structured EPR spectra.[7] The persistence of the radical in NDI-BP/ZP solids exposed to air is a strong indication of a densely packed arrangement of imide molecules in these materials. Stabilization of viologen radicals within ZP materials has been observed by Thompson *et al.*, who attributed the persistence of the radical to the compact arrangement of viologen groups in the solid.[34] When they prepared porous viologen/ZP materials, the colour of the radical bleached readily upon exposition to air.

The conductivity of the radical-doped solid was measured, giving the value $2.7 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$, which is lower than previously reported values for analogous imide radical doped materials.[26] The low conductivity is probably a consequence of the poor crystallinity obtained as a result of the rapid precipitation procedure employed (Fig. 1), causing the appearance of defects in the lattice, thus decreasing the conductivity. The rapid precipitation procedure was used to produce radical-doped materials because of the difficulties in maintaining a steady-state concentration of radicals for several days, as demanded for the slow precipitation procedure with HF. We are presently trying to develop a method to obtain radical-doped NDI-BP/ZP materials with a higher degree of crystallinity.

Self-assembled thin films of NDI-BP/ZP

Multilayer films of NDI-BP/ZP were grown on gold substrates as shown in Scheme 1. The gold surface was primed by reaction with 2-mercaptoethanol, followed by treatment with $POCl_3$,[35] giving a phosphorylated surface. A layer of zirconium atoms was then adsorbed on the surface (step i), followed by a layer of NDI-BP (step ii). Repetition of steps i and ii gave imide-containing multilayer films. In a previous report, we demonstrated that NDI-BP/ZP films grow in a linear fashion with the number of adsorption steps on both quartz and silicon surfaces,[22] indicating that regular films are formed. The morphology of these films are believed to be similar to that proposed in Fig. 2 for the solid materials.

Cyclic voltammograms of a NDI-BP/ZP film with 20 layers on each side of a gold substrate are shown in Fig. 5. Two redox pairs can be seen, with $E_{1/2} = -0.414$ V and $E_{1/2} = -0.852$ V (*vs.* SCE), corresponding to the formation of imide anion radical and dianion species, respectively.[1–3] The first redox wave is quasi-reversible at all scan rates studied, whereas the second wave changes from quasi-reversible to irreversible with

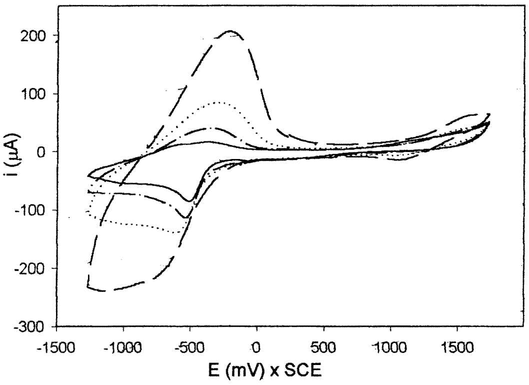


Fig. 5 Cyclic voltammograms of a NDI-BP/ZP film with 20 layers on each side of a gold electrode at scan rates of 5 (—), 10 (–·–·–), 20 (···) and 50 (– – –) mV s^{-1}. The voltammograms were recorded against a Ag/AgNO$_3$ reference electrode in acetonitrile containing 0.1 M LiClO$_4$, and the data were corrected to SCE.

increasing scan rate. The overall electrochemical behavior of the film is characteristic of kinetic control, with broad waves and peak separation (ΔE_p) increasing with scan rate (v). Furthermore, the peak current (i_pc) for the first reduction is proportional to $v^{1/2}$, indicating that interlayer electron hopping within the film is slow. This behavior is expected, taking in account the insulating character of the zirconium layers separating the imide layers.[36]

The surface coverage obtained by integration of the first reduction peak (at 5 mV s^{-1}) gives 4 × 10^{14} molecules cm^{-2} per layer. If the film structure is analogous to that known for α-zirconium phosphonates (24 Å^2 per phosphonate group, corresponding to a maximum density of 4 × 10^{14} phosphonate cm^{-2}),[19] the surface coverage estimated by this method corresponds to nearly total coverage, although this value might be overestimated due to uncertainties in the baseline of the voltammograms.

It is important to note that the total area of the reduction wave (first and second steps) is approximately similar to the total area of the reoxidation wave, at any scan rate, showing that most of the material reduced in the forward scan was reoxidized in the backward scan. These results point to the high stability of electrogenerated NDI-BP anion radical and dianion species in the films, since no significant degradation or desorption of the material was observed (the voltammograms were unchanged even after several cycles, data not shown).

The reduction potential for NDI-BP$^{-\bullet}$ formation in the ZP films ($E_{1/2} = -0.414$ V *vs.* SCE) is less negative than that found for aqueous NDI-BP solutions ($E_{1/2} = -0.660$ V *vs.* SCE). Based on coulombic considerations, one would expect NDI-BP reduction to be easier in water than in the films, because a polar solvent should stabilize the charged anion radical, in contrast to the hydrophobic environment of the stacked imide molecules in the films. Since the opposite was observed, it can be supposed that imide radical-anions are stabilized in the films by delocalization of the unpaired electron over several π-stacked NDI-BP molecules, as proposed above for the radical-doped solids.

Conclusions

The NDI-BP/ZP compounds presented here constitute a novel class of rather versatile materials, which can be prepared either in the form of bulk solids or thin self-assembled films. All the evidence indicated a layered structure for these materials, with segregated organic and inorganic layers. The NDI-BP molecules in the organic layer are tilted relative to the inorganic layer normal. The bulk solids showed the capability of stabilizing photogenerated imide radical anions for several days, making them potential candidates for the harvesting of solar energy. Stabilization of imide radicals was also observed in the thin films, as shown by electrochemical measurements.

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