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Thermochromic and Solvatochromic Nafion Films Incorporating Cationic Metal-Chelate Complexes†

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Nafion films incorporating cationic nickel complexes [Ni\(^{\text{II}}\)(acac)(R\(_{\text{en}}\))]\(^+\) (acac = acetylacetonato, R\(_{\text{en}}\) = tetraalkylenediamine) have been prepared that exhibit both thermochromic and solvatochromic behaviors in response to temperature changes and solvent molecules in the vapor and liquid phases.

Nafion is a perfluorinated ion-exchange polymer bearing a sulfonic group on the side-chain. To date, many studies have been conducted on its use in fuel cells,\(^1\) sensors,\(^2\) and catalystic reactions.\(^3\) The sulfonic proton in the polymer can be replaced with metal ions and cationic molecules. Based on this, several functional Nafion films containing metal complexes have been prepared, which exhibit catalytic activity,\(^4\) spin-crossover phenomena,\(^5\) vapoluminescence,\(^6\) and electrochromism.\(^7\) In this study, we report the preparation and properties of Nafion films incorporating these cationic complexes, which exhibit vapochromism and thermochromism.

\(\text{Fig. 1}\) The reversible coordination of solvent molecules (X) to [Ni(acac)(Me\(_2\)en)]\(^+\) (1: R = \(^8\)Bu, 2: R = Me; Fig. 1), which show thermochromism, vapochromism, and solvatochromism.

A light green transparent film incorporating 1 was prepared by immersing Nafion film (Na\(^+\) form) in a methanol solution of 1.\(^1\) The obtained film ([1:MeOH]–Nafion) contained 8–10 equimolar methanol per cation. Leaving this film in ambient conditions or drying for 1 h under vacuum leads to the partial loss of methanol to give a light brown film ([1:MeOH]–Nafion), which contains about three methanol molecules per cation. Further drying of this film at 130 °C under vacuum leads to the complete loss of methanol to give a red film ([1]–Nafion). The observed color change from light green to red by desorption of methanol is seen when the methanol-coordinated octahedral structure changes to the square-planar structure. The sulfonate group in the film is not coordinated to the complex because of its weak coordination ability, estimated to lie between BF\(_4\) – and ClO\(_4\) –. A blue film of [2:MeOH]–Nafion containing 2 was obtained by the same procedure.\(^1\)

[1:MeOH]–Nafion also exhibits thermochromism. The color of the film was light green at –20 °C, light brown at 20 °C, and orange at 70 °C (Fig. 2a), and the color change was reversible below 80 °C (†ESI, Fig. S1). The thermochromism is based on the coordination equilibrium of 1 in the film. The dependence of the UV-vis spectra of [1:MeOH]–Nafion on temperature is shown in Fig. 2b. The absorption maxima of the spectra at low temperatures (\(\lambda_{\text{max}} = 640\) and 1050 nm) and at high temperatures (\(\lambda_{\text{max}} = 490\) nm) are characteristic of the octahedral and square-planar species of 1, respectively. As shown in the inset of Fig. 2b, the molar ratio of the latter species (x\(_{\text{R}}\)) increases above 0 °C. The thermochromism is tunable by ligand modification. [2:MeOH]–Nafion was blue at 20 °C and changed to red at around 70 °C (†ESI, Fig. S2). The difference in color and the color change temperature range, as seen in the inset in Fig. 2b, are attributed to the smaller steric hindrance around the ligand in 2.\(^8\) Incorporation of DMSO (DN = 29.8)\(^9\) instead of methanol (DN = 19.0) produced a light green film [1:nDMSO]–Nafion, which showed no thermochromism because of strong coordination of DMSO. Heating [1:MeOH]–Nafion above 80 °C led to desorption of the methanol to give [1]–Nafion, which no longer exhibited thermochromism.

The dry film [1]–Nafion exhibited color changes in response to donor molecules. The color changed from red to light green under a saturated vapor of methanol over 1 h and in a few days in humid air. The color change occurred in a few minutes when the film was directly immersed in methanol (Fig. 3), and similar responses were observed in other polar solvents such as water (DN = 18), DMF (DN = 26.6), and DMSO (DN = 29.8) (†ESI, Fig. S3); DMSO, however, needed a longer time (~ 15 min). In contrast, the color change was less prominent in solvents with...
lower DN. The color changed to light red in ethanol (DN = 18.5) and acetonitrile (DN = 14.1), whereas no color change occurred in dichloromethane (DN = 0\(^{10b}\)) and acetone (DN = 17.0) (ESI, Fig. S3). It is interesting that the film can distinguish methanol and ethanol, giving distinctly different colors, light green and light red, respectively.

Fig. 2 (a) [1·3MeOH]–Nafion film at various temperatures. (b) UV-vis absorption spectra of [1·3MeOH]–Nafion recorded between −60 °C and 100 °C at 20 K intervals. The spectra in the low energy region (600–1200 nm) are magnified (×5) for clarity. The changes are irreversible above 80 °C because of the desorption of MeOH. The inset shows the temperature dependence of the molar ratio of four-coordinated species (\(x_4\)) in the films of [1·3MeOH]–Nafion (○) and [2·3MeOH]–Nafion (●).

Fig. 3 [1]–Nafion (a) before and (b) after immersion in methanol.

The response of [1]–Nafion to mixed solvents was investigated to further reveal the effect of dilution of the high DN solvents (methanol or DMSO) with non-coordinating (DN = 0) solvents (dichloromethane). The color of the film in a methanol–dichloromethane mixture changed from light green to brown gradually as the methanol concentration decreased to 10% v/v, indicating a shift in the coordination equilibrium. In contrast, the color changed to light green in a DMSO–dichloromethane mixture independent of DMSO concentration (100–10% v/v), which indicates that DMSO coordinates to the complex even in diluted solutions. However, the time required for the color change became longer with decreasing DMSO concentration, from a few minutes in DMSO, to 10 min in 50% v/v mixture, and 1 h in a 10% v/v mixture. This is ascribed to the less efficient expansion of the nano-pores in Nafion in a non-polar solvent.\(^{11,12}\) The film showed no response to 5% v/v solutions of methanol or DMSO in dichloromethane.

In contrast to [1]–Nafion, [1·nMeOH]–Nafion also exhibited color changes in solvents with DN lower than methanol. The color changed from light green to light brown in ethanol by exchange of the solvent molecules. Immersion in dichloromethane caused complete desorption of methanol within 1 min, becoming completely red, in the reverse reaction of [1]–Nafion in methanol. This is due to efficient desorption of methanol into the solvent associated with the reduction of the pore size in Nafion. The complementary responses of [1]–Nafion and [1·nMeOH]–Nafion may be useful for solvent molecule recognition. [1·nDMSO]–Nafion was almost completely insensitive to solvents because of the strong coordination of DMSO. The color remained unchanged in ethanol, but turned dark brown in dichloromethane over 30 min by partial elimination of DMSO.

In conclusion, transparent films that exhibit reversible color changes in response to temperature change and solvent molecules with different DN have been developed by incorporating solvatochromic nickel complexes into Nafion. The films show repeated solvatochromism between different liquid phases, recognition of solvent donor numbers, and tunable chromic behaviors by ligand modification. Although various chromic films containing metal complexes\(^5,7,13\) and organic dyes\(^4\) have been reported, most of them respond to a single external stimulus. These thermochromic and solvatochromic films show promise for use in applications such as vapor/solvent indicators. Further investigations into the response and modification of the complexes will be the subject of future research.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Photographs and UV-vis spectra of Nafion films incorporating 1 and 2. See DOI: 10.1039/b000000x/

‡ A strip of Nafion 117 (1.0 × 2.0 cm, thickness 0.183 mm, Aldrich) was immersed in an aqueous solution of NaOH (10w%) for 12 h, and then washed with water and air-dried. The film was immersed in a solution of [1][Tf\(_2\)N]\(^+\) in methanol (25 mM, 5 mL) for 24 h and then washed with methanol. The obtained film [1·nMeOH]–Nafion (n = 8–10) was dried under vacuum for 1 h to give a brown transparent film of [1·MeOH]–Nafion. A red transparent film of [1]–Nafion was obtained by heating the film at 130 °C under vacuum. The amount of 1 in this film was 11 wt%,

as estimated from the absorption spectra of the mother liquor. The ratio of 1 to SO\(_2\) in the film was 39%, calculated from the EW (equivalent weight, ~1100) of Nafion 117. Other hydrophobic salts may be used for the cation exchange. [2·MeOH]–Nafion was prepared similarly, using [2]X (X = PF\(_6\) or BPh\(_4\)) as the cation source.

Functional films that exhibit thermochromism, solvatochromism and vapochromism have been developed by immobilization of cationic nickel complexes \([\text{Ni}^{II}(\text{acac})(\text{R}_2\text{en})]^+\) in Nafion.
Fig. S1. Absorbance changes of [1·3MeOH]–Nafion monitored at 490 nm for repeated temperature changes between –40 °C (open circles) and 70 °C (filled circles).
Fig. S2. (a) [2−3MeOH]–Nafion at various temperatures. (b) UV-vis absorption spectra of [2−3MeOH]–Nafion recorded between −40 °C and 100 °C at 20 K intervals. The change is irreversible above 80 °C because of the desorption of MeOH. The insert shows the temperature dependence of the molar ratio ($x_{4c}$) of four-coordinated species in the film.

Fig. S3. [1]–Nafion (a) before and (b) after immersion in various solvents.