

A thermochromic ormosil coating used in smart windows

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ABSTRACT

An inorganic-organic hybrid coating (PMS-Co) was studied as a thermochromic functional coating on the glass of smart windows. The basic resin matrix of the coating was the organopolysiloxane (PMS) prepared by cross-linking between two prepolymers (PA and PB) which had epoxy and amino groups respectively. The prepolymer PA was prepared by the hydrolysis of alkoxy groups and copolycondensation reactions between methyl triethoxysilane and gamma glycidoxypropyltriethoxysilane upon acidic catalysis. Likewise, the prepolymer PB was prepared by reactions between methyl triethoxysilane and gamma amino-propyl triethoxysilane. The PMS-Co coating was obtained by in-situ hybridization in which the cross-linking reaction and the coordination reaction proceeded simultaneously during the curing process. The PMS-Co coating indicated the thermochromic characteristic which was ascribed to the ligand exchanging reaction between the hydroxyl groups and chloride ion in the cobalt(II) complex. The thermodynamics of the reaction was studied and the value of the enthalpy change (ΔH) was measured as 51.76 kJ/mol. Good compatibility, photostability, reversibility and solvent resistance were found in the coating as well which could be anticipated as one of the valuable candidates used in smart windows.

Keywords: thermochromism, ormosil matrix coating, sol-gel, hybridization, smart window.

1. INTRODUCTION

Windows are known as one of the most dominant energy efficiency components of buildings. Obviously the efforts to prevent the energy losses by improving the thermal and optical performances of the windows will result in reduced electricity supporting air-conditioning and lighting, which eventually cut down the green house gas emissions. Smart windows could intelligently block the unwanted solar radiation through adjusting the transmittance of windows by means of thermochromism, photochromism, electrochromism, etc, [1-5] and adding controllable absorbing layer containing functional materials on the surface of the glass might be one of the most convenient methods to achieve the aim of regulating the incident solar radiation flux [6]. The inorganic thermochromic materials had been studied to be used in glazing industry as early as 1970s [7], which were in view of the discovery of a number of inorganic thermochromic compounds. The most promising thermochromic compounds for smart windows were vanadium dioxide [8] and cobalt(II) chloride [9].

In the technology of applying light-adjusting coatings on glass or in laminated glass, the homogeneity of the organic polymer doped with inorganic thermochromic compounds was an inevitable challenge to the researchers, as the thermochromism of the inorganic compounds in solution had been extensively studied [10-12]. Inorganic-organic hybrid polymers as Ormosils (Organically Modified Silicates) prepared by the sol-gel method might be an effectual approach to this challenge. The Ormosils had been explored and applied in the abrasion-resistant, durable optical coatings [13] and anti-corrosive coatings [14]. They usually had low glass transition temperatures, which might provide a flexible micro-environment to accommodate functional materials

and allow optical switching at the molecular level [15]. In our previous research, a photochromic Ormosil matrix coating with fast spectrokinetics was prepared via the sol-gel method in which a polymerizable dye and a silicone monomer were hydrolyzed and copolycondensed to form the Ormosil matrix using in smart windows [16].

As is known to all, the thermochromism of the cobalt(II) family comes from the ligand exchanging reactions between the hydroxyl groups and chloride ions which are accompanied by the change of the geometry from octahedral to tetrahedral [17]. However, the enormous amount of hydroxyl groups in the protic solvent or medium (such as the polysiloxane materials) suppresses the coordination of the chloride ions to the cobalt(II) atom overwhelmingly. In some cases the chloride concentration was used as high as 80 equivalents to favour the equilibrium shifting in the reversible reaction [10]. In this paper, we developed a thermochromic Ormosil coating via the sol-gel method. The methyl group in the epoxy-crosslinking polymethylsiloxane (PMS) Ormosil provided better compatibility, flexibility and solvent resistance to the coating than the polysiloxane (PSO), in addition, the hydroxyl groups in the micro-environment surrounding the cobalt(II) atom were reduced which could benefit the equilibrium shifting in the ligand exchanging reactions. Simultaneously, better homogeneity might be another feasibility of thermochromic inorganic-organic hybrid coating over usually used thermochromic systems. This inorganic-organic hybrid coating (PMS-Co) was formed by *in-situ* hybridization and was anticipated to be used in smart windows.

2. EXPERIMENTAL SECTION

2.1. Materials.

All chemicals were used as received without further purification. The tetraethylorthosilicate 99.0% (TEOS, Sinopharm Chemical Reagent Co., Ltd), methyltriethoxysilane 98.0% (MOS, Sinopharm Chemical Reagent Co., Ltd), gamma amino-propyl triethoxysilane 98.0% (APOS, Sinopharm Chemical Reagent Co., Ltd), and gamma glycidoxypropyltriethoxysilane 97.0% (GLYOS) were purchased from Aladdin.

A solution of cross-linkable organopolysiloxane (prepolymer **PA**) was prepared by adding with stirring a mixture of 0.6 mol methyl triethoxysilane (MOS), 0.2 mol gamma glycidoxypropyltriethoxysilane (GLYOS), 100 g n-propanol, 5 g water and 3 g glacial acetic acid. The resultant solution was stirred for one hour and allowed to stand for 24 hours. Likewise, the prepolymer **PB** was prepared by reactions of 0.2 mol methyl triethoxysilane (MOS), 0.2 mol gamma-amino-propyl triethoxysilane (APOS) and 50 g n-propanol.

PMS-Co solution was obtained by mixing 270.4 g solution of prepolymer **PA**, 129.8 g solution of prepolymer **PB** and 47.6 g (0.2 mol) cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$). The resultant solution was stirred for one hour and allowed to stand for 24 hours.

For comparison, a solution of the inorganic polysiloxane (**PSO-Co**) was prepared from a mixture of 1.2 mol tetraethoxysilane (TEOS), 100 g n-propanol, 5 g water, 3 g glacial acetic acid and 0.2 mol cobalt(II) chloride hexahydrate in a similar procedure.

The coatings were applied onto quartz substrates by the method of dip coating from the prepared **PMS-Co** solution above. The lifting speed of the substrate was controlled as 300 $\mu\text{m/s}$ at 20 $^\circ\text{C}$ after soaking in **PMS-Co** solution for 200 s. Once the substrate was coated, the samples were cured at 120 $^\circ\text{C}$ for 1 hr. The thickness of the coating was measured as 23 μm averagely by an ultrasonic coating thickness gauge (QuintSonic, ElektroPhysik, Germany).

2.2. Methods.

The spectral and thermodynamic measurements of the thermochromic coatings were performed using a TU1901 UV/Vis spectrophotometer (PG Instruments Limited, China) coupled with a temperature controller. The coating on quartz substrate was placed in a holder and the change of absorbance (A) was recorded. The differential scanning calorimetry (DSC) analysis was

determined on a Pyris 1 Differential Scanning Calorimeter (Perkin Elmer). The shading effect was evaluated by the time-variation of temperature differences (ΔT) between the internal (T_{in}) and external air (T_{ex}) in the test cells which were in the sunshade of the glass coated by **PMS-Co** and the blank reference, respectively. The test cell (1.0 m \times 1.0 m \times 1.0 m) was constructed by plain glass (5 mm thick) without any special attemperator (Fig. 1). The experiment of shading effect was carried out on 12 am July 9th 2013 in Shanghai, China, when the samples were irradiated by sunshine in the vertical direction.

$$\Delta T = T_{\text{in}} - T_{\text{ex}}$$

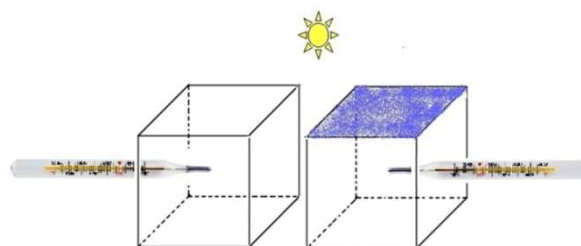


Figure 1. The experiment of shading effect in the sunshade of the glass coated by **PMS-Co** (right) and the blank reference (left).

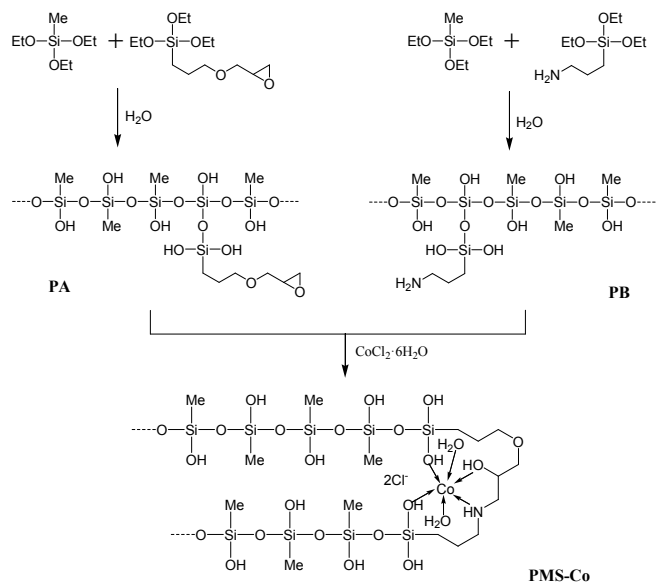
The photobleaching test of the Co-PMS coating against UV radiation (365 nm) was carried out in the UV radiometer (ZF-20D, 16 W, Shanghai Yuezhong Instrument Equipment Co., Ltd., China) at 20 $^\circ\text{C}$. The values of A_{656} were measured at 90 $^\circ\text{C}$ when the coating was taken out from UV radiation in a time interval of 24 hours. The reversibility of the coating was evaluated by the values of A_{656} after the sample was set in the thermostatic cells at 90 and 20 $^\circ\text{C}$ for 20 min alternately.

The solvent wash-off resistances of **PMS-Co** coating was investigated through measuring the difference of the absorption (A/A_0) of samples at 656 nm (state B, 90 $^\circ\text{C}$) before and after immersion in selected solvents for 3 hrs at 20 $^\circ\text{C}$. The **PSO-Co** coating prepared from tetraethoxysilane (TEOS) was studied for comparison as well. The solvents were including water, hexane, ethyl acetate (EtAc), acetone, EtOH, MeOH, acetic acid (HOAc), HCl (1%) and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (1%) solution. The contact angles were measured on the Optical Contact Angle Measuring Instrument (OCA15EC, Beijing Eastern-Dataphy Instruments Co., Ltd, China) at 20 $^\circ\text{C}$.

3. RESULTS SECTION

The basic resin matrix of the coating was the organopolysiloxane (**PMS**) prepared by cross-linking between two prepolymers (**PA** and **PB**) which had epoxy and amino groups respectively (Scheme 1). The cross-linkable prepolymer **PA** was prepared by the hydrolysis of alkoxy groups and copolycondensation reactions between methyl triethoxysilane and gamma glycidoxypropyltriethoxysilane upon acidic catalysis. Likewise, the prepolymer **PB** was prepared by reactions between methyl triethoxysilane and gamma amino-propyl triethoxysilane. The prepolymers could be stored until required or be used for

curing immediately. The curing process (preparation of **PMS**) involved both addition reaction (between the epoxy and amino groups) and the further siloxane linkages. The cobalt(II) was introduced by means of *in-situ* hybridization during the curing process and the **PMS-Co** hybrid coating was obtained accordingly (Scheme 1).



Scheme 1. The preparation of the PMS-Co coating by in-situ hybridization.

The absorption at the visible region played the main role in the shading effect of the coating. To testify the thermochromic property of the **PMS-Co** coating, the visible spectra in condition of different temperatures were measured and shown in Fig. 2. The Ormosil coating displayed two characteristic absorption peaks at 510 nm and 656 nm which were corresponding to the temperatures below 50°C and above 60°C, respectively. The color of the **PMS-Co** coating changed gradually from pale pink to green, blue, and dark blue eventually as the temperature rose, which could be applied as a temperature indicator, too.

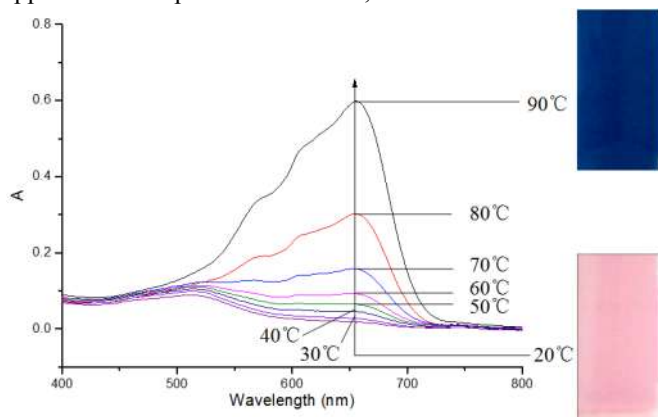
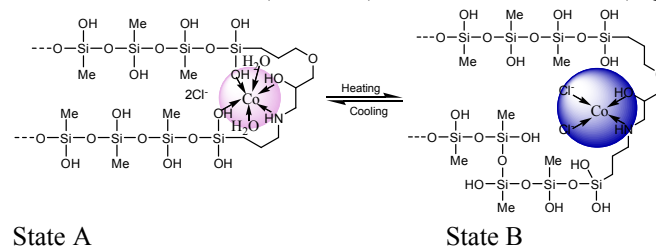


Figure 2. The absorption spectra of PMS-Co coating at different temperatures.

According to the coordination chemistry of cobalt(II) [17], the thermochromism of the **PMS-Co** between the state A and B was contributed from the ligands exchanging reaction between the hydroxyl groups and chloride ion. On heating of the Ormosil matrix, the micro-environment surrounding the cobalt(II) became loose and released more free volumes, which enabled the chloride ion of a larger scale to acquire more possibilities to approach the cobalt(II) instead of the ligands of water molecules or Si-OH (Scheme 2). The similar flexible environment suitable for optical switching was elaborately designed in other functional polymer matrix, too [18]. The absorption peaks at 656 nm (A_{656}) in Fig. 2 were observed to rise sensitively to the change of temperature, while those at 510 nm (A_{510}) remained nearly constant which meant most of cobalt(II) species coordinated with the

hydroxyl groups (the state B) even at high temperature of 90°C. Thus the ratio value of A_{656}/A_{510} was used to study the thermodynamics of the reaction, and then a linear relationship between the value of $\ln(A_{656}/A_{510})$ and $1/T$ was obtained (Fig. 3).



State A

State B

Scheme 2. The ligand exchanging reaction in thermochromism of the PMS-Co coating.

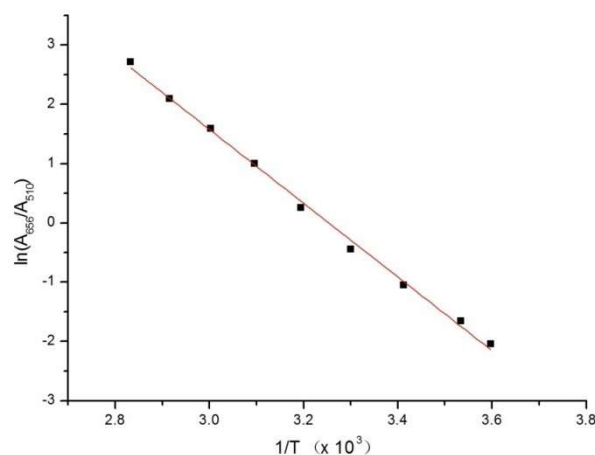


Figure 3. The linear relationship between the value of $\ln(A_{656}/A_{510})$ and $1/T$ for PMS-Co coating (T is the absolute temperature).

For the visible absorbing species which obey the Lambert-Beer's law, the linear dependences are given by

$$A_{510} = \varepsilon_A \cdot C_A \quad (1)$$

$$A_{656} = \varepsilon_B \cdot C_B \quad (2)$$

Where A_{510} is the absorption value at 510 nm, A_{656} is the absorption value at 656 nm, ε_A is the molar extinction coefficient of state A, ε_B is the molar extinction coefficient of state B, C_A is the concentration of the state A, C_B is the concentration of the state B.

Thus the equilibrium constant K for the ligands exchanging reaction is given by

$$K = C_B/C_A = A_{656}\varepsilon_A/A_{510}\varepsilon_B \quad (3)$$

And the equilibrium constant K in Van't Hoff equation is given by

$$\ln K = \Delta S/R - \Delta H/RT \quad (4)$$

where ΔS is the entropy change, R is the universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), ΔH is the enthalpy change of the reaction, T is the absolute temperature,

Then,

$$\ln(A_{656}/A_{510}) = -\Delta H/RT + \Delta S/R + \ln(\varepsilon_A/\varepsilon_B) \quad (5)$$

The value of $-\Delta H/R$ could be derived from the fitted line in Fig. 3,

$$\ln(A_{656}/A_{510}) = -6225.7/T + 20.255 \quad (6)$$

Thus, the value of the enthalpy change (ΔH) of the reaction is given by:

$$\Delta H = 6225.7 \cdot R = 51760 \text{ (J/mol)} = 51.76 \text{ (kJ/mol)} \quad (7)$$

The ligand exchanging reaction was also characterized by the method of the differential scanning calorimetry (DSC) shown in

Fig. 4, in which a large and broad endothermic peak in the temperature range of 48.3-155.5 °C was observed. It could be explained by the reversible gradual replacement reactions between the ligands of Cl and water molecules or Si-OH from the environment around the cobalt(II) ion (Scheme 3). The DSC analysis also indicated the homogeneity of the **PMS-Co** hybrid coating as no isolated endothermic peak associated with the phase separation structure was found.

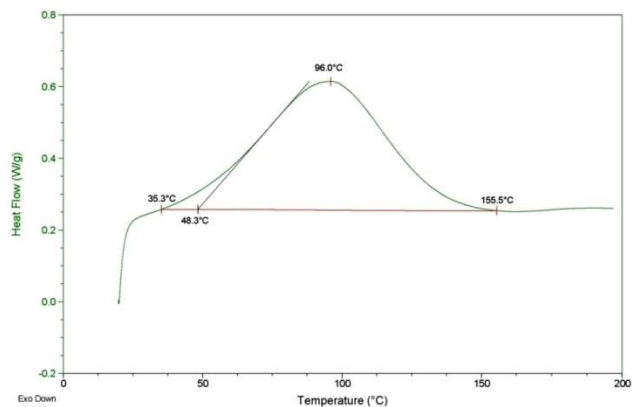
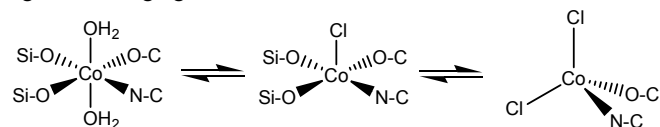


Figure 4. The differential scanning calorimetry (DSC) analysis of the ligand exchanging reaction.



Scheme 3. The gradual replacement reactions between the ligands from the environment around the cobalt(II) ion.

The shading effect shown in Fig. 5 was evaluated by the time-variation of temperature differences (ΔT) between the internal (T_{in}) and external air (T_{ex}) in the test cells which were in the sunshade of the glass coated by **PMS-Co** and the blank reference, respectively. In the initial 5 min, the temperature of the internal air in the test cell rose rapidly at the similar rate in both conditions. Subsequently, the rate of temperature rising of the sample with **Co-PMS** coating was observed to decelerate and the temperature of the internal air tended to reach a constant value. This was due to the shading effect intensified by the thermochromism of **Co-PMS** coating. In contrast, the sample without the thermochromic coating offered a negligible shading effect and the temperature of the internal air in the test cell rose without a let-up in 50 min.

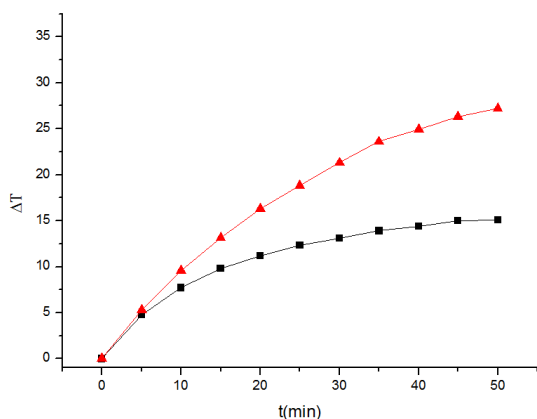


Figure 5. The time-variation of temperature differences (ΔT) between the internal and external air in the test cells which were in the sunshade of the glass coated by **PMS-Co** (-■-) and the blank reference (-▲-)

The photostability was one of the most important specifications for the functional coatings in smart windows, and then the photobleaching test of the **Co-PMS** coating against UV radiation (365 nm) was carried out. As a result shown in Fig. 6, there was nearly no photobleaching phenomenon for the State B of the **Co-PMS** coating in ten days, which indicated a good photostability due to the inorganic nature of the chromospheres (cobalt complexes).

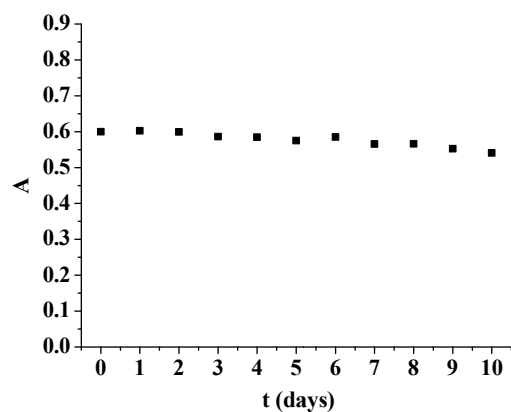


Figure 6. The photobleaching tests of the **Co-PMS** coating irradiated by UV (UV source power 16 W at 25 °C, the values of A_{656} measured at 90 °C).

Of equal importance was the reversibility of the thermochromism between the state A and B of the **Co-PMS** coating. The reversibility of the coating was evaluated by the values of A_{656} after the sample was set in the thermostatic cells at 90 and 20 °C for 20 min alternately. In 80 exposure cycles shown in Fig. 7, nearly no optical fatigue was noticed, which should become one of the main advantage of the Ormosil hybrid coating for smart windows.

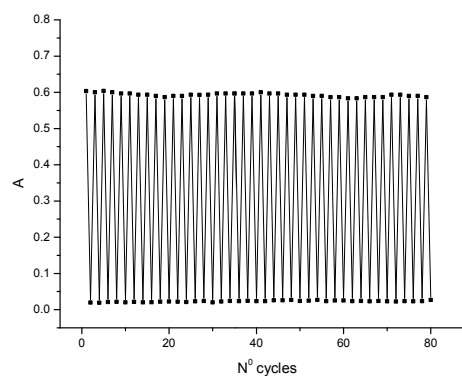


Figure 7. The reversibility of the **Co-PMS** coating (A_{656} measured after set in the thermostatic cells at 90 and 20 °C for 20 min alternately).

Likewise, the solvent resistance was another fundamental property for smart glass coatings as well, which referred to the notion of a colored object that retained its original hue without running along with the washing solvents [19]. It had become a major limiting factor for the working life for the smart window. The solvent wash-off resistances of **PMS-Co** coating was investigated through measuring the difference of the absorption (A/A_0) of samples at 656 nm (state B, 90 °C) before and after immersion in selected solvents for 3 hrs at the room temperature. The **PSO-Co** coating prepared from tetraethoxysilane (TEOS) was studied for comparison as well.

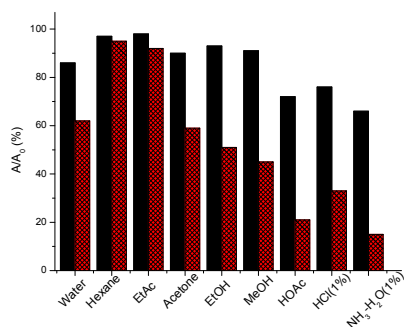


Figure 8. The study of solvent wash-off resistance of PMS-Co (filled square) and PSO-Co coating (dark shade) through measuring the difference of the absorption (A/A_0) of samples at 656 nm (state B, 90°C) before and after immersion in selected solvents for 3 h at 20°C.

4. CONCLUSIONS

An inorganic-organic hybrid coating (**PMS-Co**) was prepared as a thermochromic coating for smart windows. The basic resin matrix of the coating was the organopolysiloxane (**PMS**) prepared through the sol-gel method by cross-linking between two prepolymers (**PA** and **PB**) which had epoxy and amino groups respectively. The **PMS-Co** was obtained by in-situ hybridization in which the cross-linking reaction and the coordination reaction proceeded simultaneously during the curing process and was of value to the compatibility for the coating. The **PMS-Co** coating

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6. ACKNOWLEDGEMENTS

None.

Different solvents used in this investigation some of which include – water, hexane, ethyl acetate (EtAc), acetone, EtOH, MeOH, acetic acid (HOAc), HCl (1%) and NH₃·H₂O (1%) solution. As shown in Fig. 8, the **PSO-Co** coating indicated some obvious fading phenomena in acetic acid, HCl and NH₃·H₂O solution, which might be due to the competition between the silica gel and the solvents in their coordination with the Co(II) ion. In comparison, good solvent resistance was obtained for the **PMS-Co** coating and was largely contributed by hydrophobicity of the methyl groups in Ormosil matrix. This point was supported by the contact angle measured as 98.2° at 20°C, which indicated a great advantage over that of the hydrophilic **PSO-Co** coating as 51.6°.

indicated a thermochromic characteristic which was contributed to the ligand exchanging reaction between the hydroxyl groups and chloride ion in the cobalt(II) complex. The thermodynamics of the reaction was studied and the value of the enthalpy change (ΔH) was measured as 51.76 kJ/mol. Good performances in photostability, reversibility and solvent resistance were found in the **PMS-Co** coating which could be regarded as the valuable candidate used in smart windows.

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