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# Sol—gel synthesis of organic—inorganic hybrid materials comprising boehmite, silica, and thiazole dye

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### 1. Introduction

Most new products are designed to have multiple functions and a form of intelligence. Thus, hybrid materials have recently become one of the main trends in materials science research. Compared with traditional materials, the most important feature of a hybrid material is its designability. The mechanical, physical, and chemical properties of a hybrid material can be designed and controlled by changing its composition or by using interface control, compounding technology, or moulding technology in order to meet the requirements of maximum usability and environmental compatibility. In particular, organic-inorganic hybrid materials have attracted significant interest [1–3] because they offer the advantages of both: the plasticity of organic materials and the functional properties of inorganic materials. In order to exploit the versatility of hybrid materials, the processing methods used for their preparation include a combination of organic-inorganic hybrids and the sol-gel process [4,5]. They encompass inorganic oxides that function as fillers in organic polymers and solids consisting of polymers or organic molecules in inorganic oxide networks. Functional materials can be prepared using organic-inorganic hybrid technology and the sol-gel method [6-9].

### ABSTRACT

A hybrid material was prepared from a boehmite sol and a thiazole derived azo dye. The thiazole azo dyes were subjected to hydrolytic polycondensation with vinyltriethoxysilane, tetraethoxysilane, and aluminium isopropoxide in different ratios to afford a hybrid of boehmite, silica, and the thiazole heterocycle azo dye. The structures of these hybrid materials were characterized using X-ray diffraction, Fourier-transform infrared analysis, <sup>29</sup>Si- and <sup>27</sup>Al-nuclear magnetic resonance, ultraviolet–visible absorption spectrophotometry, and an energy-dispersive X-ray spectroscopy.

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An inorganic sol is blended with an organic polymer solution and then gelatinized. The organic monomer and the inorganic sol are polymerized simultaneously using a hybridization method to form an interpenetrating network. The major structural feature of this composite material is that the microzones are in the order of nanometres and can be interpenetrating [10,11]. The  $\gamma$ -AlOOH coating is a thin layer material that adheres to a parent material to play a special role and provides a certain anchoring strength to the parent material. It can overcome some types of defects in the parent material and improve the material's surface characteristics, such as optical characteristics, electrical characteristics, erosion and corrosion resistance, wearability, and mechanical strength. It is a film with support. There are many preparation methods for the coating material, which can be classified into two major types: physical processes, such as the vapour deposition method and the sputtering method, and chemical processes, such as chemical vapour deposition, spray pyrolysis, and sol-gel methods. The sol-gel method for coating preparation has the following characteristics when compared with other coating preparation methods: (1) simple process equipment: expensive vacuum equipment or vacuum conditions are not required; (2) low-temperature technological process: this characteristic is very important for the preparation of versatile systems containing light-volatile components or likely to undergo phase separation at high temperature; (3) the film can be prepared on substrates made of different materials, with different shapes and a large area [12-15]. At present, it is





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known that  $\gamma$ -AlOOH can induce improved hardness and other properties, and although it is mostly applied to ceramics as a substrate, it has recently been applied to other materials [16–20].

Furthermore, silica is a natural material derived from common materials such as quartz, sand, and flint. Silica has a high chemical stability, a low thermal expansion coefficient, and high heat resistance. The relatively high chemical stability of the silica phase can be advantageous in some cases [21–24]. If the  $\gamma$ -AlOOH and silica gel condensation polymerization method are sufficiently intermixed in the surface layer, a short travelling distance between the surface-modified silica thermal stability sites and the mechanical strength sites on the boehmite phase may result in a high chemical stability performance.

The molecules of heteroaryl azo dyes contain unshared electron pairs of nitrogen and sulfur, which can easily trigger resonance and cause the  $\pi$  electrons of the compound to leap from the ground state to the excited state. The synthesis and spectroscopic properties of azo dyes are well-established [25–29]. The use of heterocyclic aromatic amines for improving higher tinctorial strength has been well-established. 2-Aminothiazole compounds which possess different substituents in the 4-position of analogous derivatives as diazo components tend to bathochromic shifts as compared to analogous dyes derived from benzenoid compounds [30–32].

In this study, we aim to synthesize a series of thiazole heterocyclic dyes. The sol–gel method is utilized herein to process an organic–inorganic hybrid material and produce hybrid materials from SiO<sub>2</sub>/ $\gamma$ -AlOOH and a thiazole azo dye in a blending reaction with various proportions of vinyltriethoxysilane, tetraethoxysilane, and aluminium isopropoxide (AIP) via an addition hydrolysis reaction to generate a blended dye having a network structure.

### 2. Experimental

### 2.1. Analytical instruments

Fourier-transform infrared (FT-IR) spectra were recorded on a Bio-Rad Digilab FTS-40 spectrometer (KBr); <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were obtained on a BRUKER AVANCE 400MHz NMR spectrometer. Chemical shifts ( $\delta$ ) are expressed in parts per million using tetramethylsilane (TMS) as an internal standard. The <sup>29</sup>Si-NMR and <sup>27</sup>Al-NMR spectra were collected using a BRUKER AVANCE 400 MHz NMR spectrometer at 78.49 MHz, with a recycle time of 60 s, and the number of scans was 914. The elemental analysis was carried out using a Philips XL40 FEG-Energy Dispersive X-ray Spectrometer. Electronic spectra were recorded using a SHIMADZU UV-1201 from dyes solutions in DMF and THF at a concentration of 1  $\times$  10<sup>-5</sup> mol L<sup>-1</sup>. X-ray diffraction (XRD) measurements were performed on a Rigaka D/MAX 2500V X-ray powder diffractometer in steps of 0.01° using Cu K<sub>α</sub> radiation as the X-ray source.

### 2.2. Materials

Vinyltriethoxysilane, tetraethoxysilane, aluminium isopropoxide  $(Al(OC_3H_7)_3)$ , acetophenone, and p-methoxyaniline were purchased from Acros Co., Ltd., Belgium. Thiourea, sulfuric acid, p-nitroaniline, and iodide were purchased from Hayashi Pure Chemical Co., Ltd.

### 2.3. Preparation of dyes 3a-3b

### 2.3.1. Preparation of dyes 5-[2-(4-nitrophenyl)-diazen-1-yl]-4-phenyl-1,3-thiazol-2-amine (**3a**)

A finely ground powder of p-nitroaniline **2a** (1.38 g, 0.01 mol) was added to a mixture of hydrochloric acid (12 mL) and stirred for

20 min. Sodium nitrite (0.72 g, 0.0105 mol) was added in portions to concentrated sulphuric acid (5 mL) at 10 °C and stirred for 1 h at 60°-65 °C. The solution was cooled to below 5 °C, and then the finely ground derivatives were slowly added; the mixture was stirred for an additional 1 h at 5–10 °C until it was clear. The resulting diazonium solution was used immediately in the coupling reaction. A clear mixed solution of the coupling component 4-phenyl-2aminothiazole 1 (2.0 g, 0.01 mol) and 10% sodium carbonate was stirred. The diazonium mixture was added at 0-5 °C, and the solution was stirred for at least 2 h; it was diluted to raise its pH to 5-6 (by adding aqueous sodium hydroxide or sodium acetate). The resulting product was filtered, washed with water, and re-crystallized from ethanol to give a deep red solid 5-[2-(4-nitrophenyl)-diazen-1-yl]-4phenyl-1,3-thiazol-2-amine (3a) (2.3 g, 70%). m.p. 245–247 °C; FT-IR (KBr)/cm<sup>-1</sup>: 3433 (NH<sub>2</sub>), 3057 (C–H); <sup>1</sup>H-NMR( DMSO-d<sub>6</sub>.) δ ppm: 7.04(1H, s, -NH<sub>2</sub>), 7.51-7.55(5H, m, ArH), 7.71, (2H, d, 2,6 - Ph-H), 8.19 (2H, d, 3,5 – Ph-H).

C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>S (325.1) Calcd.: C, 55.38; H, 3.41; N, 21.53; O, 9.84; S, 9.85

Found: C, 55.32; H, 3.44; N, 21.58; O, 9.78; S, 9.87

2.3.2. Preparation of dyes 5-[2-(4-methoxyphenyl)-diazen-1-yl]-4-phenyl-1,3-thiazol-2-amine (**3b**)

As shown in Scheme 1, Dye 5-[2-(4-methoxyphenyl)-diazen-1yl]-4-phenyl-1,3-thiazol-2-amine (**3b**) was synthesized by using the same method as that used for synthesizing **3a**, which was coordinated with diazo components p-nitroaniline **2a**. The resulting product was filtered, washed with water, and re-crystallized from ethanol to give an orange solid 5-[2-(4-methoxyphenyl)-diazen-1yl]-4-phenyl-1,3-thiazol-2-amine (**3b**) (1.65 g, 50%). m.p. 253–255 °C; FT-IR (KBr)/cm<sup>-1</sup>: 3430 (NH<sub>2</sub>), 3105 (C–H), 1179 (O–CH<sub>3</sub>); <sup>1</sup>H-NMR(DMSO-d<sub>6</sub>)  $\delta$  ppm: 3.80 (3H, s, –OCH<sub>3</sub>), 7.04(1H, s, –NH<sub>2</sub>), 7.40–7.50(5H, m, ArH), 7.61 (2H, d, 3,5 – Ph-H), 7.82 (2H, d, 2,6 – Ph-H).

C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>OS (310.3) Calcd.: C, 61.92; H, 4.55; N, 18.05; O, 5.15; S, 10.33

Found: C, 61.88; H, 4.57; N, 18.11; O, 5.11; S, 10.28

2.4. Preparation of precursors 4a-4b

### 2.4.1. 5-[2-(4-nitrophenyl)-diazen-1-yl]-4-phenyl-N-[2-(triethoxysilyl)ethyl]-1,3-thiazol-2-amine (**4a**)

Precursor **4a** was prepared by the reaction of dyes **3a** (3.25 g, 0.01 mol) followed by the addition of vinyltriethoxysilane (9.5 g, 0.05 mol) in THF (80 mL) with stirring at 65 °C for 4 h at an adjusted pH of 4–5. The resulting product was filtered, washed with water, and re-crystallized from ethanol to give a dark red solid 5-[2-(4-



Scheme 1. Synthesis of hybrid material 6a-6b.



**Fig. 1.** The X-Ray diffraction pattern of  $\gamma$ -AlOOH sol.

nitrophenyl)-diazen-1-yl]-4-phenyl-N-[2-(triethoxysilyl)ethyl]-1,3-thiazol-2-amine (**4a**) (2.76 g, 59%). m.p. 304–306 °C; FT-IR (KBr)/cm<sup>-1</sup>: 3395 (NH), 3073 (C–H), 1096 (O–Si).

 $\begin{array}{l} C_{23}H_{29}N_5O_5Si\ (515.4)\ Calcd.:\ C,\ 53.57;\ H,\ 5.67;\ N,\ 13.58;\ O,\\ 15.51;\ S,\ 6.22;\ Si,\ 5.45\\ Found:\ C,\ 53.63;\ H,\ 5.62;\ N,\ 13.56;\ O,\ 15.55;\ S,\ 6.28;\ Si,\ 5.41\\ \end{array}$ 

### 2.4.2. 5-[2-(4-methoxyphenyl)-diazen-1-yl]-4-phenyl-N-[2-(triethoxysilyl)ethyl]-1,3-thiazol-2-amine (**4b**)

Precursor 5-[2-(4-methoxyphenyl)-diazen-1-yl]-4-phenyl-N-[2-(triethoxysilyl)ethyl]-1,3-thiazol-2-amine (**4b**) was synthesized by the same method as that used for synthesizing **4a**. The resulting product was filtered, washed with water, and re-crystallized from ethanol to give a deep orange solid 5-[2-(4-methoxyphenyl)-diazen-1-yl]-4-phenyl-N-[2-(triethoxysilyl)ethyl]-1,3-thiazol-2amine (**4b**) (2.04 g, 45%). m.p. 313–315 °C; FT-IR (KBr)/cm<sup>-1</sup>: 3280 (NH), 3103 (C–H), 1134 (O–CH<sub>3</sub>), 1032 (O–Si).

 $C_{26}H_{32}N_4O_4SSi\ (500.2)$  Calcd.: C, 57.57; H, 6.44; N, 11.19; O, 12.78; S, 6.40; Si, 5.61

Found: C, 57.65; H, 6.49; N, 11.23; O, 12.75; S, 6.45; Si, 5.54



Fig. 2. FT-IR spectra of hybrid materials AN<sub>1</sub>-AN<sub>4</sub>.



Fig. 3. FT-IR spectra of hybrid materials ATN<sub>1</sub>-ATN<sub>4</sub>.

### 2.5. Preparation of boehmite sol

The boehmite sol was prepared by the Yoldas process using AIP as the precursor [33]. The AIP was hydrolyzed in excess of deionized water ( $nH_2O:nAIP = 100:1$ ) for 1 h under vigorous stirring at 80 °C. Peptization was then initialized by adding HNO<sub>3</sub> ( $nAIP:nHNO_3 = 1:0.1$ ). Subsequently, the resulting colloidal suspension was heated under reflux for 2 h with vigorous stirring at 80 °C. At the end of this process, a stable transparent boehmite sol was obtained.

## 2.6. Preparation of hybrid materials $AN_1 - AN_4$ , $AM_4$ , $ATN_1 - ATN_4$ , and $ATM_4$

The hybrid material  $AN_1$  was prepared by the condensation of precursor 4a (5.01 g, 0.01 mol) and boehmite sol (0.001 mol) in ethanol (80 mL) by stirring at 65 °C for 2 h, by adding hydrochloric acid (0.365 g, 0.01 mol) and water (5 mL). The hybrid materials  $AN_2$ - $AN_4$  were synthesized using the same method as that used for synthesizing  $AN_1$ . The hybrid materials  $AN_1$ - $AN_4$ were prepared using different molar ratios of precursor 4a to the boehmite sol in the hydrolysis polycondensation; the molar



Fig. 4. <sup>29</sup>Si-NMR spectra of hybrid materials AN1-AN4.

ATN4 ATN3 ATN2 ATN1 -20 -40 -60 -80 -100 -120 -140 -160 ppm

Fig. 5. <sup>29</sup>Si-NMR spectra of hybrid materials ATN<sub>1</sub>-ATN<sub>4</sub>.

ratios were 1:0.1, 1:0.2, 1:0.4, and 1:0.6. The hybrid material **AM**<sub>4</sub> was prepared by the condensation of precursor **4b** with boehmite sol at a molar ratio of 1:0.6. The hybrid material **ATN**<sub>1</sub> was prepared by the condensation of precursor **4a** (5.01 g, 0.01 mol), TEOS (4.16 g, 0.02 mol), and boehmite sol (0.001 mol) in ethanol (80 mL) by stirring at 65 °C for 2 h, by adding hydrochloric acid (0.365 g, 0.01 mol) and water (5 mL). The hybrid materials **ATN**<sub>2</sub>-**ATN**<sub>4</sub> were synthesized using the same method as that used for synthesizing **ATN**<sub>1</sub>. The hybrid materials **ATN**<sub>1</sub>-**ATN**<sub>4</sub> were prepared using different molar ratios of precursor **4a** to TEOS and the boehmite sol in the hydrolysis polycondensation; the molar ratios were 1:2:0.1, 1:2:0.2, 1:2:0.4, and 1:2:0.6. The hybrid material **ATM**<sub>4</sub> was prepared by the condensation of precursor **4b** with TEOS and the boehmite sol at the molar ratio of 1:2:0.6.

### 3. Results and discussion

### 3.1. X-ray diffraction analysis

The XRD pattern of the gel film is shown in Fig. 1. The XRD pattern indicates that the gel film has a boehmite ( $\gamma$ -AlOOH) structure.  $\gamma$ -AlOOH was calcined at 550 °C for 10 h and measured by an X-ray diffraction analyzer. As shown in Fig. 1, the diffraction peak at  $2\theta$  around 37° is the (031) plane of boehmite [34,35]. It was



**Fig. 6.** <sup>27</sup>Al-NMR spectra of hybrid materials **AN**<sub>1</sub>–**AN**<sub>4</sub>.



Fig. 7. <sup>27</sup>Al-NMR spectra of hybrid materials ATN<sub>1</sub>-ATN<sub>4</sub>.

reported that the network structure could make this peak broadening, suggesting that a given mixed phase is present in the boehmite. Accordingly, in the present study we postulated that the broadening peak at  $2\theta$  around  $37^{\circ}$  may result from the structure of Si–O–Al networks in the gel. Meanwhile, the other diffraction peaks at  $46^{\circ}$  and  $67^{\circ}$  are the (200) and (002) planes of hexahedron  $\gamma$ -AlOOH, respectively [34,35].

### 3.2. FT-IR analysis

According to Fig. 2, precursors **4a–4b** had absorption peaks of the N–H group and the C–H group, respectively, near 3440 cm<sup>-1</sup> and 3113 cm<sup>-1</sup>; an additional Si–O absorption peak was observed near 1100 cm<sup>-1</sup> and an additional Si–C absorption peak near 1247 cm<sup>-1</sup>. The precursor **4b** had an additional methoxy group absorption peak near 1320 cm<sup>-1</sup>. According to Fig. 3, hybrid materials AN<sub>1</sub>-AN<sub>4</sub> had absorption peaks of the N-H group and the C–H group, respectively, near 3064  $\text{cm}^{-1}$  and 2962  $\text{cm}^{-1}$ . The nitric acid addition increased when the Y-AlOOH addition level was maximized; hence, the absorption peaks of the N-H group and the C–H group in the maximum ratio shifted left. The additional Si–O absorption peak near 1098 cm<sup>-1</sup> was also the characteristic peak of Al-O. The additional Si-C absorption peak was observed near 1249 cm<sup>-1</sup>, and the Si-O-Al absorption peak was seen near 1518 cm<sup>-1</sup>. According to Fig. 3, the hybrid materials ATN<sub>1</sub>-ATN<sub>4</sub> had absorption peaks of the N-H group and the C-H group, respectively, near 3079 cm<sup>-1</sup> and 2934 cm<sup>-1</sup>. The additional Si–O absorption peak observed near 1076 cm<sup>-1</sup> was also the characteristic peak of Al–O; there was an additional Si–C absorption peak observed near 1243 cm<sup>-1</sup>. However, the absorption peak was relatively weak when the amount of  $\gamma$ -AlOOH was small in the minimum ratio; the Si-O-Al absorption peak rose as the amount of γ-AlOOH increased.

Table 1EDS analysis of hybrid materials AN1-AN4, ATN1-ATN4.

Samples	Elemental composition (%)						
	С	0	S	Si	Al		
AN <sub>1</sub>	70.21	16.08	2.68	9.92	1.11		
AN <sub>2</sub>	70.07	16.26	2.32	9.85	1.50		
AN <sub>3</sub>	68.92	18.59	2.39	8.27	1.83		
AN <sub>4</sub>	58.33	25.09	2.17	8.63	5.78		
AM <sub>4</sub>	66.08	20.42	2.09	8.19	3.21		
ATN <sub>1</sub>	53.78	26.45	1.29	18.26	0.22		
ATN <sub>2</sub>	53.63	26.07	1.70	17.84	0.76		
ATN <sub>3</sub>	53.33	26.74	1.07	17.08	1.78		
ATN <sub>4</sub>	52.09	27.31	1.41	16.96	2.23		
ATM <sub>4</sub>	50.16	27.07	2.90	17.40	2.47		



Fig. 8. The EDS diagram of hybrid materials AN4.

### 3.3. <sup>29</sup>Si-NMR and <sup>27</sup>Al-NMR spectra analyses

According to the <sup>29</sup>Si-NMR inspection, there were Q<sup>1</sup>, Q<sup>2</sup>, Q<sup>3</sup>, and Q<sup>4</sup> absorption peaks; Q<sup>1</sup> and Q<sup>2</sup> were at  $\delta$ : -80 to -90 ppm, Q<sup>3</sup> was at  $\delta$ : -101 ppm, and Q<sup>4</sup> was at  $\delta$ : -110 ppm. However, the structure of Q<sup>1</sup> and Q<sup>2</sup> was such that some Si quadruple bonds had two unreacted Si-OH functional groups, such as (H-O)Si(-OSi=)<sub>2</sub>. The structure of Q<sup>3</sup> was such that some Si quadruple bonds had one unreacted Si-OH functional group such as (H-O)Si(-OSi=)<sub>3</sub>. The structure of Q<sup>4</sup> was such that all the Si quadruple bonds were completely reacted Si-O functional groups such as Si(-OSi=)<sub>4</sub>.

Fig. 4 shows the minimum proportion of the hybrid material **AN**<sub>1</sub>. The condensation polymerization of vinyltriethoxysilane (VTES) reduced the purity of the net structure, and there were many noise peaks. This situation could be improved by increasing the AlOOH addition. Hence, it was inferred that the Al–O–Al bonding became the main structure. VTES revealed signals for Q<sup>1</sup> and Q<sup>2</sup> at  $\delta$ : –71.2 ppm and  $\delta$ : 79.2 ppm because VTES was the bridging bond that caused the final absorption peak to take Q<sup>1</sup> and Q<sup>2</sup> as the main peaks.

According to Fig. 5, the hybrid material **ATN**<sub>1</sub> did not have a noise peak in the minimum ratio when there was silica gel. When the  $\gamma$ -AlOOH addition was at its minimum, there were Q<sup>1</sup>, Q<sup>2</sup>, Q<sup>3</sup>, and Q<sup>4</sup> absorption peaks. Q<sup>3</sup> was predominant, and Q<sup>4</sup> increased suddenly in the hybrid material **ATN**<sub>2</sub>. Al–O substituted Si–O of tetraethoxysilane (TEOS) to form Si–O–Al TEOS with signals for Q<sup>1</sup> and Q<sup>2</sup> at  $\delta$ : –79.2 ppm, Q<sup>3</sup> at  $\delta$ : –101.5 ppm, and Q<sup>4</sup> at  $\delta$ : –109 ppm. The  $\gamma$ -AlOOH addition increased proportionally, and the Q<sup>3</sup> absorption peak was predominant at the maximum addition level.



Fig. 9. The EDS diagram of hybrid materials ATN<sub>4</sub>.

 Table 2

 UV spectra of dyes, precursor, hybrid materials.

Compound	$\lambda_{max}(nm)$		Compound	$\lambda_{\max}(nm)$	
	Ethanol	DMF		Ethanol	DMF
6a	494	509	AN <sub>3</sub>	495	510
6b	450	456	AN <sub>4</sub>	495	509
7a	494	509	AM <sub>4</sub>	440	463
7b	450	463	ATN <sub>1</sub>	492	509
8a	495	510	ATN <sub>2</sub>	492	508
8b	444	466	ATN <sub>3</sub>	495	509
AN <sub>1</sub>	495	510	ATN <sub>4</sub>	496	510
AN <sub>2</sub>	495	510	ATM <sub>4</sub>	448	466

According to <sup>27</sup>Al-NMR inspection, the coordinate bonds that resulted from the Al hydrolysis were usually 6-coordinate bonds at  $\delta$ : -10 to 10 ppm, 5-coordinate bonds at  $\delta$ : 30–50 ppm, and 4coordinate bonds at  $\delta$ : >50 ppm. According to Fig. 6, the hybrid material AN<sub>1</sub> used a 6-coordinate bond as the main peak at the minimum  $\gamma$ -AlOOH ratio. The absorption peak of the 4-coordinate bond was around  $\delta$ : 51.2 ppm and disappeared gradually with an increase in the  $\gamma$ -AlOOH addition. It was obvious that the hybrid material AN<sub>4</sub> was predominated by the 6-coordinate bond that had an absorption peak around  $\delta$ : 6.4 ppm at the maximum ratio. According to Fig. 7, the hybrid materials ATN1-ATN4 had 4coordinate and 6-coordinate bonds at the minimum ratio. The absorption peak of the 4-coordinate bond of  $\gamma$ -AlOOH around  $\delta$ : 52.2 ppm decreased with decrease in the  $\gamma$ -AlOOH addition. It was obvious that the hybrid material ATN<sub>4</sub> was predominated by the 6-coordinate bond at the absorption peak around  $\delta$ : 6.7 ppm at the maximum ratio. The 6-coordinate bond was the main peak at the maximum ratio.

#### 3.4. EDS element analysis of hybrid material

According to Table 1, the EDS analysis of the hybrid materials showed that the aluminium content increased with increasing  $\gamma$ -AlOOH addition to hybrid materials **AN**<sub>1</sub>–**AN**<sub>4</sub>, but each increment was small. Hence, the difference was slight. The element carbon decreased at the maximum ratio of the hybrid material, whereas the element oxygen increased. This was because the high ratio formed more alumina film bonding Al–O–Al, and as shown in the Fig. 8 illustrates the aluminium content in the hybrid material **AN**<sub>4</sub> increased suddenly. In addition, according to Table 1, the relatively large mole number of aluminium in the hybrid materials **ATN**<sub>1</sub>–**ATN**<sub>4</sub> indicated a relatively high aluminium content according to the EDS analysis. However, the increase in the mole number



Fig. 10. UV spectra of dyes, precursor, hybrid materials in ethanol solvent.

was small, and hence, each increment was small. According to Fig. 9, the amount of aluminium increased in the hybrid material **ATN**<sub>4</sub>, but the difference was small. Therefore, a larger hybrid material ratio indicated that the alumina silicon bonding Al–O–Si was more obvious. According to Table 1, when the TEOS was fixed, the silicon content decreased with an increase in the aluminium content. The maximum **AM**<sub>4</sub> and **ATM**<sub>4</sub>  $\gamma$ -AlOOH addition level in the hybrid material resulted in the maximum aluminium content.

### 3.5. Analysis of UV spectrum

Table 2 and Fig. 10 present the results of the ultraviolet-visible absorption spectral analysis of each compound. The  $\lambda_{max}$  values associated with the mono-substituent follow the order 3a (494 nm) > 3b (450 nm). Based on this result, if the monosubstituent is a donor group, then its  $\lambda_{max}$  is assumed to increase. Meanwhile, the effect of the dye-bonding precursor and the hybrid material on  $\lambda_{max}$  is insignificant. The hybrid materials **AN**<sub>4</sub> and **ATN**<sub>4</sub> with various diazonium components are compared, and  $\lambda_{max}$  is found to vary with the substituent. A benzene ring structure to which a nitro group diazonium component is bonded as an acceptor group will prompt  $\lambda_{max}$  to move toward a relatively long wavelength. Bonding a methoxy group substituent diazonium component to a benzene ring reduces its  $\lambda_{\text{max}}.$  According to the spectra shown in Table 2, which indicate the effect of different solvents on the compound, dissolution in DMF increases  $\lambda_{max}$ . Since the dipole moment of ethanol is smaller than that of DMF and a relatively large dipole moment induces resonance among molecules more easily, less energy is required for dissolution in DMF than in ethanol, and consequently, the absorption wavelength is relatively high, leading to the bathochromic effect.

### 4. Conclusions

In this study, a series of 4-substitution thiazole heterocyclic azo dyes were synthesised, and then added VTES/ $\gamma$ -AlOOH and VTES/ TEOS/ $\gamma$ -AlOOH in different ratios to prepare a series of hybrid materials using the sol-gel method. The broadening diffraction peak of the XRD pattern indicated the structure of Si-O-Al networks of boehmite in the hybrid gel. The Si-O-Al absorption peaks were observed from the FT-IR characterizations, and the intensities of these absorption peaks increased with increasing  $\gamma$ -AlOOH amount. On <sup>29</sup>Si-NMR and <sup>27</sup>Al-NMR determinations the hybrid gels, including AN<sub>4</sub> and ATN<sub>1</sub>-ATN<sub>4</sub>, showed the main peak due to a 6coordinate bond at the maximum ratio, suggesting the occurrence of Si-O-Al and Al-O-Al networks. The ultraviolet spectra analysis showed that  $\lambda_{max}$  is greater for the more polar DMF than for ethanol. According to the experimental FT-IR, NMR, and energy-dispersive Xray spectroscopy results, the boehmite or boehmite/silica in the hybrid material could bond thiazole dyes to form the Al-O-Al or Al–O–Si network structures with a thiazole moiety.

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