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The synthesis of vinyltriethoxysilane-modified heteroaryl thiazole dyes and silica hybrid materials

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Hybrid materials composed of tetraethoxysilane and heteroaryl 4-substituent-2-aminothiazoles were prepared. 4-Substituted acetophenone, thiourea and iodide were used to generate the intermediate, 4-substituted-2-aminothiazole, as coupling component, which was then coupled with p-nitroaniline and p-methoxyaniline to yield heteroaryl 4-substitued thiazole azo dyes. The dyes subsequently underwent hydrolytic polycondensation with vinyltriethoxysilane and tetraethoxysilane to yield hybrid, heteroaryl thiazole azo dyes, whose chemical structure was characterized using FT-IR, ^{29}Si NMR, ^{1}H NMR and EDS.

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1. Introduction

Multifunctional polymeric materials have been used for optoelectronic polymer materials, composite materials, nanopolymer materials [1] and biopolymer materials; some are even employed in emerging fields of energy, medicine, biology and aviation. Organic/inorganic hybrid materials have also been used to prepare multifunctional polymeric materials [2–5]. Current methods for preparing functional polymers can be divided into four categories of preparation namely, using a functional monomer [6], by the chemical reaction of a polymer [7], blending and compounding [8], and (4) special processing or surface treatment [9]. The sol–gel method [10,11], which is generally applied to functionalized silica materials has been established in the synthesis of monodispersed particles that control chemical reactions in homogeneous solutions [12,13].

Heteroaryl azo dyes [14,15] contain unshared electron pairs of nitrogen and sulfur, which can trigger resonance and cause the π electron of the compound to move from the ground state to the excited state. This process facilitates the chromogenic development of the compound.

In view of the aforementioned facts, the sol–gel method was used to produce heteroaryl azo dyes via a blending reaction with various proportions of vinyltriethoxysilane and tetraethoxysilane.

2. Results and discussion

2.1. Preparation of hybrid materials 10a–10c and 13a–13c

Scheme 1 presents the route for synthesizing diazo components and bis-hetaryl monoazo dyes. The coupling components, 4-phenyl-2-aminothiazole **7a** and its derivatives **7b**–**7c**, used as starting materials in the synthesis of the precursor hybrid materials, were obtained by the cyclization of a mixture of p-phenylsubstituted-acetophenone **2a**–**2c**, thiourea **1** and iodide **3**. As shown in Scheme 1, two series of new bis-hetaryl monoazo dyes, **8a**–**8c** and **11a**–**11c,** based on 4-aryl-2-aminothiazoles as coupling components with both diazo components p-nitroaniline and p-methoxyaniline, were prepared. The diazo component p-nitroaniline was diazotized using sulfuric acid at 0–5 °C. Before the end of diazotization, the sulphamic acid was added to a diazonium salt solution to remove excess nitrite ions; the diazonium salt solution was then added to an aqueous diluted sodium carbonate solution of coupling components **7a**–**7c**. To complete the coupling reaction, the pH value of the mixture was adjusted from about 5 to 6 by adding 40% sodium hydroxide solution, which promoted the precipitation of the dyes. The presence of acetic acid prevented an abrupt increase in

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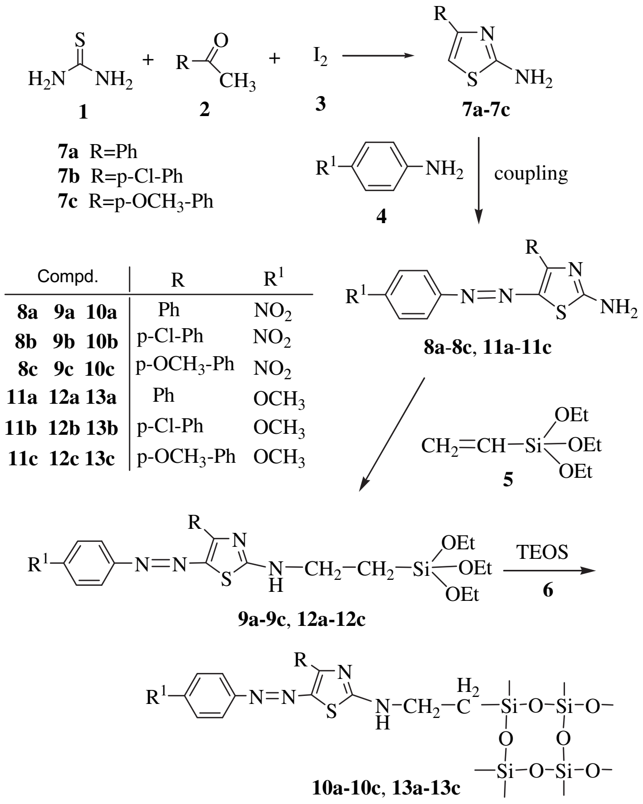

Compd.	R	R^1
8a 9a 10a	Ph	NO_2
8b 9b 10b	p-Cl-Ph	NO_2
8c 9c 10c	p-OCH_3-Ph	NO_2
11a 12a 13a	Ph	OCH_3
11b 12b 13b	p-Cl-Ph	OCH_3
11c 12c 13c	p-OCH_3-Ph	OCH_3

Scheme 1. Synthesis of the hybrid materials **10a**–**10c**, **13a**–**13c**.

pH [16]. Dyes **8a**–**8c** were precipitated after the diazonium solution was added, and were then filtered, washed and air-dried. The synthesis of dyes **11a**–**11c** was similar to that of dyes **8a**–**8c,** except that the diazo components were replaced by p-methoxyaniline. Then, two series of new bis-hetaryl monoazo dyes, **8a**–**8c** and **11a**–**11c,** alternately modified by the addition of vinyltriethoxysilane at a constant ratio to yield precursors **9a**–**9c** and **12a**–**12c,** were prepared. Finally, two series of precursors, **9a**–**9c** and **12a**–**12c,** were synthesized alternately by condensation with tetraethoxysilane at a constant ratio to yield hybrid materials **10a**–**10c** and **13a**–**13c**, were prepared.

2.2. FT-IR analysis of hybrid materials

The FT-IR figure of dyes and the hybrid materials indicates that dyes **8a** yields N–H group and C–H group absorption peaks close to 3440 cm^{-1} and 3113 cm^{-1}, respectively. In the FT-IR figure of the precursors **9a** there is an obvious deviation of amino group absorption peaks close to 3419 cm^{-1} and absorption peaks around 3395 cm^{-1}, revealing that some of the dye had reacted with VTES. The appearance of the Si–OR absorption peak around 1096 cm^{-1} proved that VTES could convert the primary amine group become a secondary amine group: the absorption peak was around 3372 cm^{-1}. Therefore, reactions can be reasonably assumed to have occurred between some of the dyes and VTES. The FT-IR figure of the hybrid materials **10a** includes the absorption peak of the converted secondary amine. The strong capture of the Si–O structure at 1065 cm^{-1} proves the dissociation of the NH_2 bond. The Si–C bond close to 1244 cm^{-1} also reveals that following the dissociation of the NH_2 bond, bonding with CH_2 result in linking the Si–O bond and prompts the formation of the Si–O–Si network. The FT-IR figure of the hybrid materials with various VTES/TEOS ratios indicates that increasing the TEOS concentration increases the absorption strength of Si–O–Si close to 1100 cm^{-1} and strengthens the bonding. The structure of Si–O–Si was analyzed using by ^{29}Si NMR.

2.3. Analysis of ^1H NMR and ^{29}Si NMR

Analysis of the ^1H NMR spectrum analysis of the heteroaryl azo dye **8a**–**8c**, presented in Table 2, reveals that the diazo coupling of the intermediates **7a**–**7c** causes the –CH of dyes **8a**–**8c** to be replaced by an azo benzene ring. The benzene ring absorbs the multiplet of dye **8a** at $\delta = 7.39$–7.55 ppm; the second and sixth positions of the benzene ring absorb the doublet at $\delta = 7.71$ ppm; the symmetric hydrogens, 2,6-Ph-H and 3,5-Ph-H, absorb the doublets at $\delta = 8.19$ ppm and 8.28 ppm, respectively, and the singlet at $\delta = 8.98$ ppm is absorbed by $-NH_2$. Moreover, ^{29}Si NMR [17] is employed to observe the structure that is formed by the hydrolysis of Si. While the FT-IR results indicate the formation of Si–O–Si by a sol–gel reaction, ^{29}Si solid-state NMR gives further information on the structure of silica and the extent of the Si–OH condensation reaction. In principle, high-resolution solid-state NMR spectra of simple dyes and VTES can include absorption peaks at −70.51 ppm (T^2) and −80.17 ppm (T^3), corresponding to Si–OR following the hydrolysis of VTES. The ^{29}Si NMR figure of hybrid materials that are formed with various molar VTES/TEOS are considered. At both −69.49 ppm (T^2) and −78.57 ppm (T^3), as well as −101.14 ppm (Q^3) and −110.83 ppm (Q^4), considerable absorption occurs. Adding of TEOS increases, the intensity of the absorption peaks of Q^3 and Q^4 is becoming more significant. The main peak, Q^4, appeared at −110.83 ppm adjacent to a minor peak at −101.14 ppm, Q^3. The strong Q^4 revealed that the degree of silicon condensation was very high.

2.4. EDS analysis of hybrid materials

Table 3 presents the EDS of the hybrid materials. The table indicates that the weight of a dye/VTES/TEOS hybrid material increases with the amount of TEOS because the $Si(OH)_3$ structure that is formed by hydrolysis-condensation of VTES and the SiO_2 that is formed after the hydrolysis-polycondensation of TEOS are combined with the dyes. The atomic content reveals that the Si peak reveals a dyes/VTES/TEOS hybrid material becomes more intense as the amount of TEOS increases.

2.5. Analysis of UV spectrum

Table 4 presents the results of the ultraviolet visible absorption spectral analysis of each compound. The λ_{max} values associated with the mono-substituent follow the order **8c** > **8a** > **8b**. Based on this result, if the mono-substituent is a donor group, then its λ_{max} is assumed to increase. Meanwhile, the effect of the dyes bonding precursor and the hybrid material on λ_{max} is insignificant. Dyes **8a**–**8c** and dyes **11a**–**11c** with various diazonium components are compared and λ_{max} is found to vary with the substituent. A benzene ring structure to which is bonded a nitro group diazonium component as an acceptor group will prompt λ_{max} to move toward longer wavelength. Bonding a methoxy group substituent diazonium component to a benzene ring reduces its λ_{max}. The ultraviolet visible absorption spectral analysis of hybrid materials with various ratios of constituents demonstrates that increasing the number of moles of any one constituent does not significantly affect $\lambda_{max.}$ According to the spectra, which indicate the effect of different solvents on the compound, dissolution in DMF increases λ_{max}. Since the dipole moment of THF is smaller than that of DMF, and that a greater dipole moment induces resonance among molecules more easily, less energy is required for dissolution in DMF than in THF, and consequently the absorption wavelength is higher.

3. Experimental

All melting points are uncorrected and in °C. FT-IR spectra were recorded on a Bio-Red Digilab FTS-40 spectrometer (KBr); ^1H NMR spectra were obtained on a BRUKER AVANCE 400 MHz NMR spectrometer, and chemical shifts are presented in δ ppm using TMS as an internal standard. The ^{29}Si 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 is 914. Mass spectra were obtained using a Finnigan TSQ-700 GC/LC/MS spectrometer. SEM images were captured using a Philips XL40 FE-SEM. Electronic spectra were recorded using a SHIMADZU UV-1201 from dyes solutions in DMF and THF at a concentration of 1×10^{-5} mol l^{-1}.

3.1. Material

Vinyltriethoxysilane, tetraethoxysilane, acetophenone, p-methoxyacetophenone, p-chloroacetophenone and p-methoxyaniline were purchased from Acros Co., Ltd., Belgium. Thiourea, sulphamic acid, p-nitroaniline and iodide were purchased from Hayashi Pure Chemical Co., Ltd.

*3.2. Preparation of intermediates **7a**–**7c***

2-Amino-4-phenyl-thiazole (**7a**) was prepared from a mixture of thiourea, acetophenone and iodide, as described elsewhere [18]. **7b**–**7c** were synthesized by the same method as described for the synthesis of **7a**. Tables 1 and 2 present the physical and spectral data of these compounds.

*3.3. Preparation of the dyes **8a**–**8c** and **11a**–**11c***

A finely ground powder of p-nitroaniline **4a** (1.38 g, 0.01 mol) was added to a mixture of 12 ml of hydrochloric and stirred for 20 min. Sodium nitrite (0.72 g, 0.0105 mol) was added in portions to 5 ml of concentrated sulfuric acid 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-2-aminothiazole 7**a** (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, after which time, the pH was raised to 5–6 (by adding aqueous sodium hydroxide or sodium acetate). The ensuing mixture was filtered and washed in water to neutral pH. The resulting product was filtered, washed with water and recrystallized from ethanol to give dye **8a**. Compounds **8b**–**8c** and **11a**–**11c** were synthesized by the same method as was used to synthesize **8a** that was coordinated with the various diazo components. Tables 1 and 2 present the physical and spectral data of these compounds.

Table 1
Characterization data for intermediates and dyes derivatives **7a**–**7c**, **8a**–**8c**, **9a**–**9c**, **11a**–**11c** and **12a**–**12c**.

Compound	M.p.[a] (°C)	MS (m/e,M^+)	Yield[b] (%)	Molecular formula
7a	143–145	176	65	$C_9H_8N_2S$
7b	162–164	210	50	$C_9H_7N_2SCl$
7c	183–185	206	67	$C_{10}H_{10}N_2SO$
8a	245–247	325	70	$C_{15}H_{17}N_2SO_2$
8b	262–264	360	60	$C1_5H_{10}O_2N_5SCl$
8c	280–282	356	75	$C_{16}H_{13}N_5SO_3$
9a	304–306	468	59	$C_{23}H_{29}N_5SO_2Si$
9b	315–317	503	51	$C_{23}H_{28}N_5SO_2SiCl$
9c	321–323	499	57	$C_{24}H_{31}N_5SO_3Si$
11a	253–255	310	50	$C_{16}H_{14}ON_4S$
11b	271–273	345	47	$C_{16}H_{13}ON_{14}SCl$
11c	297–299	341	52	$C_{17}H_{16}O_2N_4S$
12a	313–315	453	45	$C_{26}H_{32}N_4SOSi$
12b	319–321	488	41	$C_{26}H_{31}ON_4SSi$
12c	325–327	484	43	$C_{27}H_{34}O_2N_4SSi$

[a] Recrystallized from ethanol.
[b] Yield of crude product.

Table 2
Spectral data of intermediates and dyes derivatives **7a**–**7c**, **8a**–**8c**, **11a**–**11c**.

Dyes	IR (KBr) ν (cm^{-1})	^1H NMR (DMSO-d_6) δ (ppm)
7a	$-NH_2$ 3425 $-CH$ 3110	7.07 (1H, s, $-CH$), 7.20 (1H, s, $-NH_2$), 7.26–7.79 (5H, m, ArH)
7b	$-NH_2$ 3431 $-CH$ 3107 C–Cl 727	7.06 (1H, s, $-CH$), 7.10 (1H, s, $-NH_2$), 7.39 (2H, d, 2,6-ArH), 7.82 (2H, d, 3,5-ArH)
7c	$-NH_2$ 3430 $-CH$ 3112 $O-CH_3$ 1174	3.81 (3H, s, $-OCH_3$), 7.04 (1H, s, $-NH_2$), 7.70 (2H, d, 3,5-ArH), 7.76 (2H, d, 2,6-ArH)
8a	$-NH_2$ 3433 $-CH$ 3057	7.04 (1H, s, $-NH_2$), 7.51–7.55 (5H, m, ArH), 7.71 (2H, d, 2,6-Ph-H), 8.19 (2H, d, 3,5-Ph-H)
8b	$-NH_2$ 3432 $-CH$ 3105 C–Cl 739	7.06 (1H, s, $-NH_2$), 7.51 (2H, d, 2,6-ArH), 7.55 (2H, d, 3,5-ArH), 7.71 (2H, d, 2,6-Ph-H), 7.78 (2H, d, 3,5-Ph-H)
8c	$-NH_2$ 3427 $-CH$ 3086 $O-CH_3$ 1170	3.80 (3H, –s, OCH_3), 6.89 (1H, s, $-NH_2$), 7.14 (2H, d, 3,5-ArH), 7.23 (2H, d, 2,6-ArH), 7.74 (2H, d, 3,5-Ph-H), 7.82 (2H, d, 2,6-Ph-H)
11a	$-NH_2$ 3430 $-CH$ 3105 $O-CH_3$ 1179	3.80 (3H, s, $-OCH_3$), 7.04 (1H, s, $-NH_2$), 7.40–7.50 (5H, m, ArH), 7.61 (2H, d, 3,5-Ph-H), 7.82 (2H, d, 2,6-Ph-H)
11b	$-NH_2$ 3430 $-CH$ 3115 $O-CH_3$ 1181 C–Cl 732	3.81 (3H, s, $-OCH_3$), 7.06 (1H, s, $-NH_2$), 7.22 (2H, d, 3,5-ArH), 7.43 (2H, d, 2,6-ArH), 7.62 (2H, d, 3,5-Ph-H), 7.76 (2H, d, 2,6-Ph-H)
11c	$-NH_2$ 3425 $-CH$ 3110	3.80 (3H, s, $-OCH_3$), 6.89 (1H, s, $-NH_2$), 7.22 (2H, d, 3,5-ArH) 7.41 (2H, d, 2,6-ArH), 8.07 (2H, d, 3,5-Ph-H), 8.18 (2H, d, 2,6-Ph-H)

*3.4. Preparation of the precursor **9a**–**9c** and **12a**–**12c***

Precursor **9a** (also known as V_3) was prepared by the reaction of dyes **8a** (3.25 g, 0.01 mol) followed by the addition of vinyltriethoxysilane (9.5 g, 0.05 mol) in 80 ml tetrahydrofuran with stirring at 65 °C for 4 h at an adjusted pH of 4–5. Precursors **9b**–**9c** and **12a**–**12c** were synthesized by the same method used to prepare **9a**.

*3.5. Preparation of hybrid materials **10a**–**10c** and **13a**–**13c***

Hybrid material **10a** was prepared by the condensation of precursor **9a** (5.01 g, 0.01 mol) and tetraethoxysilane (2.08 g,

Table 3
EDS analysis of hybrid materials.

Compd.	Elemental composition (%)				
	C	N	O	Si	S
T_1	45.89	4.06	18.51	25.66	5.88
T_2	36.30	4.78	22.30	32.16	4.46
T_3	33.32	3.55	24.98	33.16	4.99
T_4	28.44	3.38	25.29	37.89	5.00

Table 4
Visible absorption spectra of dyes, precursor and hybrid materials.

Data	λ_{max} (nm)		Data	λ_{max} (nm)	
Dyes	DMF	THF	Dyes	DMF	THF
8a	510	499	**11a**	465	459
8b	505	497	**11b**	461	455
8c	524	518	**11c**	473	466
9a	506	495	**12a**	465	459
9b	510	497	**12b**	460	453
9c	514	510	**12c**	476	468
10a	511	501	**13a**	465	459
10b	514	505	**13b**	467	461
10c	523	515	**13c**	470	465

0.01 mol), hydrochloric acid (0.365 g, 0.01 mol) and 5 ml of water in 80 ml tetrahydrofuran, with stirring at 65 °C for 2 h. The hybrid materials **10b**–**10c** and **13a**–**13c** were synthesized using the method described for **10a**. The hybrid materials T_1–T_4 were prepared using different molar ratios of precursor **9a:**tetraethoxysilane **of** 1:1, 1:3, 1:5 and 1:10.

4. Conclusions

In this work, a series of heteroaryl 4-substituent thiazole dyes is prepared. VTES/TEOS are added in various ratios to produce a series of functional hybrid materials is produced by the sol–gel method. The color of the series of dyes that contain the nitro group as the diazonium component substituent is significantly deeper than that of the series of dyes that have the methoxy group as the substituent. FT-IR and NMR analysis confirms that the silicon in the hybrid material can indeed bond with the thiazole dyes. Additionally, ultraviolet spectral analysis reveals differences among different solvents. The λ_{max} values from the absorption spectra follow the order DMF > THF.

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