

Full Paper

Blue Organic Light-emitting Supramolecular Microfibers: The Self-assembly of a 1,2,4-Triazolo[1,5-a]pyrimidine Derivative

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Abstract: The design and synthesis of 5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-thioaceto-(2-fluorobenzyl) hydrazone (TPTH), which self-assembled into supramolecular microfibers with blue organic light-emitting properties, is reported. This is the first occurrence of the molecular self-assembly of 1,2,4-triazolo[1,5-a]pyrimidine derivatives.

Keywords: 1,2,4-Triazolo[1,5-a]pyrimidine; acetohydrazone; synthesis; self-assembly; supramolecular

Introduction

Recently, self-assembly of organic small molecules into supramolecules has attracted a great deal of attention [1]. These supramolecules always have three-dimensional fibrous network structures and might have potential applications in drug delivery, coatings, lithography, catalyst supporters, scaffolds for tissue engineering, the engineering of nanostructural materials and as self-supporting porous materials in the novel separation for macro-molecules, and so forth [2]. Although it is well known that the self-assembly processes is mediated by cooperative weak and noncovalent bonds, such as hydrogen bonds, ionic bonds, hydrophobic interactions, van der Waals interactions, and water-mediated hydrogen bonds, there is still no sufficient understanding about the general rules of the self-assembly mechanism [3-5]. Therefore, significant efforts have been devoted to identify novel system

with a three-dimensional interconnecting self-organized network structure with the aim to enrich the content of supramolecular chemistry and obtain new functional materials with desirable properties [6-9].

In last decades, 1,2,4-triazolo[1,5-a]pyrimidine derivatives have been extensively studied for their applications in medical chemistry and agrochemistry [10-12]. Additionally, a few examples of 1,2,4-triazolo[1,5-a]pyrimidines have also been applied in the field of photosensitive materials [13, 14], and some triazole-based compounds were also reported to be useful as electron transporting materials in organic light-emitting diodes [15, 16]. However, so far there have been no reports concerning the self-assembly of 1,2,4-triazolo[1,5-a]pyrimidine derivatives, to the best of our knowledge.

Bearing in mind that the triazolopyrimidinyl moiety is a large π -conjugated system, it might display some unique photonic properties when linked with another π -conjugated system through a nonconjugated bridge (-SCH₂CONHN=CH-) containing hydrogen bond acceptors or donors. A synthetic route to such systems using aryl aldehydes as starting materials is shown in Scheme 1 [17]. We hoped these compounds might form a superstructure *via* self-assembly by the cooperative π - π stacking interactions and hydrogen bond interactions. Interestingly, one compound, 5,7-dimethyl-[1,2,4]triazolo[1,5-a]pyrimidine-2-thioaceto-(2-fluorobenzyl)hydrazone (**4a**), was indeed found to self-assemble into supramolecular microfibers in the solid state and displayed a unique photonics property. To our knowledge, this is the first reported occurrence of the molecular self-assembly of 1,2,4-triazolo[1,5-a]pyrimidine derivatives.

Results and Discussion

As shown in Scheme 1, 2-mercapto-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine and ethyl α -bromoacetate were employed as starting materials to obtain 5,7-dimethyl-[1,2,4]triazolo[1,5-a]pyrimidine-2-thioacetohydrazone (TPTH) by a three-step synthetic sequence. Thus 2-ethoxyacetylthio-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine (**2**) was synthesized in 94% yield by the reaction of 1,2-mercapto-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine with ethyl α -bromoacetate in the presence of sodium hydroxide. Compound **2** which was then reacted with hydrazine to give 2-hydrazinoacetylthio-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine (**3**). Compounds **4** (TPTH) were generated by the reaction between aldehydes and the intermediate **3**.

Firstly, we examined the absorption spectra of **4a** in solution and in the solid state, as displayed in Figure 1. In DMF solution, there are two broad absorption bands at 250 nm and 350 nm for the phenyl and triazolo[1,5-a]pyrimidinyl chromophores, respectively. The broad band reflects the existence of electron transfer between the phenyl and triazolo[1,5-a]pyrimidinyl. This broadening effect might originate from extensive excitation coupling, and the extent of the broadening would strongly correlate with the degree of coupling. This depends on several factors, such as the closeness of the adjacent molecule, the tilting angle, the overlap position, the substituted groups, and the extinction. The experiment showing the relationship between the absorbance and concentration indicated that **4a** is not aggregated in the solution. However, a narrow band with a maximum absorption at around 320 nm was observed in the solid state absorption spectra of **4a**. Compared with that in the DMF solution, the absorption spectra in the solid state gave a considerable red-shift, which might be attributed to the

intermolecular interaction of **4a**. In addition, the narrow band shows that the electron transfer does not occur because of the intermolecular π - π stacking and nonclassical hydrogen bond interactions.

Scheme 1. Synthesis of 5,7-dimethyl-[1,2,4]triazolo[1,5-a]pyrimidine-2-thioacetohydrazone (TPTH).

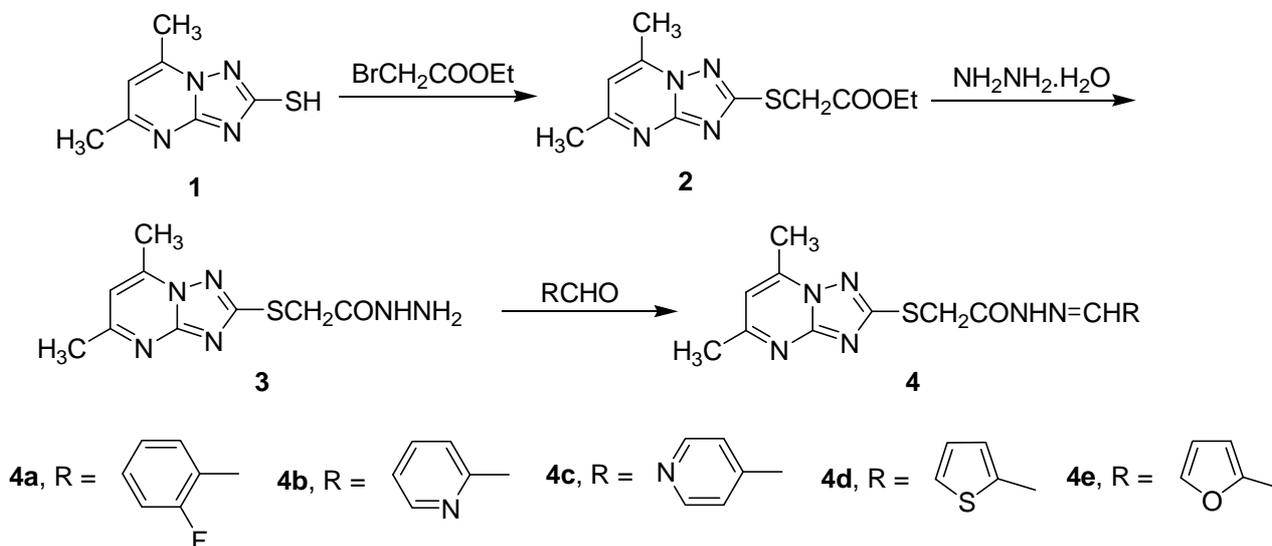
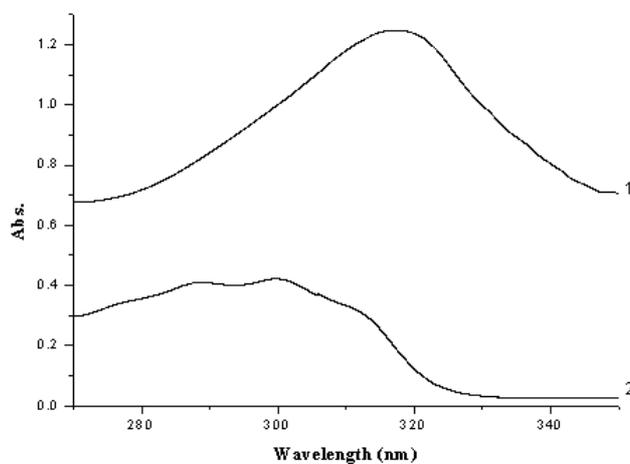


Figure 1. UV absorption spectra of **4a** in (1) the solid state and (2) DMF (1×10^{-5} M).



Secondly, we also examined the emission spectra of **4a** in solution and in the solid state (Figure 2). When excited at 302 nm, two emission peaks at 335 nm and 352 nm can be observed in the solution spectrum. The luminescence quantum yield of **4a** is 0.45 (relative to the standard coumarin). The emission behavior in DMF solution can be simply explained by the conformational changes of chromophores within the **4a** molecule. However, an identical peak at 462 nm with lower intensity was observed in the solid state, which might result from the aggregation of **4a**. These results are consistent with that of UV-vis experiment. There are two isolated π -conjugated system in the **4a** molecule, which display individual optical properties both in the UV-vis and fluorescence spectra in a diluted solution, but the molecule can self-assemble in the solid state via noncovalent interactions.

Subsequently, an atypical field emission scanning electronic microscopy (Field-emission SEM) image of the synthesized microfibers was obtained, in order to examine the configuration of the aggregate. As shown in Figure 3a, the **4a** sample consists of rather regular microfibers with lengths up

to the micrometer range, and many microfibers are in an orderly arrayed pattern and each of these microfibers is almost uniform in size. In addition, there are also some branched or short microfibers in the fibrous networks. As seen from the magnified image of a single one (Figure 3b), the microfiber is smooth and clean with a diameter of 278 nm. It suggests a possible formation mechanism by which **4a** initially self-organizes and then assembles into shorter microfibers, after which it self-assembles into longer microfibers.

Figure 2. Emission spectrum of the **4a** in (1) DMF solution ($1 \times 10^{-5} \text{M}$; excited at 302 nm) and (2) solid state (excited at 315nm).

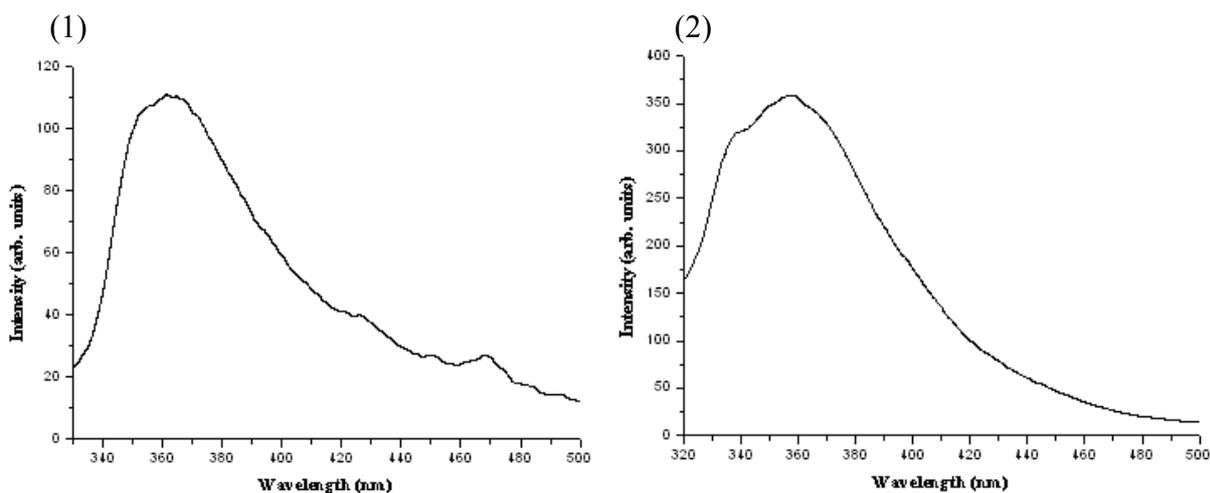
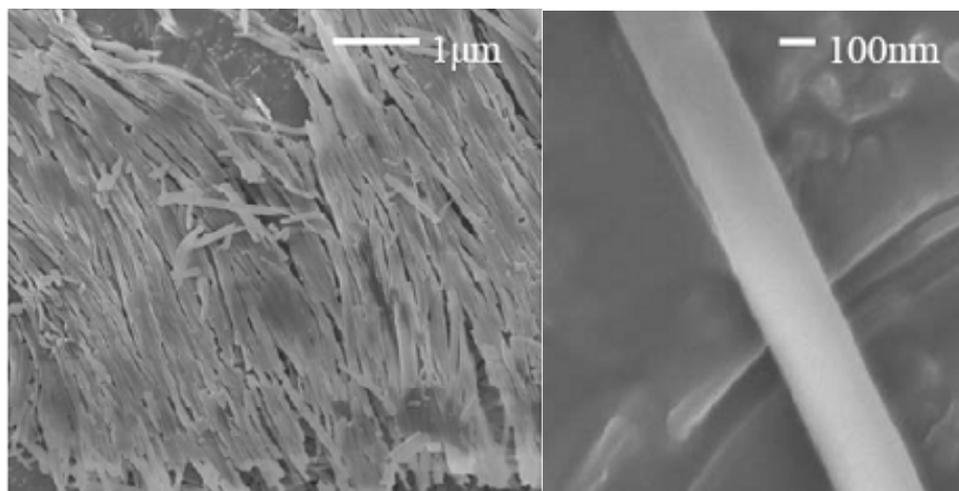


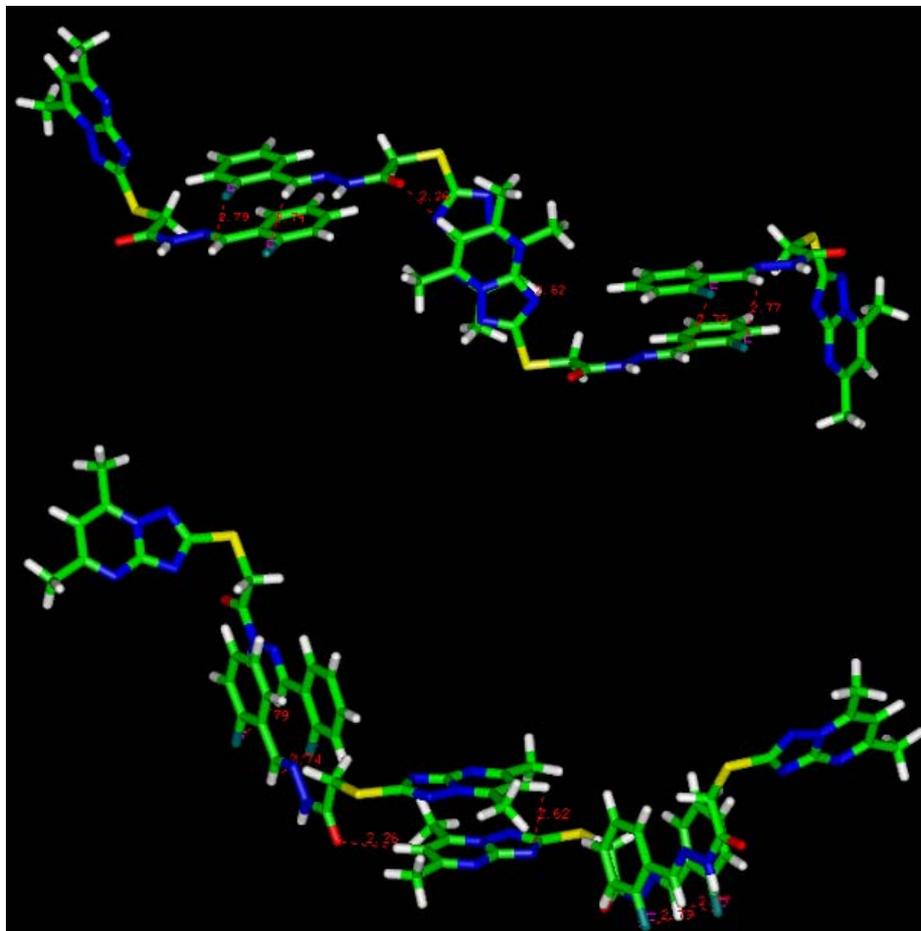
Figure 3. Field-emission SEM images of **4a** supramolecular aggregates: a) overall sample morphology; b) a detailed view on a single microfiber.



To visualize the molecular dispositions of the self-assembled suprastructures of **4a**, molecular simulations were performed using the Insight II software. Figure 4 illustrates the molecular modeling results of the self-assembled system. As shown, the 1,2,4-triazolo[1,5-a]pyrimidinyl of one molecule can pack with that of the adjacent molecule through π - π stacking interactions, while the phenyl of the two adjacent molecules can pack with each other very well. Additionally, the F atom of one molecule forms two hydrogen bonds with the H atom of the N=CH group of the adjacent molecule, while the oxygen atom of the C=O group forms a hydrogen bond with the 6-H of the triazolopyrimidinyl of the

adjacent molecule, and the hydrogen bond between the 6-H and 3-N atom of two adjacent triazolopyrimidinyl was also observed.

Figure 4. A possible mechanism for the self-assembly of **4a**. The hydrogen bond distances are: F...H, 2.79Å, 2.74 Å; O...H, 2.26Å; N...H, 2.62Å.



Conclusions

In conclusion, we successfully designed and synthesized a 1,2,4-triazolo[1,5-a]pyrimidine derivative containing two independent π -conjugated systems and hydrogen bond acceptors and donors. The experimental results demonstrated that **4a** was a non-planar intermolecular photoinduced charge transfer compound [18], which could self-assemble in the solid state and displayed a special fluorescence spectrum, compared with that obtained in dilute solution. In addition, the microfibers obtained by the self-assembly of TPTH showed blue photoluminescence properties. Molecular simulation results indicated that π - π stacking interactions and hydrogen bonds might be the important driving forces for the formation of supra-molecular microfibers. To our knowledge, this work provides a completely new supramolecular system for producing new potential blue organic light-emitting material.

Experimental

General

Melting points were measured with a Buchi melting point apparatus and are uncorrected. TLC was performed on Merck 60 F254 silica gel-coated aluminum sheets, and spots were detected by UV light (254 nm). The $^1\text{H-NMR}$ spectra were recorded on a Vario MERUCY-PLUS 400 instrument using DMSO-d_6 as a solvent and TMS as an internal standard. MS spectra were performed on a Hewlett-Packard 5988A instrument. IR spectra were recorded as KBr pellets on a Perkin-Elmer Fourier transform infrared spectrophotometer. Elemental analyses were performed on a Vario El III CHNS instrument. The compound 2-mercapto-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine (**1**) was synthesized according to [19]. The other chemicals were obtained from commercially available sources and used without further purification.

Syntheses

Preparation of 2-ethoxyacetylthio-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine (**2**)

To a stirred mixture of 2-mercapto-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine (**1**, 18 g, 0.1 mol), sodium hydroxide (4 g, 0.1 mol) and water (250 mL), a mixture of $\text{BrCH}_2\text{CO}_2\text{Et}$ (16.7 g, 0.1 mol) in methanol (50 mL) was added dropwise at room temperature. After stirring the reaction mixture for 2 hours, the precipitate formed was filtered off and recrystallized from methanol to afford **2** as a white needle-like crystals (24 g, 94% yield); mp 142-143°C; $^1\text{H-NMR}$ δ : 1.24 (t, 3H, CH_2CH_3), 2.57 (s, 3H, 5- CH_3), 2.67 (s, 3H, 7- CH_3), 4.07 (s, 2H, SCH_2), 4.16-4.19 (q, 2H, CH_2CH_3), 6.69 (s, 1H, 6-H); MS m/e (relative intensity) 266 (M^+ , 34.6), 193 (100), 149 (23.9), 108 (80.5), 107 (32.6).

Preparation of 2-hydrazinoacetylthio-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine (**3**)

2-Ethoxyacetylthio-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine (**2**, 13.3g, 0.05 mol), hydrazine monohydrate (20 mL, 0.35 mol) in ethanol (200 mL) were refluxed for 4 hours. After cooling to room temperature, the precipitate was filtered and washed twice with ethanol. The solid was recrystallized from methanol to give **3** as white crystals (11.7 g, 93% yield); mp 202-203 °C; $^1\text{H-NMR}$ δ : 2.55 (s, 3H, 5- CH_3), 2.65 (s, 3H, 7- CH_3), .9.5 (s, 2H, SCH_2), 4.35 (bs, 2H, NH_2), 7.10 (s, 1H, 6-H), 9.40 (s, 1H, NH).

General Procedure for Preparation of

5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-thioaceto-hydrazones **4a-e**

2-Hydrazinoacetylthio-5,7-dimethyl-1,2,4-triazolo[1,5-a]pyrimidine (**3**, 1.4 g, 5 mmol), the appropriate aldehyde (6 mmol) and acetic acid (0.5 mL) were refluxed in ethanol (50mL) until the starting materials disappeared. After cooling to room temperature, the precipitate was filtered and

washed twice with ethanol. The solid was recrystallized from DMF or DMF- acetonitrile mixture to afford **4** as white crystals.

5,7-Dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-thioaceto-(2-fluorobenzyl)hydrazone (4a). Yield: 94%; mp 196-197 °C; ¹H-NMR δ: 2.49, 2.52 (2s, 3H, 5-CH₃), 2.62, 2.64 (2s, 3H, 7-CH₃), 4.12, 4.54 (2s, 2H, SCH₂), 7.06 (s, 1H, 6-H), 7.30-7.80 (m, 4H, Ar-H), 8.23 (2s, 1H, CH), 11.8 (2S, 1H, NH); MS *m/e* (relative intensity) 358 (M⁺, 6.14), 221 (42.7), 194 (52.4), 193 (52.9), 180 (100), 149 (37.6), 108 (79.4), 67 (43.7); FTIR: ν_(C=O) at 1677 cm⁻¹; Anal. Calcd. for C₁₆H₁₅FN₆OS: C, 53.62%; H, 4.22%; N, 23.45%. Found: C, 53.75%; H, 4.29%; N, 23.31%.

5,7-Dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-thioaceto-(2-pyridinyl)hydrazone (4b). Yield: 91%; mp 205-206 °C; ¹H-NMR δ: 2.55 (s, 3H, 5-CH₃), 2.65, 2.67 (2s, 3H, 7-CH₃), 4.15, 4.58 (2s, 2H, SCH₂), 7.11, 7.12 (2s, 1H, 6-H), 7.41-7.43 (d, 1H, 3-pyridine), 7.86-7.96 (m, 2H, 4,5-pyridine), 8.08, 8.24 (2s, 1H, CH), 8.61 (d, 1H, 6-pyridine), 11.84, 12.00(2S, 1H, NH); MS *m/e* (relative intensity) 342 (M+1, 13.3), 221 (67.7), 194 (100), 193 (79.8), 180 (68.9), 149 (63.4), 108 (34.6), 65 (35.8); FTIR: ν_(C=O) at 1693 cm⁻¹; Anal. Calcd. for C₁₅H₁₅N₇OS: C, 52.77%; H, 4.43%; N, 28.72%; Found: C, 52.95%; H, 4.51%; N, 28.21%.

5,7-Dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-thioaceto-(4-pyridinyl)hydrazone (4c). Yield: 98%; mp 251-252 °C; ¹H-NMR δ: 2.55 (s, 3H, 5-CH₃), 2.65, 2.67 (2s, 3H, 7-CH₃), 4.16, 4.58 (2s, 2H, SCH₂), 7.11, 7.12 (2s, 1H, 6-H), 7.64, 7.65 (2s, 2H, 3,5-pyridine), 8.02, 8.23 (2s, 1H, CH), 8.62, 8.63 (2s, 2H, 2,6-pyridine) 11.92, 12.05 (2s, 1H, NH); MS *m/e* (relative intensity) 342 (M+1, 100), 221 (29.0), 194 (13.0), 193 (52.3), 180 (51.6), 149 (18.3), 108 (16.0); FTIR: ν_(C=O) at 1705 cm⁻¹; Anal. Calcd. for C₁₅H₁₅N₇OS: C, 52.77%; H, 4.43%; N, 28.72%; Found: C, 53.02%; H, 4.53%; N, 28.28%.

5,7-Dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-thioaceto-(2-thiophenyl)hydrazone (4d). Yield: 99%; mp 184-185 °C; ¹H-NMR δ: 2.55, 2.57 (2s, 3H, 5-CH₃), 2.66, 2.67 (2s, 3H, 7-CH₃), 4.11, 4.45 (2s, 2H, SCH₂), 7.11-7.13 (m, 2H, 6-H, 3-thiophene), 7.44-7.47 (m, 1H, 4-thiophene), 7.63-7.66 (m, 1H, 5-thiophene), 8.22, 8.44 (2s, 1H, CH), 11.62, 11.72 (2s, 1H, NH); MS *m/e* (relative intensity) 347 (M+1 46.9), 346 (M⁺ 56.7), 221 (100), 194 (30.2), 193 (75.0), 180 (42.8), 149 (25.9), 108 (31.1), 67 (12.9); FTIR: ν_(C=O) at 1675 cm⁻¹; Anal. Calcd. for C₁₄H₁₄N₆OS₂: C, 48.54%; H, 4.07%; N, 24.26%; Found: C, 48.32%; H, 4.03%; N, 24.28%.

5,7-Dimethyl-1,2,4-triazolo[1,5-a]pyrimidine-2-thioaceto-(2-furyl)hydrazone (4e). Yield: 99%; mp 190-192 °C; ¹H-NMR δ: 2.55 (s, 3H, 5-CH₃), 2.66, 2.67 (2s, 3H, 7-CH₃), 4.11, 4.50 (2s, 2H, SCH₂), 6.62 (s, 1H, 4-furan), 6.90, 6.91(d, 1H, 3-furan), 7.11, 7.12 (2s, 1H, 6-H), 7.82 (s, 1H, 5-furan), 7.93, 8.11 (2s, 1H, CH), 11.60, 11.71(2S, 1H, NH); MS *m/e* (relative intensity) 331 (M+1 94.5), 330 (M⁺ 100), 221 (32.2), 193 (41.6), 180 (17.3), 149 (14.7), 108 (26.2), 52(42.4); FTIR: ν_(C=O) at 1674 cm⁻¹; Anal. Calcd. for C₁₄H₁₄N₇O₂S: C, 50.90%; H, 4.27%; N, 25.44%; Found: C, 50.82%; H, 4.33%; N, 25.28%.

Acknowledgements

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Sample Availability: Samples of the compounds are available from the authors.