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1,3,4-Thiadiazol-2-ylphenyl-1,2,4,5-tetrazines: efficient synthesis via Pinner reaction and their luminescent properties

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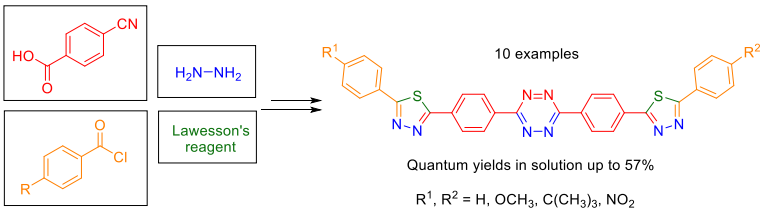
Abstract

Due to the interest in, and diverse applications of, 1,2,4,5-tetrazines and 1,3,4-thiadiazoles, individually and, more recently, in combination, a series of novel 1,2,4,5-tetrazine derivatives conjugated directly or via a 1,4-phenylene linker with a 1,3,4-thiadiazole core, were synthesized. A six-step reaction sequence, involving the Pinner reaction and oxidation under mild conditions, was used. This approach worked well for both symmetrical and unsymmetrical arrangements. Their luminescence properties were examined and are reported. The obtained compounds may have a number of great applications potential.



Keywords: Tetrazines, 1,2,4,5-tetrazine, 1,3,4-thiadiazole, Pinner reaction, Lawesson's reagent, aromatic carbonitriles

Introduction

One of the most interesting heterocyclic arrangements, characterised by both the maximum content of nitrogen atoms and its ring stability, is the six-membered 1,2,4,5-tetrazine (*s*-tetrazine).[1] Among its most commonly described applications, one has to distinguish high-energy-density materials (HEDM), which allow their utilisation in the production of explosives and propellants.[2] However, the derivatives of this compound also have great potential for applications in other fields. In the literature, there are more and more studies on the possibilities of using *s*-tetrazine derivatives in laser dyes, organic light emitting diodes (OLEDs) or perovskite solar cells.[3-5] Optoelectronics is an intensively developing and researched field, however, new organic n-type semiconductors, which would allow improvements in the efficiency and durability of devices, are still being researched. Accordingly, nitrogen-containing compounds are of great interest. Due to the high electronegativity of nitrogen, heterocycles rich in this atom are characterised by a large electron deficit. The use of such systems allows the modification of the charge-transport properties of a given material to obtain the appropriate levels of bandgap energies. In addition to *s*-tetrazine derivatives, examples of systems that work perfectly in this role are compounds containing 1,3,4-thiadiazole.[6,7] Its derivatives can also be used as high-performance wide-bandgap copolymer donors for efficient non-fullerene organic solar cells.[8]

Both *s*-tetrazine and 1,3,4-thiadiazole also exhibit a broad spectrum of biological activity. Consequently, their derivatives can be used in medicine[9-19] and 1,3,4-thiadiazole-containing systems serve as plant-protection products.[20,21] In addition, an extremely interesting potential application of *s*-tetrazine derivatives is in medical diagnostics. These compounds are excellent substrates in Diels-Alder reactions with inverse electron demand used in bioorthogonal chemistry.[22-24]

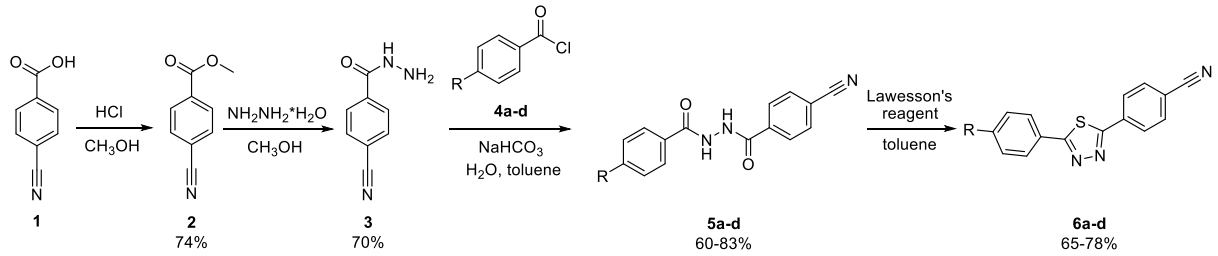
The combination of *s*-tetrazine and 1,3,4-thiadiazole seems to be very promising as well, especially for applications in optoelectronics. However, very few types of derivatives have been described in the literature so far. In our previous work, we synthesised a series of *s*-tetrazines directly conjugated to 1,3,4-thiadiazoles which exhibited excellent fluorescent properties.[25] We were interested in how the introduction of the 1,4-phenylene linker between the heterocyclic rings would affect the luminescent properties of the new compounds.

The work reported here describes a convenient and practical methodology for the synthesis of 3,6-bis(4-(1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazine derivatives from aromatic carbonitriles, hydrazine hydrate and Lawesson's reagent. We present another series of compounds containing these two rings, this time connected via a 1,4-phenylene linker. We were also interested in the results due to the possibility of comparing the properties of the obtained compounds with analogous systems containing 1,3,4-oxadiazole.[26] To the best of our knowledge, the preparation and fluorescent properties of the title compounds, containing an extended π-conjugated system, have not been previously reported.

Results and Discussion

The title 1,2,4,5-tetrazine derivatives conjugated via a 1,4-phenylene linker to a 1,3,4-thiadiazole ring were obtained in a six-step reaction sequence. The first four steps were aimed at the formation of a five-membered ring without compromising the stability of the carbonitrile moiety (Scheme 1). For this purpose, commercially available 4-cyanobenzoic acid (**1**) was used. The specific structure of this compound allows its application as a linker between 1,2,4,5-tetrazine and 1,3,4-thiadiazole. In the first step, the carboxyl group present in the substrate was subjected to esterification using methanol and hydrochloric acid, which gave ester **2**. The next

step was the conversion of compound **2** by reaction with hydrazine hydrate in methanol which resulted in product **3**. In order to form the necessary diacylhydrazine moiety, as well as to introduce an additional ring with substituents of various types, hydrazide **3** was reacted with freshly prepared aroyl chlorides **4a-d**. A series of products, **5a-d**, were obtained. The derivatives thus prepared were reacted with Lawesson's reagent in dry toluene. At this stage, the influence on the reaction yield of the type of substituents introduced by the aroyl chlorides was evident. The presence of electron-donor groups (methoxy and *tert*-butyl) led not only to higher yields, but also to a reduction in the heating time (**5b**, **5c**, entries 2 and 3, Table 1).

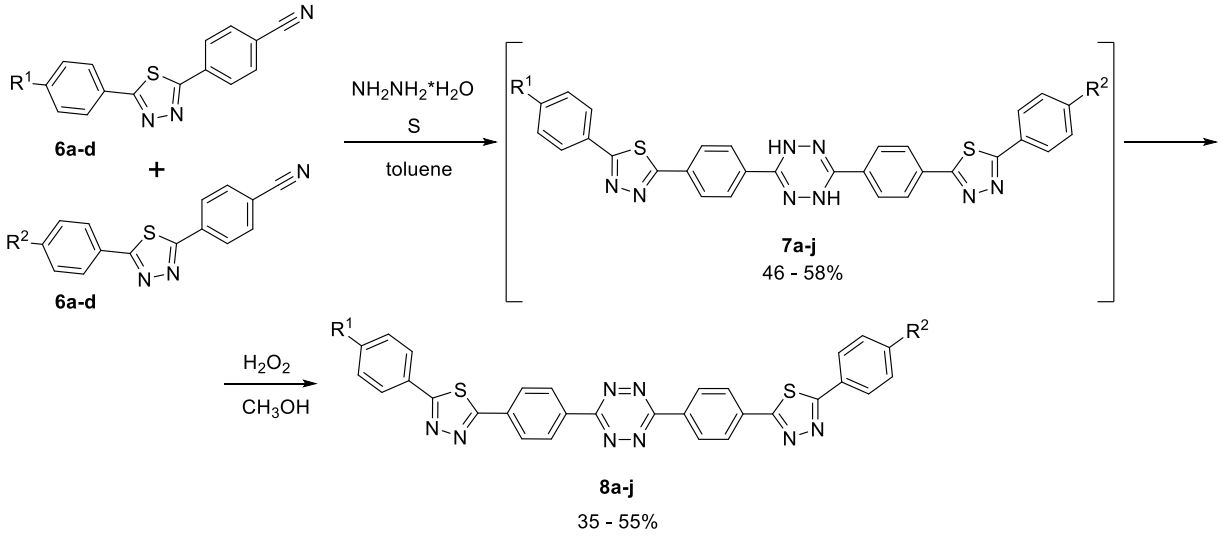


Scheme 1. Synthesis of nitriles containing a 1,3,4-thiadiazole ring [R = H, OCH_3, $C(CH_3)_3$, NO_2].

Table 1. Diacylhydrazides (**5a-d**) and 4-(5-phenyl-1,3,4-thiadiazol-2-yl)benzonitrile derivatives (**6a-d**)

Entry	R	Product **5**		Product **6**		
		Product	Yield (%)	Product	Reaction time (h)	Yield (%)
1	H	**5a**	75	**6a**	10	70
2	OCH_3	**5b**	83	**6b**	7	78
3	$C(CH_3)_3$	**5c**	80	**6c**	9,5	74
4	NO_2	**5d**	60	**6d**	12	65

The next step involved the Pinner reaction of previously prepared 4-(5-phenyl-1,3,4-thiadiazol-2-yl)benzonitrile derivatives **6a-d** with hydrazine hydrate in the presence of sulphur (Scheme 2). Initially, the research involved the formation of symmetrical compounds **7a-d**. In this case, there was also a clear influence of the type of substituents. Similar to the previous reaction, electron-donor groups had a very beneficial effect on the yield of the synthesized products. This impact was also visible later in the study which involved obtaining unsymmetrical derivatives **7e-j**. The last step was the oxidation of 1,4-dihydro-1,2,4,5-tetrazine derivatives (**7a-j**) to the final products. Of the various oxidising agents described in the literature, we decided to use hydrogen peroxide since this environmentally friendly reagent worked well for similar systems containing 1,3,4-oxadiazole.[26] After 24 hours of stirring at room temperature, a number of the title products **8a-j** were isolated with satisfactory yields (Table 2). Traces of two symmetrical products were also detected. The impact of the type of substituents on the outcome of the reaction, and its detailed mechanism, were discussed in our previous work.[26]



Scheme 2. Synthesis of the final products [R = H, OCH_3, $C(CH_3)_3$, NO_2].

Table 2. The resulting symmetrical and unsymmetrical derivatives of *s*-tetrazine conjugated via a 1,4-phenylene linker with a 1,3,4-thiadiazole ring (**8a-j**)

Entry	R^1	R^2	Product **7**		Product **8**	
			Product	Yield (%)	Product	Yield (%)
1	H	H	**7a**	70	**8a**	51
2	OCH_3	OCH_3	**7b**	78	**8b**	55
3	$C(CH_3)_3$	$C(CH_3)_3$	**7c**	65	**8c**	53
4	NO_2	NO_2	**7d**	46	**8d**	35
5	H	OCH_3	**7e**	54	**8e**	53
6	H	$C(CH_3)_3$	**7f**	48	**8f**	45
7	H	NO_2	**7g**	44	**8g**	42
8	OCH_3	$C(CH_3)_3$	**7h**	63	**8h**	60
9	OCH_3	NO_2	**7i**	45	**8i**	44
10	$C(CH_3)_3$	NO_2	**7j**	45	**8j**	42

Luminescent properties

UV-Vis absorption and three-dimensional fluorescence spectra were determined for the final products of the performed reactions (Figure S29-S31, Supplementary Material). In the case of compounds **8a**, **8c**, **8f**, and **8g**, the fluorescence spectra possess one slightly deformed maximum of fluorescence. The global emission maximum of **8b**, **8d**, **8e**, **8h**, **8i**, and **8j** covers the second, weaker local maximum (visible as a shoulder of the symmetrical global maximum). Due to large differences in intensities of global and local maxima and a substantial overlap, the λ_{ex} and λ_{em} of local maxima cannot be determined unambiguously, even with the usage of deconvolution of the three-dimensional function I = f(λ_{ex},λ_{em}). The described compounds emit fluorescent UV (compounds **8a**, **8c**, **8f**, **8g**) or Vis (compounds **8b**, **8d**, **8h**, **8i**, **8j**) radiation upon UV irradiation (Table 3). This suggests that the presence of one terminal H substituent (R^1 or R^2) is sufficient for appearance of the UV fluorescence. The quantum yields (Φ) correlate with fluorescence intensities (I), an increase of Φ causes an increase of I (Figure S32, Supplementary Material), whereas they do not correlate with the

absorption wavelength (Figure S33, Supplementary Material). This indicates that the electronic transition character is analogous in all the studied compounds, but the amount of the absorbed energy converted into internal energy differs considerably. The main source of excited states is the n→π* absorption transitions. In general, the fluorescence intensity agrees with the nature of the electron-withdrawing (EWG) and electron-donating (EDG) groups of substituents. The presence of two strong EWG substituents (**8d**, R^1, R^2 = NO_2) decreases fluorescence due to a decrease in electron density in delocalised systems. Alternatively, the existence of EDG substituents mostly increases fluorescence. The differences between λ_{em} and λ_{ex} at global maxima fall in two ranges: 121-126 nm for compounds with the OCH_3 substituent (**8b**, **8e**, **8h**, **8i**), and 72-91 nm for compounds without the OCH_3 substituent (**8a**, **8c**, **8d**, **8f**, **8g**, **8j**). This proves that the studied compounds have diverse energy gaps between individual orbitals participating in fluorescence transitions. It should be noted that compounds with the OCH_3 substituent (**8b**, **8e**, **8h**, **8i**) possess uncommon fluorescence characteristics as λ_{em}-λ_{ex} is larger than the standard border value of 100 nm. Within each of the above-mentioned groups of compounds (with or without the OCH_3 substituent), λ_{ex} correlates with λ_{em}, i.e., a larger λ_{ex} produces emission at a larger λ_{em} (Figure S34, Supplementary Material). Noteworthy is the fact that irradiation of compounds **8h** by ultraviolet radiation leads to the emission of violet fluorescence light visible by the naked eye.

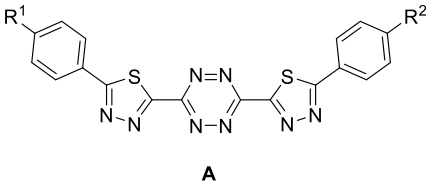
Table 3. Luminescence properties of symmetrical (**8a-d**) and unsymmetrical (**8e-j**) derivatives of *s*-tetrazine. Quantum yields Φ were calculated according to Equation 1 presented in reference [27], with the use of emission intensity registered for two standard substances: quinine sulphate (qn-SO_4^{2-})[28] and *trans,trans*-1,4-diphenyl-1,3-butadiene (dpb).[29] Stokes shifts were calculated from the equation $\Delta = \lambda_{em} - \lambda_{abs}$

Entry	Product	λ_{abs} (nm) directly preceding λ_{em}	λ_{ex} (nm) at global emission maximum	λ_{em} (nm) at global emission maximum	Stokes shift Δ [nm]	Quantum yield	
						Φ_q (qn-SO_4^{2-})	Φ_d (dpb)
1	**8a**	311	322	399	88	0.09	0.09
2	**8b**	306	316	432	126	0.39	0.39
3	**8c**	296	304	379	83	0.43	0.42
4	**8d**	319	336	410	91	0.09	0.09
5	**8e**	303	313	429	126	0.41	0.40
6	**8f**	295	300	367	72	0.51	0.50
7	**8g**	293	303	367	74	0.57	0.56
8	**8h**	323	326	445	122	0.54	0.53
9	**8i**	312	318	433	121	0.39	0.38
10	**8j**	337	338	411	74	0.05	0.05

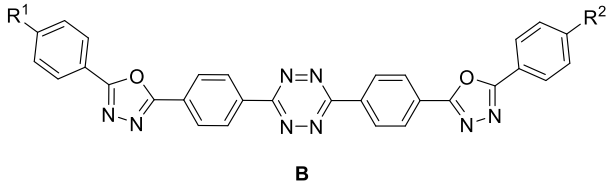
The studied compounds (**C**, Table 4) have generally lower Φ than their analogous compounds containing 1,3,4-oxadiazole (**B**)[26] which is a consequence of the sulphur, the presence of which typically causes the severe quenching of fluorescence.[30] On the other hand, the compounds of both mentioned groups (**B** and **C**) exhibit lower Φ in comparison to their directly conjugated counterparts (**A**).[25] It shows that the insertion of benzene rings between tetrazine and thia/oxadiazole rings leads to the disruption of the fluorescence-favourable conjugation. The absorption wavelengths of the title compounds (**C**) are higher than for the direct-coupled systems (**A**), and most often are comparable to the corresponding 1,3,4-oxadiazole arrangements (**B**). The

above described trend of increasing Stokes shifts for the studied compounds containing a methoxy group is in line with the observations for 1,3,4-oxadiazole analogues, but does not occur in the case of directly conjugated heterocyclic rings (entries 2 and 6, Table 4).

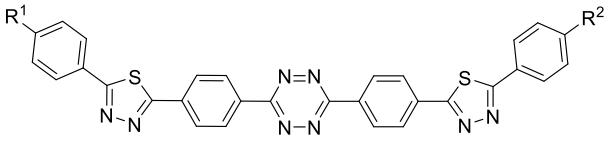
Table 4. Comparison of the properties of the title compounds (**C**) with analogous systems described in the literature (**A**, **B**)[25,26]



A



B



C

Entry	R^1	R^2	Quantum yield Φ			λ_{abs} (nm) directly preceding λ_{em}			Stokes shift Δ [nm]		
			A	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**
1	H	H	0.78	0.46	0.09	265	284	311	85	64	88
2	OCH_3	OCH_3	>0.98	0.60	0.39	273	309	306	90	129	126
3	NO_2	NO_2	0.53	0.14	0.09	274	338	319	91	69	91
4	H	NO_2	-	0.26	0.57	-	298	293	-	72	74
5	$C(CH_3)_3$	NO_2	-	0.26	0.05	-	300	337	-	84	74
6	OCH_3	NO_2	-	0.38	0.39	-	306	312	-	129	121

Conclusions

In summary, we have elaborated an efficient and universal methodology for the synthesis of 1,2,4,5-tetrazine derivatives conjugated via a 1,4-phenylene linker with a 1,3,4-thiadiazole ring. The developed procedure made it possible to obtain a number of symmetrical and unsymmetrical derivatives. In addition, the methodology can be used for arrangements containing both electron-donating and electron-withdrawing groups. As a result of the research, ten new final products, not previously described in the literature, were obtained and characterised, including by their fluorescent properties.

Experimental Section

General. Melting points were measured on a Stuart SMP3 melting point apparatus. NMR spectra were recorded at 25 °C on an Agilent 400-NMR spectrometer at 400 MHz for ^1H and 100 MHz for ^{13}C, using $CDCl_3$ or DMSO-d6 as solvent and TMS as the internal standard. UV-Vis absorption and 3D fluorescence spectra were registered in methanol solutions (c = $5 \cdot 10^{-6}$ mol/dm^3) with Jasco V-660 and Jasco F-6300 spectrometers,

respectively. FT-IR spectra were measured between 4000 and 650 cm^{-1} on an FT-IR Nicolet 6700 apparatus with a Smart iTR accessory. Elemental analyses were performed with a VarioEL analyser. High-resolution mass spectra were obtained by means of a Waters ACQUITY UPLC/Xevo G2QT instrument. Thin-layer chromatography was performed on silica gel 60 F_{254} (Merck) thin-layer chromatography plates using benzene/ethyl acetate (1:3 v/v) or chloroform/ethyl acetate (5:1 v/v) as the mobile phases.

Materials and procedures. All chemicals, materials and solvents were purchased from Sigma-Aldrich and used as received. Compounds **1-5** were synthesized according to the literature.[26]

4-(5-Phenyl-1,3,4-thiadiazol-2-yl)benzonitrile derivatives (6a-d). *N*'-Benzoyl-4-cyanobenzohydrazide (**5a**) or derivative (**5b-d**) (0.02 mol) and Lawesson's reagent (0.42 g, 0.01 mol) were dissolved in toluene (40 mL) and heated in an oil bath with stirring for 7-12 hours. The resulting mixture was filtered and the residue was evaporated. The crude product was purified by column chromatography using a chloroform/ethyl acetate mixture (5:1, v/v) as the eluent.

4-(5-Phenyl-1,3,4-thiadiazol-2-yl)benzonitrile (6a). Yellow solid (3.68 g, 70% yield); mp 197-199 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.50-7.53 (m, 3H), 7.79 (d, *J* 8.0 Hz, 2H), 8.00-8.03 (m, 2H), 8.13 (d, *J* 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.7, 118.2, 128.3, 128.5, 129.5, 129.8, 131.9, 133.1, 134.2, 166.2, 169.7; UV-VIS: λ_{max} (MeOH) 309.0 nm (ε·10^{-3} = 11.06 $cm^{-1}M^{-1}$), λ_{max} (MeOH) 226.0 nm (ε·10^{-3} 12.95 $cm^{-1}M^{-1}$), λ_{max} (MeOH) 204.0 nm (ε·10^{-3} = 17.12 $cm^{-1}M^{-1}$); IR (ATR) ν:3112, 2839, 2554, 2227, 1669, 1604, 1519, 1492, 1423, 1344, 1309, 1292, 1178, 1128, 1105, 1070, 1013, 965, 930, 877, 853, 800, 788, 772, 739, 716, 691 cm^{-1}; Anal. Calcd for $C_{15}H_9N_3S$: C, 68.42; H, 3.45; N, 15.96. Found: C, 68.44; H, 3.42; N, 15.95; HRMS calcd for ($C_{15}H_9N_3S$+H^+): 264.0590; found: 264.0588.

4-(5-(4-Methoxyphenyl)-1,3,4-thiadiazol-2-yl)benzonitrile (6b). Yellow solid (4.57 g, 78% yield); mp 196-198 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.87 (s, 3H), 7.00 (d, *J* 4.0 Hz, 2H), 7.17 (d, *J* 8.0 Hz, 2H), 8.09 (d, *J* 8.0 Hz, 2H), 8.28 (d, *J* 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 55.4, 113.4, 114.9, 118.3, 127.2, 128.2, 128.8, 129.5, 133.3, 161.1, 162.3, 164.6; UV-VIS: λ_{max} (MeOH) 312.0 nm (ε·10^{-3} 8.66 $cm^{-1}M^{-1}$), λ_{max} (MeOH) 228.5 nm (ε·10^{-3} 13.48 $cm^{-1}M^{-1}$), λ_{max} (MeOH) 204.0 nm (ε·10^{-3} = 17.65 $cm^{-1}M^{-1}$); IR (ATR) ν: 3063, 2964, 2841, 2552, 2228, 1687, 1602, 1550, 1519, 1492, 1434, 1407, 1345, 1309, 1295, 1258, 1172, 1130, 1105, 1073, 1015, 987, 966, 936, 854, 843, 830, 800, 772, 740, 712 cm^{-1}; Anal. Calcd for $C_{16}H_{11}N_3OS$: C, 65.51; H, 3.78; N, 14.32. Found: C, 65.50; H, 3.76; N, 14.34; HRMS calcd for ($C_{16}H_{11}N_3OS$+H^+): 294.0696; found: 294.0694.

4-(5-(4-(tert-Butyl)phenyl)-1,3,4-thiadiazol-2-yl)benzonitrile (6c). Yellow solid (4.72 g, 74% yield); mp 168-170 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.34 (s, 9H), 7.51 (d, *J* 8.0 Hz, 2H), 7.88 (d, *J* 8.0 Hz, 2H), 8.03-8.10 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 30.8, 34.7, 113.8, 120.5, 126.2, 126.6, 127.3, 128.2, 129.4, 132.6, 155.8, 163.3, 167.2; UV-VIS: λ_{max} (MeOH) 230.0 nm (ε·10^{-3} = 19.47 $cm^{-1}M^{-1}$), λ_{max} (MeOH) 203.5 nm (ε·10^{-3} = 19.66 $cm^{-1}M^{-1}$); IR (ATR) ν: 3220, 2953, 1695, 1671, 1634, 1600, 1572, 1507, 1459, 1439, 1303, 1281, 1255, 1169, 1123, 1015, 989, 917, 852, 838, 824, 800, 704 cm^{-1}; Anal. Calcd for $C_{19}H_{17}N_3S$: C, 71.44; H, 5.36; N, 13.16. Found: C, 71.42; H, 5.37; N, 13.18; HRMS calcd for ($C_{19}H_{17}N_3S$+H^+): 320.1216; found: 320.1218.

4-(5-(4-Nitrophenyl)-1,3,4-thiadiazol-2-yl)benzonitrile (6d). Yellow solid (4.00 g, 65% yield); mp 226-228 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.12-8.18 (m, 2H), 8.31-8.36 (m, 2H), 8.42 (d, *J* 8 Hz, 2H), 8.47 (d, *J* 8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 113.4, 114.4, 118.0, 127.6, 128.2, 129.0, 130.7, 132.3, 150.0, 161.1, 166.8; UV-VIS: λ_{max} (MeOH) 296.5 nm (ε·10^{-3} = 1.97 $cm^{-1}M^{-1}$), λ_{max} (MeOH) 225.5 nm (ε·10^{-3} = 3.94 $cm^{-1}M^{-1}$), λ_{max} (MeOH) 204.0 nm (ε·10^{-3} = 5.66 $cm^{-1}M^{-1}$); IR (ATR) ν: 2953, 2233, 2168, 1689, 1635, 1600, 1571, 1549, 1523, 1507, 1460, 1439, 1348, 1283, 1256, 1196, 1177, 1141, 1108, 1014, 991, 927, 879, 853, 837, 800, 752, 738, 709 cm^{-1}; Anal. Calcd for $C_{15}H_8N_4O_2S$: C, 58.44; H, 2.62; N, 18.17. Found: C, 58.45; H, 2.60; N, 18.16; HRMS calcd for ($C_{15}H_8N_4O_2S$+H^+): 309.0441; found: 309.0443.

Preparation of *final products* (8a-j). The mixtures of one or two of compounds **6a-d** (2 mmol of each substrate), sulphur (0.08 g, 2.5 mmol) and dry toluene (60 mL) was cooled to 0 °C and hydrazine hydrate (0.5 mL, 6 mmol) was added dropwise with stirring. The slurry was allowed to reach room temperature and then heated under reflux for 2 h. The mixture was then cooled to room temperature, filtered, and the filtrate was evaporated. The crude product (**7a-j**) was dissolved in methanol (30 mL), and then 35% hydrogen peroxide (30 mL) was added. After stirring at room temperature for 24 h, the reaction mixture was filtered and concentrated by evaporation. The oily residue or precipitate was filtered and purified by column chromatography using a chloroform/ethyl acetate mixture (5:1, v/v) as the eluent.

3,6-Bis(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,4-dihydro-1,2,4,5-tetrazine (7a). Yellow solid (1.55 g, 70% yield).

3,6-Bis(4-(5-(4-methoxyphenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,4-dihydro-1,2,4,5-tetrazine (7b). Yellow solid (1.91 g, 78% yield).

3,6-Bis(4-(5-(4-(*tert*-butyl)phenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,4-dihydro-1,2,4,5-tetrazine (7c). Yellow solid (1.73 g, 65% yield).

3,6-Bis(4-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,4-dihydro-1,2,4,5-tetrazine (7d). Yellow solid (1.18 g, 46% yield).

2-(4-Methoxyphenyl)-5-(4-(6-(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,4-dihydro-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (7e). Yellow solid (1.26 g, 54% yield).

2-(4-(*tert*-Butyl)phenyl)-5-(4-(6-(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,4-dihydro-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (7f). Yellow solid (1.17 g, 48% yield).

2-(4-Nitrophenyl)-5-(4-(6-(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,4-dihydro-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (7g). Yellow solid (1.05 g, 44% yield).

2-(4-(*tert*-Butyl)phenyl)-5-(4-(6-(4-(5-(4-methoxyphenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,4-dihydro-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (7h). Yellow solid (1.61 g, 63% yield).

2-(4-Methoxyphenyl)-5-(4-(6-(4-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,4-dihydro-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (7i). Yellow solid (1.13 g, 45% yield).

2-(4-(*tert*-Butyl)phenyl)-5-(4-(6-(4-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,4-dihydro-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole(7j). Yellow solid (1.18 g, 45% yield).

3,6-Bis(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazine (8a). Yellow solid (0.79 g, 51% yield); mp 218-220 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.50 (m, 6H), 7.76 (d, *J* 8.0 Hz, 4H), 7.96-7.99 (m, 4H), 8.09 (d, *J* 8.0 Hz, 4H);^{13}C NMR (100 MHz, $CDCl_3$): δ 127.2, 127.4, 128.4, 129.3, 129.4 131.2, 131.7, 133.0, 166.0, 168.2, 169.5; UV-VIS: λ_{max}(MeOH) 311 nm (ε·10^{-3} = 50.0 cm^{-1}M^{-1}); fluorescence (CH_3OH): λ_{ex} = 322 nm; λ_{em} = 399 nm; IR (ATR) ν: 3375, 2229, 1675, 1608, 1552, 1519, 1493, 1441, 1413, 1307, 1253, 1174, 1100, 1070, 1026, 988, 962, 832, 770, 743, 703 cm^{-1}; Anal. Calcd for $C_{30}H_{18}N_8S_2$: C, 64.97; H, 3.27; N, 20.20. Found: C, 64.99; H, 3.25; N, 20.21; HRMS calcd for ($C_{30}H_{18}N_8S_2$+H$^+$): 555.1169; found: 555.1168.

3,6-Bis(4-(5-(4-methoxyphenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazine (8b). Yellow solid (1.05 g, 55% yield); mp 169-171 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.87 (s, 6H), 7.01 (d, *J* 8.0 Hz, 4H), 7.17 (d, *J* 8.0 Hz, 4H), 8.09 (d, *J* 8.0 Hz, 4H), 8.19 (d, *J* 8.0 Hz, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 55.4, 114.9, 122.9, 126.4, 128.4, 128.7, 129.4, 133.3, 162.2, 162.8, 164.2, 167.0; UV-VIS: λ_{max}(MeOH) 246 nm (ε·10^{-3} = 31.15 cm^{-1}M^{-1}), λ_{max}(MeOH) 306 nm (ε·10^{-3} = 39.8 cm^{-1}M^{-1}); fluorescence (CH_3OH): λ_{ex} = 316 nm; λ_{em} = 432 nm; IR (ATR) ν: 2229, 2022, 1994, 1676, 1610, 1582, 1548, 1519, 1492, 1411, 1305, 1252, 1172, 1102, 1072, 1028, 962, 834, 813, 773, 745, 731, 714, 703, 684 cm^{-1}; Anal. Calcd for $C_{32}H_{22}N_8O_2S_2$: C, 62.53; H, 3.61; N, 18.23. Found: C, 62.54; H, 3.60; N, 28.22; HRMS calcd for ($C_{32}H_{22}N_8O_2S_2$+H$^+$): 615.1380; found: 615.1379.

3,6-Bis(4-(5-(4-(*tert*-butyl)phenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazine (8c). Yellow solid (0.92 g, 53% yield); mp 145-147 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.33 (s, 18H), 7.64 (d, *J* 8.0 Hz, 4H), 7.87 (d, *J* 8.0 Hz, 4H), 8.02-8.10 (m, 8H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 30.8, 34.8, 125.2, 126.2, 126.5, 126.8, 127.3, 128.5, 133.3, 155.3, 162.7, 163.8, 165.7; UV-VIS : λ_{max}(MeOH) 241 nm (ε·10^{-3} = 28.98 cm^{-1}M^{-1}), λ_{max}(MeOH) 296 nm (ε·10^{-3} = 54.62 cm^{-1}M^{-1}); fluorescence (CH_3OH): λ_{ex} = 304 nm; λ_{em} = 379 nm; IR (ATR) ν: 2964, 2228, 1672, 1624, 1613, 1581, 1548, 1492, 1446, 1417, 1363, 1308, 1272, 1119, 1098, 1070, 1015, 842, 773, 751, 735, 710 cm^{-1}; Anal. Calcd for $C_{38}H_{34}N_8S_2$: C, 68.44; H, 5.14; N, 16.80. Found: C, 68.42; H, 5.15; N, 16.82; HRMS calcd for ($C_{38}H_{34}N_8S_2$+H$^+$): 667.2421; found: 667.2423.

3,6-Bis(4-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazine (8d). Yellow solid (0.41 g, 35% yield); mp 116-118 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.12 (d, *J* 8 Hz, 4H), 8.30-8.35 (m, 4H), 8.40 (d, *J* 8 Hz, 4H), 8.45 (d, *J* 8 Hz, 4H); ^{13}C NMR (100 MHz, DMSO): δ 116.2, 127.1, 128.1, 128.3, 128.4, 128.5, 129.2, 152.2, 162.1, 164.2, 166.9; UV-VIS: λ_{max}(MeOH) = 319 nm (ε·10^{-3} = 36.34 cm^{-1}M^{-1}); fluorescence (CH_3OH): λ_{ex} = 336 nm; λ_{em} = 410 nm; IR (ATR) ν: 2228, 2157, 2025, 1698, 1647, 1614, 1595, 1567, 1545, 1525, 1479, 1406, 1344, 1297, 1280, 1253, 1194, 1106, 1073, 1012, 962, 949, 881, 849, 830, 813, 783, 776, 739, 721, 711, 692, 681, 668 cm^{-1}; Anal. Calcd for $C_{30}H_{16}N_{10}O_4S_2$: C, 55.90; H, 2.50; N, 21.73. Found: C, 55.91; H, 2.48; N, 21.74; HRMS calcd for ($C_{30}H_{16}N_{10}O_4S_2$+H$^+$): 645.0870; found: 645.0872.

2-(4-Methoxyphenyl)-5-(4-(6-(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8e). Yellow solid (0.67 g, 53% yield); mp 231-233 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.86 (s, 3H), 7.13 (d, *J* 8.0 Hz, 2H), 7.16 (d, *J* 8.0 Hz, 2H), 7.63-7.67 (m, 3H), 7.92 (d, *J* 12 Hz, 2H), 8.03 (d, *J* 8.0 Hz, 2H), 8.08 (d, *J* 8.0 Hz, 4H), 8.14-8.19 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 55.5, 114.9, 122.1, 126.4, 126.7, 127.2, 127.4, 128.2, 128.4, 128.6, 128.7, 129.1, 129.4, 129.5, 132.0, 133.3, 161.5, 161.9, 162.3, 163.4, 164.6, 166.5, 168.7; UV-VIS: λ_{max}(MeOH) 251 nm (ε·10^{-3} = 23.3 cm^{-1}M^{-1}), 303 nm (ε·10^{-3} = 50.2 cm^{-1}M^{-1}); fluorescence (CH_3OH): λ_{ex} = 313 nm; λ_{em} = 429 nm; IR (ATR) ν: 3378, 2228, 1671, 1608, 1550, 1519, 1484, 1441, 1414, 1307, 1253, 1174, 1118, 1100, 1069, 1027, 962, 832, 769, 744, 704, 690, 667 cm^{-1}; Anal. Calcd for $C_{31}H_{20}N_8OS_2$: C, 63.68; H, 3.45; N, 19.17. Found: C, 63.70; H, 3.46 N, 19.16; HRMS calcd for ($C_{31}H_{20}N_8OS_2$+H$^+$):585.1274; found: 585.1273.

2-(4-(tert-Butyl)phenyl)-5-(4-(6-(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8f). Yellow solid (0.53 g, 45% yield); mp 161-163°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.29 (s, 9H), 7.61-7.67 (m, 5H), 7.87 (d, *J* 8.0 Hz, 2H), 8.01-8.05 (m, 2H), 8.13 (d, *J* 2.4 Hz, 4H), 8.15 (d, *J* 1.6 Hz, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 30.9, 34.6, 123.4, 125.4, 126.7, 126.8, 127.2, 127.3, 127.8, 128,3, 129.2, 129.4, 129.5, 131.7, 132.3, 133.3, 133.4, 155.3, 162.9, 164.6, 165.7, 165.9, 166.1, 169.0; UV-VIS: λ_{max}(MeOH) 295 nm (ε·10^{-3} = 55.42 cm^{-1}M^{-1}); fluorescence (CH_3OH): λ_{ex} = 300 nm; λ_{em} = 367 nm; IR (ATR) ν: 2228, 1671, 1610, 1572, 1550, 1491, 1447, 1414, 1307, 1253, 1175, 1067, 1029, 853, 833, 775, 739, 708, 687 cm^{-1}; Anal. Calcd for $C_{34}H_{26}N_8S_2$: C, 66.86; H, 4.29; N, 18.35. Found: C, 66.85; H, 4.27; N, 18.36; HRMS calcd for ($C_{34}H_{26}N_8S_2$+H$^+$): 611.1795; found: 611.1793.

2-(4-Nitrophenyl)-5-(4-(6-(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8g). Yellow solid (0.44 g, 42% yield); mp 165-167 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.63-7.71 (m, 3H), 8.01 (d, *J* 8.0 Hz, 2H), 8.06 (d, *J* 8.0 Hz, 4H), 8.14 (d, *J* 8.0 Hz, 4H), 8.24 (d, *J* 8.0 Hz, 2H), 8.44 (d, *J* 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 118.3, 123.4, 126.8, 127.0, 127.3, 127.7, 128.0, 128.3, 129.1, 129.4, 129.5, 131.7, 132.1, 133.3, 133.4; 152.3, 162.9, 164.6, 166.1, 166.9, 169.0, 169.9; UV-VIS: λ_{max}(MeOH) 293 nm (ε·10^{-3} = 72.28 cm^{-1}M^{-1}); fluorescence (CH_3OH): λ_{ex} = 303 nm; λ_{em} = 367 nm; IR (ATR) ν: 2228, 1634, 1608, 1576, 1550, 1490, 1446, 1413, 1341, 1307, 1273, 1177, 1121, 1104, 1067, 1031, 853, 775, 739, 708, 687 cm^{-1}; Anal. Calcd for $C_{30}H_{17}N_9O_2S_2$: C, 60.09; H, 2.86; N, 21.02. Found: C, 60.08; H, 2.88; N, 21.01; HRMS calcd for ($C_{30}H_{17}N_9O_2S_2$+H$^+$): 600.1019; found: 600.1017.

2-(4-(*tert*-Butyl)phenyl)-5-(4-(6-(4-(5-(4-methoxyphenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8h). Note: the product is a precipitate formed after the reaction. Yellow solid (0.97 g, 60% yield); mp 201-203°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.32 (s, 9H), 3.86 (s, 3H), 7.14 (d, *J* 8.0 Hz, 2H), 7.16 (d, *J* 8.0 Hz, 2H), 7.63 (d, *J* 4.0 Hz, 2H), 7.65 (d, *J* 4.0 Hz, 2H), 8.02 (d, *J* 8.0 Hz, 2H), 8.07 (d, *J* 8.0 Hz, 4H), 8.26 (d, *J* 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 30.7, 34.8, 55.5, 114.8; 121.7, 125.2, 127.2, 127.3, 127.4, 128.2, 128.3, 128.7, 129.1, 129.5, 129.8, 133.3, 133.6, 154.9, 161.9, 162.3, 162.4, 164.6, 165.2, 165.7, 166.6; UV-VIS: λ_{max}(MeOH) 225 nm (ε·10^{-3} = 39.82 cm^{-1}M^{-1}), 251 nm (ε·10^{-3} = 28.5 cm^{-1}M^{-1}), 323nm (ε·10^{-3} = 53.5 cm^{-1}M^{-1}); fluorescence (CH_3OH): λ_{ex} = 326 nm; λ_{em} = 445 nm; IR (ATR) ν: 2228, 1672, 1634, 1607, 1549, 1519, 1436, 1407, 1306, 1256, 1172, 1122, 1101, 1073, 1024, 830, 798, 769, 745, 704, 667 cm^{-1}; Anal. Calcd for $C_{35}H_{28}N_8OS_2$: C, 65.60; H, 4.40; N, 17.49. Found: C, 65.62; H, 4.39; N, 17.51; HRMS calcd for ($C_{35}H_{28}N_8OS_2$+H$^+$): 641.1900; found: 641.1901.

2-(4-Methoxyphenyl)-5-(4-(6-(4-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8i). Yellow solid (0.50 g, 44% yield); mp 172-174 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.87 (s, 3H), 7.13 (d, *J* 8.0 Hz, 2H), 7.17 (d, *J* 8.0 Hz, 2H), 7.92 (d, *J* 8.0 Hz, 2H), 8.04 (d, *J* 8.0 Hz, 2H), 8.09 (d, *J* 8.0 Hz, 4H), 8.16-8.22 (m, 2H), 8.28 (d, *J* 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 55.5, 114.9, 118.1, 126.4, 126.9, 127.2, 127.4, 128.2, 128.4, 128.5, 128.6, 128.8, 129.1, 129.5, 133.3, 152.7, 161.5, 161.9, 162.3, 164.2, 164.6, 166.5, 166.9; UV-VIS: λ_{max}(MeOH) 250nm (ε·10^{-3} = 26.54 cm^{-1}M^{-1}), 312 nm (ε·10^{-3} = 50.74 cm^{-1}M^{-1}); fluorescence (CH_3OH): λ_{ex} = 318 nm; λ_{em} = 433 nm; IR (ATR) ν: 3363, 2229, 1675, 1608, 1551, 1519, 1493, 1442, 1413, 1308, 1253, 1174, 1100, 1070, 1026, 989, 962, 832, 773, 743, 703, 674 cm^{-1}; Anal. Calcd for $C_{31}H_{19}N_9O_3S_2$: C, 59.13; H, 3.04; N, 20.02. Found: C, 59.15; H, 3.03; N, 20.04; HRMS calcd for ($C_{31}H_{19}N_9O_3S_2$+H$^+$): 630.1125; found: 630.1127.

2-(4-(tert-Butyl)phenyl)-5-(4-(6-(4-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8j). Yellow solid (0.50 g, 42% yield); mp 191-193 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.31 (s, 9H), 7.53 (d, *J* 8.0 Hz, 2H), 7.87 (d, *J* 8.0 Hz, 2H), 8.00-8.03 (m, 2H), 8.07 (d, *J* 8.0 Hz, 2H), 8.11-8.14 (m, 2H), 8.31-8.34 (m, 2H), 8.41 (d, *J* 8.0 Hz, 2H), 8.46 (d, *J* 12.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 30.9, 34.7, 118.2, 124.6, 125.2, 126.1, 126.9, 127.3, 127.6, 127.9, 128.2, 128.5, 129.0, 129.3, 129.8, 133.3, 152.7, 154.6, 161.5, 163.3, 163.3, 163.7, 165.5, 166.7; UV-VIS: λ_{max}(MeOH) 242 nm (ε·10^{-3} = 34.62 cm^{-1}M^{-1}), 337 nm (ε·10^{-3} = 27.42 cm^{-1}M^{-1}); fluorescence (CH_3OH): λ_{ex} = 338 nm; λ_{em} = 411 nm; IR (ATR) ν: 3343, 3234, 2947, 2356, 2229, 1671, 1635, 1608, 1582, 1548, 1492, 1444, 1414, 1364, 1341, 1305, 1279, 1179, 1122, 1027, 848, 769, 745, 704, 674 cm^{-1}; Anal. Calcd for $C_{34}H_{25}N_9O_2S_2$: C, 62.28; H, 3.84; N, 19.22. Found: C, 62.29; H, 3.86; N, 19.21; HRMS calcd for ($C_{34}H_{25}N_9O_2S_2$+H$^+$): 656.1645; found: 656.1644.

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Supplementary Material

^{1}H and ^{13}C NMR, UV-Vis, and fluorescence spectra for compounds **6a**-**d** and **8a**-**j** are provided as supplementary material in the online version.

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