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Fluorescence

Convenient One-Pot Synthesis of 1,2,3,4-Thiatriazoles Towards a Novel Electron Acceptor for Highly-Efficient Thermally-Activated Delayed-Fluorescence Emitters

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Abstract: A novel and unexpected convenient one-pot synthesis of 1,2,3,4-thiatriazoles has been discovered while investigating the classical tetrazine "Pinner synthesis". The synthetic route starts from commercially-available nitrile derivatives and gives good to high yields (51–80%) with no need to isolate any thioacylating agents. The crucial impact of the solvent on the outcome of the modified "Pinner synthesis" is moreover examined and discussed. Using this new synthetic route, a novel donor-acceptor thiatriazole derivative has been prepared, which exhibits prominent thermally-activated delayed fluorescence (TADF) in both solution and film. The photoluminescence quantum yield (PLQY) in methylcyclohexane (MCH) and Zeonex (a cyclo olefin polymer) in oxygen-free conditions were determined to be 76 and 99%, respectively. This work provides an efficient and practical synthetic approach to functionalized 1,2,3,4-thiatriazole derivatives, and will noticeably facilitate the application of 1,2,3,4-thiatriazole as an electron acceptor in organic electronics.

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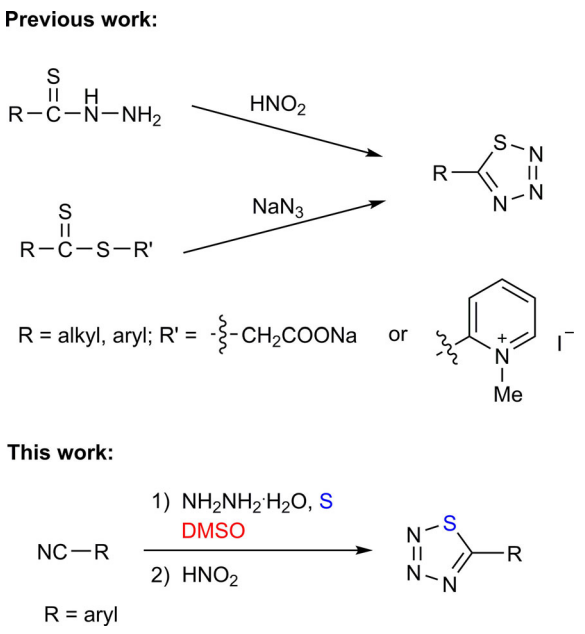
1,2,3,4-thiatriazole heterocycle was first reported in 1896 by Freund and co-workers.[1] Its structural assignment was firmly established in the 1950s by Lieber and co-workers.[2] A number of 1,2,3,4-thiatriazoles were then prepared and studied during that period.[3] The chemistry of 1,2,3,4-thiatriazoles has unfortunately been almost forgotten for many decades thereafter. As a strong electron-deficient heterocycle, 1,2,3,4-thiatriazole is, however, potentially an excellent electron acceptor in organic donor-acceptor materials. Due to charge-transfer (CT) states introduced in the donor-acceptor system, these molecules can exhibit interesting photophysical and electrochemical properties, and therefore are of interest in organic electronics,[4,5] though strangely, no related applications have been reported so far. Thermally-activated delayed fluorescence (TADF) molecules have recently received significant attention since the first efficient TADF organic light emitting diodes (OLEDs) reported in 2012 by Adachi.[6] In TADF molecules, the triplet excitons can be converted to the emissive singlet excitons through efficient reverse intersystem crossing (RISC) from the lowest triplet excited state (T_1) to the lowest singlet excited state (S_1), when their energy difference (ΔE_{ST}) is small enough.[5] Most of the TADF molecules were therefore designed by coupling various electron donors and acceptors with a large twisting angle, to separate the spatial distributions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The aim is to harvest 100% of triplet exciton.[7] The use of purely organic TADF emitters goes far beyond their use in electroluminescent devices. They can supersede metal-complex emitters by acting as triplet sensitizers,[8] or bio-imaging dyes.[9] Molecules with efficient RISC[10] are also counted among mechanochromic materials with switchable parameters, such as emission color,[11] on/off TADF,[12] or interplay between TADF and prompt fluorescence.[13] Therefore, exploration of novel electron acceptors for TADF emitters is of clear interest to this community.

1,2,3,4-thiatriazoles have been previously prepared by diazotization of thiohydrazides, or reaction of dithioates with azide ions, in high yields (Scheme 1).[3] However, both methods require preparation of starting thioacylating agents, which are often difficult to obtain. This increases the synthetic complexity of 1,2,3,4-thiatriazole derivatives, especially for those with complex functional groups. As a result, no 1,2,3,4-thiatriazole derivatives with complex functional groups have been reported so



Scheme 1. Overview of synthetic approaches to 1,2,3,4-thiatriazoles.

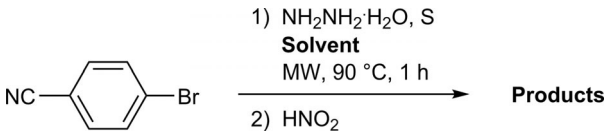
far. Therefore, developing practical and convenient synthetic approaches for preparing functionalized 1,2,3,4-thiatriazole derivatives is quite desirable.

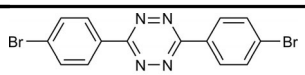
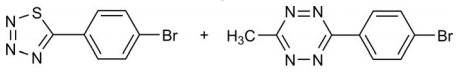
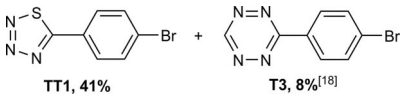
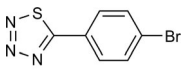
In this study, we report a novel convenient one-pot synthesis of 1,2,3,4-thiatriazoles directly from commercially available nitriles in high yields (51–80%), with no need of isolating any thioacylating agents (Scheme 1). The access to the 1,2,3,4-thiatriazoles can therefore be significantly improved because of the large availability of commercially available nitriles. Through this approach we have designed and synthesized an example of a donor-acceptor thiatriazole derivative using phenoxazine as a donor, in high yield (70%). This molecule exhibits excellent TADF characteristics in both solution and film. To the best of our knowledge, this is the first example of a highly-efficient TADF emitter using a 1,2,3,4-thiatriazole as acceptor.

Having a long experience in 1,2,4,5-tetrazine chemistry,[14,15] we had already noticed that the solvent nature can play an important role in the tetrazine forming reaction called "Pinner synthesis".[16] For example, we have recently found that dichloromethane (DCM) can serve as a novel reagent in the synthesis of 3-monosubstituted unsymmetrical 1,2,4,5-tetrazines.[15] In this work a comprehensive study of solvent effect in the modified "Pinner synthesis" was performed, and we found out that the products of the reaction are significantly influenced by the solvent employed.

The traditional "Pinner synthesis" is a two-step procedure starting from the formal addition of hydrazine to nitrile precursors in ethanol, followed by oxidation of the intermediate 1,2-dihydrotetrazine to afford 1,2,4,5-tetrazines.[16] It has been demonstrated later that addition of sulfur helps accelerating the reaction.[17] Here we used 4-bromobenzonitrile as a standard nitrile precursor to survey the effect of a range of solvents on this reaction. The results are summarized in Table 1. When our optimized reaction conditions for tetrazine synthesis (hydrazine hydrate, sulfur, and heating at 90 °C for 1 hour in a sealed tube with microwave irradiation, followed by oxidation), with ethanol as a solvent in the first step, was used, the 3,6-disubstituted symmetrical tetrazine **T1** was obtained in good yield (43%) as expected. However, when the polar protic sol-

Table 1. Survey of solvents and outcomes in the modified "Pinner synthesis".[a]



Solvent		Dielectric Constant	Products[b]
polar protic solvent	ethanol	25	 **T1, 43%**
non-polar solvent	toluene	2.3	SN[c]
	chloroform	4.8	SN
	THF	7.5	SN
	acetonitrile	37	 **TT1, 9%** **T2, 16%**
polar aprotic solvent	DMF	38	 **TT1, 41%** **T3, 8%**[18]
	DMSO	47	 **TT1, 74%**

[a] All reactions were carried out on a 0.5 mmol scale in 2 mL solvent. MW = microwave. [b] Yields (isolated) based on the nitrile precursor. [c] SN = Starting nitrile precursor

vent ethanol was replaced by a non-polar (e.g., toluene, chloroform) or a slightly polar aprotic solvent (e.g., tetrahydrofuran (THF)), no reaction was observed and the starting nitrile agent was fully recovered.

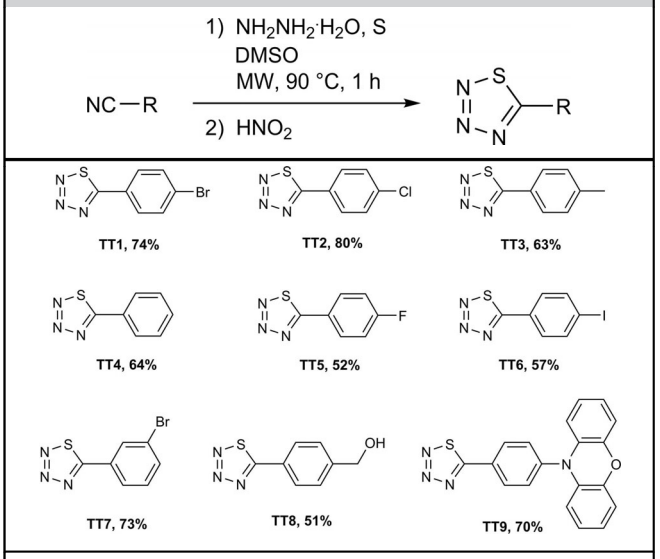
When the highly polar aprotic solvent acetonitrile was used, we isolated 16% of unsymmetrical 3-(4-bromophenyl)-6-methyl-1,2,4,5-tetrazine **T2**, because acetonitrile acts as both solvent and second nitrile precursor in the reaction. In addition to the tetrazine, the unusual 1,2,3,4-thiatriazole **TT1** was also obtained with a 9% yield. More interestingly, when using dimethylformamide (DMF) as a solvent, the yield of **TT1** significantly increased to 41%.[18] And remarkably, when the even more polar solvent dimethyl sulfoxide (DMSO) was employed, the yield was optimized to as high as 74%. These findings are remarkably interesting because this is the first time that the 1,2,3,4-thiatriazole has been isolated using "Pinner synthesis". All the reactions were performed in a one-pot procedure without isolating any thioacylating agents. It is worth noting that in the case of all three polar solvents (acetonitrile, DMF and DMSO) only a trace amount (yield below 1%) of symmetrical tetrazine **T1** could also be observed.

Formation of 1,2,3,4-thiatriazole in this reaction is assumed to process through diazotization of a thiohydrazide intermediate, formed in the first step, by the nitrous acid used in the second step. However, the detailed mechanism of formation of these thiohydrazide intermediates is still under investigation and it is not clear if small amounts of hydrogen sulfide are formed or not.

The reaction with DMSO as a solvent became the most interesting to us because it provides a novel, convenient pathway to 1,2,3,4-thiatriazoles directly from commercially available nitrile reagents in an excellent yield. The reaction conditions were optimized by changing the amount of sulfur and reaction temperature. Probably acting both as an inducer and reactant in the reaction, the amount of sulfur is crucial in this reaction. Theoretically, one equivalent of sulfur should be enough to obtain the thiatriazole product. In those conditions the reaction already led to a reasonable yield (53%, Table S1 in Supporting Information), while slight excesses (1.3 equiv) of sulfur could still improve the yield and 1.5 equiv of sulfur gave the best yield (74%). The reaction temperature and time were optimized to 90 °C for 1 hour, because decreasing the reaction temperature only resulted in prolonged reaction times to reach similar yields (Table S2). We used microwave heating throughout, but we have verified that running the reaction in a sealed tube with conventional heating worked fine as well, resulting in a similar yield (72%).

To extend the scope of this synthetic approach, we engaged a series of nitrile substrates in our new one-pot synthetic approach. Thus, a series of 5-aryl-1,2,3,4-thiatriazoles were successfully prepared in good to high yields (51–80%, Table 2), among which many were previously complicated to prepare.[3] The reactions are simple and efficient, and the nitrile substrate can contain different functional groups such as halogens and hydroxyl groups. Although the reaction is versatile, unfortunately, preparation of 5-alkyl-1,2,3,4-thiatriazoles using benzyl cyanide or *tert*-butyl cyanide was not successful, probably due to instability of the thioacylating intermediates which have been described previously.[3]

Table 2. Synthesis of 5-aryl-1,2,3,4-thiatriazoles **TT1-TT9**.[a]



[a] Reactions were carried out on a 0.5 mmol scale in 2 mL DMSO. Yields (isolated) based on the starting nitrile.

With our convenient one-pot synthetic approach in hand, we hypothesized that it could be used to prepare donor-acceptor type thiatriazole derivatives using an appropriate nitrile precursor. More importantly, we also believed that 1,2,3,4-thiatriazole could act as a novel electron acceptor for efficient TADF emitters. Indeed one-pot or multicomponent synthesis of functional chromophores has received considerable interest both in academia and industry.[19] To our delight, the donor-acceptor thiatriazole derivative using phenoxazine as a donor motif, **TT9**, was easily prepared in a high yield (70%) using our approach. **TT9** easily forms yellow crystals, which are stable and could be stored at room temperature for several months without noticeable degradation. The single-crystal structure (Figure 1) shows a large twisting angle (67°) between the planes of donor and acceptor, which is desired to achieve small HOMO–LUMO overlap and to realize a small ΔE_{ST}, and therefore efficient TADF characteristics.[4]

TT9 was further characterized by electrochemistry (Figure S8). The cyclic voltammogram in DCM displays a reversible oxidation wave for the phenoxazine, and an irreversible reduction one corresponding to the thiatriazole. The HOMO and LUMO energies were determined to be 5.35 and 3.41 eV from the onset of the respective waves.

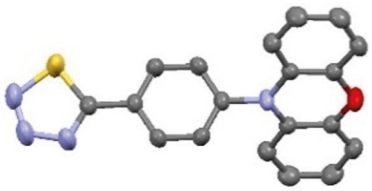


Figure 1. Crystal structure of **TT9**. Hydrogen atoms are omitted for clarity.

DFT-based calculations were also performed on **TT9**. The ground state structure of the molecule shows an almost perpendicular twist between the phenoxazine and the thiatriazole-phenyl moieties and complete spatial separation of the HOMO and LUMO (Figure 2) which is an ideal situation to reach a small singlet-triplet energy difference. Optimization in the first singlet excited state gave a very similar geometry, where the main difference is a flattening of the phenoxazine moiety (Figure S10). The computed ΔE_{ST} on this excited state optimized structure is 0.005 eV, which is excellent to get efficient TADF.

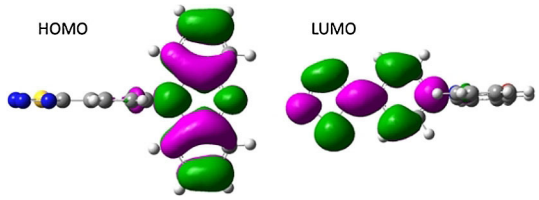


Figure 2. Calculated spatial distributions of the HOMO (left) and LUMO (right) of **TT9**.

Photophysical studies demonstrated that **TT9** indeed exhibits prominent thermally activated delayed fluorescence (TADF) characteristics both in solution and film. Relevant photophysical properties of **TT9** are displayed in Figure 3 and Table 3. Like other donor-acceptor molecules, **TT9** shows a clear solvatochromic effect (Figure 3a). It is highly emissive in non-polar media such as methylcyclohexane (MCH), Toluene (Tol), and Zeonex (a cyclo olefin polymer), whereas it is however very

Table 3. Photophysical properties of **TT9**.

Sample	λ_{PL} [nm][a]	$\Phi_{PL}^{air}/\Phi_{PL}^{deg}$ [%]	τ_{PF} [ns][d]	τ_{DF} [μs][e]	DF/PF[f]
Zeonex film	539	65/99[b]	20.4 ± 0.7	5.5 ± 0.28 28.0 ± 1.7	2.37
MCH solution	505 532	12/76[c]	18.6 ± 0.6	22.2 ± 1.2	2.65

[a] Emission maxima. [b] PLQY in air and N_2 atmosphere. [c] PLQY in air-equilibrated and degassed MCH solution. [d] Prompt fluorescence lifetime determined from PL decay (Figure S4, S5). [e] Delayed fluorescence lifetime determined from PL decay (Figure S4, S5). [f] Ratio of delayed fluorescence component to prompt fluorescence one.

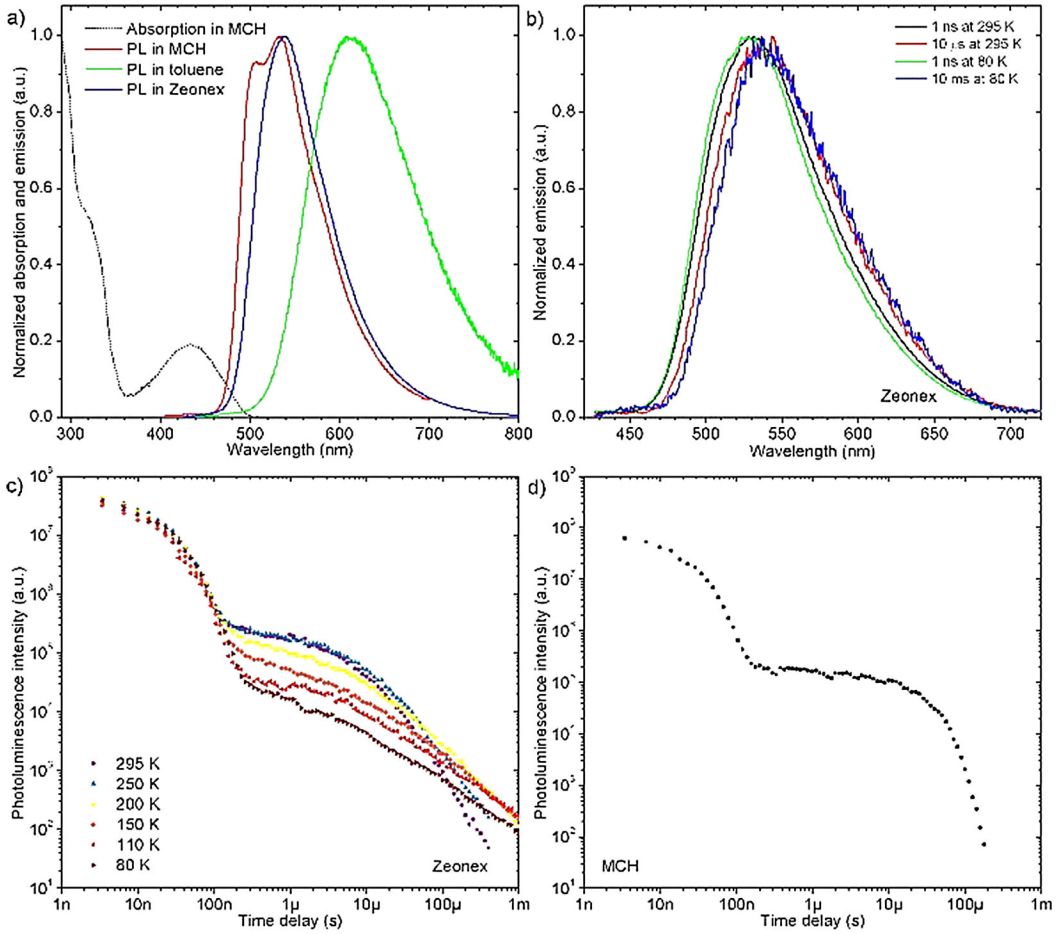


Figure 3. (a) Normalized fluorescence spectra of **TT9** in MCH, Tol and Zeonex 1% (w/w) and normalized absorption spectrum in MCH. (b) Time-resolved spectra of **TT9** in Zeonex. (c) PL decays of **TT9** in Zeonex 1% (w/w) at various temperatures. (d) PL decay of **TT9** in degassed MCH at room temperature.

weakly emissive or non-emissive in more polar solvents (Figure S1 in Supporting Information), as is typical for strong charge transfer (CT) excited state systems.[20] Photoluminescence (PL) intensity of **TT9** in MCH increases 6.3-fold in degassed solution relative to the air-equilibrated system (Figure S2), indicating that oxygen largely influences the PL of this material. Comparison of PL decays of **TT9** in air-equilibrated and degassed MCH (Figure S3) shows that in the latter case, a longer lifetime indicative of TADF, as well as a longer prompt fluorescence lifetime than in the presence of oxygen is observed. Thus oxygen apparently not only quenches the triplet state but also the singlet one. The ratio of the delayed fluorescence component to the prompt fluorescence one (DF/PF) was determined to be 2.65 from the PL decay of **TT9** in degassed MCH (Table 3). The photoluminescence quantum yield (PLQY) of **TT9** in MCH and Zeonex in air were determined to be 12% and 65%, respectively. The PLQY in degassed MCH increased to 76%, and the PLQY in Zeonex under nitrogen reached 99%. This is remarkable since many CT molecules suffer from a small radiative decay rate due to the spatial separation of HOMO and LUMO originating from the molecular design.[4] **TT9** exhibits prominent TADF characteristic not only in MCH but also in Zeonex (Figure 3c,d) with a DF/PF ratio in the latter equal to 2.37. Temperature dependence of delayed fluorescence recorded in Zeonex (Figure 3c) is typical of TADF molecules showing clearly the thermal activation of the process.[5] Interestingly, at 80 K the intensity of TADF is still substantial and thus phosphorescence is hardly distinguishable from delayed fluorescence (Figure 3b). This gives a clear indication for a ΔE_{ST} approaching zero. It is also noteworthy that the prompt fluorescence is completely unaffected by temperature change, which indicates that it has almost no effect on the non-radiative decay rate of the singlet excited state. This also contributes to the high PLQY of the molecule. Power dependence of delayed fluorescence of **TT9** is linear in both MCH and Zeonex confirming the TADF mechanism (Figure S6, S7).

In conclusion, we have examined and proved that the solvent plays an important role in the "Pinner synthesis" outcome. We have discovered a novel, convenient one-pot synthesis of 1,2,3,4-thiatriazoles directly from nitrile substrates in high yields (51–80%), with no need for isolating the thioacylating agents. We believe that our work significantly improves access to differently functionalized 1,2,3,4-thiatriazoles. Using this new one-pot approach, a peculiar donor-acceptor thiatriazole derivative has been synthesized which proved to be quite an efficient TADF emitter. This is the first example of 1,2,3,4-thiatriazole use as an electron acceptor for TADF emitters. Our new approach opens possibility to further develop 1,2,3,4-thiatriazole derivatives as new families of molecules for applications in organic electronics and other related fields. One-pot synthesis and high reaction yields are two key factors to reduce costs in large scale synthesis and correlatively possible industrial applications.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: delayed fluorescence · one-pot synthesis · Pinner synthesis · tetrazines · thiatriazoles

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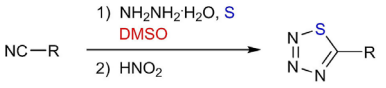
COMMUNICATION

One-stop shop: A novel and unexpected convenient one-pot synthesis of 1,2,3,4-thiatriazoles has been discovered meanwhile investigating on the classical tetrazine "Pinner synthesis". The synthetic route starts from commercially-available nitrile derivatives and gives good to high yields (51–80%) with no need to isolate any thioacylating agents. Using this new synthetic route a novel donor-acceptor thiatriazole derivative has been prepared which exhibits prominent thermally activated delayed fluorescence (TADF).



✓ One-pot synthesis
✓ Novel acceptor for efficient TADF emitters

Fluorescence

Y. Qu, P. Pander, A. Bucinskas, M. Vasylieva, Y. Tian, F. Miomandre, F. B. Dias, G. Clavier, P. Data, P. Audebert**

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Convenient One-Pot Synthesis of 1,2,3,4-Thiatriazoles Towards a Novel Electron Acceptor for Highly-Efficient Thermally-Activated Delayed-Fluorescence Emitters