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Synthesis, optical properties of multi donor–acceptor substituted AIE pyridine derivatives dyes and application for Au^{3+} detection in aqueous solution

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A series of multi donor–acceptor substituted pyridine derivative dyes were synthesed by three-component catalyst-free domino reaction in methanol aqueous at room temperature. The pyridine derivative dyes with thermally stable fluorescence exhibit aggregation-induced emission (AIE) in both aqueous solution and solid state due to the restricted intramolecular rotation as well. Furthermore, the family of molecule dyes showed nearly the full range of color emitters from blue to green and to orange. Moreover, the importance of dyes for heavy and transition metal ion species detection applications was demonstrated *via* the "turn off" detection of Au^{3+} in aqueous solution with the simple synthetic approach and high selectivity and sensitivity.

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1. Introduction

Recently, photo-induced responsive organic luminescent dyes have been attracted much scientific and commercial attention [1]. Especially, they have been shown various applications, such as materials presenting semiconducting, fiber switcher, fluorescent sensor, and modulator [2]. In order to gain a long-lived organic dyes and to tune the electron–hole combination efficiency, the researchers have been devoted to the investigation of the multi donor–acceptor (D–A) systems such as D–A–D [3], A–D–A [4], and A–D–A–A [5]. In addition, aggregation-induced emission (AIE) dyes, as a kind of typical luminescent materials, were non-emissive in solution and highly fluorescent upon aggregate formation, which were contradicted to the expected aggregation caused quench (ACQ) effect of most traditional fluorophores [6]. Moreover, fluoregens bearing the AIE characteristic have been widely explored in bio-imaging, organic light-emitting diodes(OLEDs), as well as other fluorescent probes [7].

According to the green characteristics of atom economy, bond forming economy, and structural economy [8], new multi-component domino approaches for the synthesis of fluorescent compounds containing multi D–A groups have been a very interesting research topic [5,9]. For example, Mukho-padhyay et al. synthesized A–D–A–A systems *via* a one-pot multi-component reaction catalyzed by zinc titanate nano-powder [5]; Gladow and co-workers reported a one-pot domino reaction to synthesize D–A systems of methylthio-substituted thiophene and pyrrole derivatives [9a].

4-aryl-2,6-diamino-3,5-dicyanopyridine derivatives **6** which exhibit π-conjugated flat rigid planar structure were a typical multi donor–acceptor (D–A–D–A–D) systems and were complied with structure characteristics of organic luminescent material dyes. Samadi et al. reported the synthesis of **6** by the amination of 2-amino-6-chloro-4-phenyl-3,5-dicyano pyridine [10] which was obtained from the condensation of malononitrile with triethyl orthobenzoate in the presence of pyridine [11]. And **6** were also obtained by the cyclization of arylidenemalononitrile, ethyl cyanoiminoacetate, and ammonium acetate in refluxing absolute ethanol (Scheme 1) [12]. However, these synthetic methods suffer from significant limitations such as low yield, toxic, and harsh reaction conditions. To the best of our knowledge, a one-pot multi-component approach for the construction of this skeleton has not reported in the literature. Therefore, a more general, efficient, and viable route with operational simplicity for the synthesis of functionalized 2, 6-dicyanoanilines is highly desirable. Moreover, the optical properties of such systems were never investigated.

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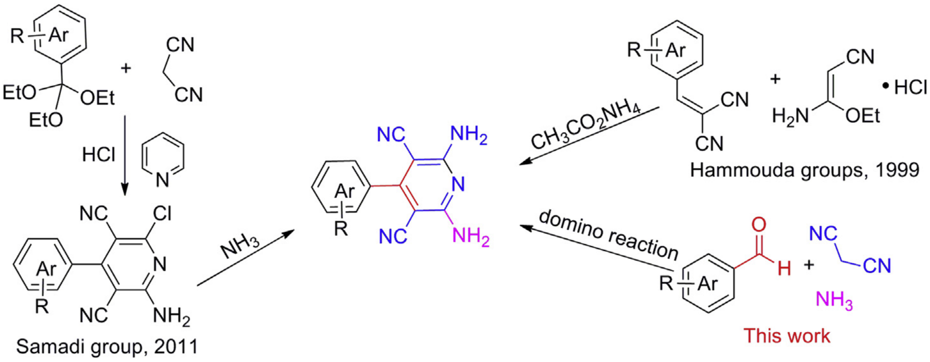


Scheme 1. Methods for the synthesis of compound **6**.

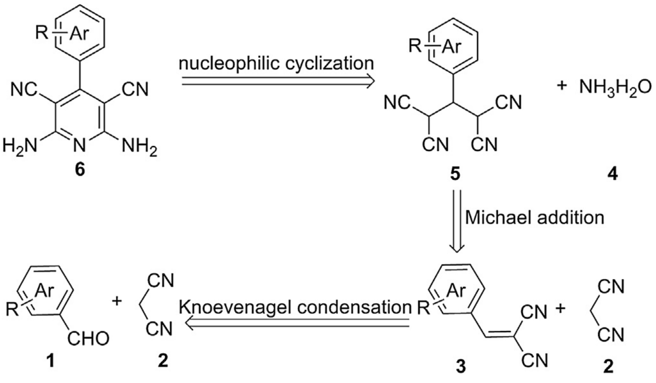
Owing to their simplicity, high sensitivity, and real-time detection, the construction of fluorescent probes for detecting heavy and transition metal ion species, have received a great deal of attentions [13]. Recently, several gold ion selective molecular sensors based on various fluorophore units including rhodamine [14], BODIPY [15], fluorescein [16], and naphthalimide [17] dyes have been reported. However, the most prominent drawback of those type of probes were the cross interferences with coexisting ions or only used in an organic or organic-containing solution. Moreover, some of the fluorescent probes sometimes suffer from intricate synthetic procedures.

Herein, we report on a rapid, efficient and convenient procedure for the synthesis of title dyes **6** *via* three component domino reaction in one pot (Scheme 2). These compounds showed AIE behavior and can be used for gold ions detection in aqueous solution with high selectivity and sensitivity.

2. Results and discussion

2.1. Synthesis

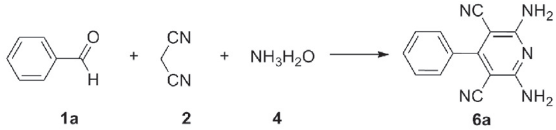
In the initial experiment, we explored the optimum conditions for the synthesis of 4-aryl-2,6-diamino-3,5-dicyanopyridine derivatives **6** by the reaction of benzaldehyde **1a**, malononitrile **2** and ammonium hydroxide **4** as model substrate. The effects of different catalysts, solvents, and temperatures on the model reaction were examined and the results were listed in Table 1. Some available base such as NaOH, $NaOCH_3$, DBU, CH_3NH_2, $(C_2H_5)_3N$ can promote the reaction [18], and ammonia was the best, probably because of the relatively lower nucleophilicity [8d]. Moreover, the excess ammonia was necessary (Table 1, entries 1–6). The reaction was performed in CH_2Cl_2, CH_3CN, THF, CH_3CH_2OH, CH_3OH, H_2O and methanol aqueous (Table 1, entries 7–12). Gratifyingly, we found that while the reaction was run in a mixture of methanol and water (volume ratio 6:1), the best result was obtained. These observations led to a conclusion that methanol aqueous is the solvent of choice, although a control experiment proved that water alone cannot promote the reaction (Table 1, entry 12) [19]. Additionally, methanol–water combination as solvent afforded a simple and clean purification of the products. The yields decreased when the temperature was higher than 40 °C, probably the more by-product was formed (Table 1, entries 13–16). Therefore, the optimal reaction condition was the reaction of benzaldehyde (**1a**) with 2.0 equivalents of malononitrile (**2**) and 2.0 equivalents ammonium hydroxide (**4**) at room temperature (25 °C) in methanol aqueous for 3.0 h and the yield of **6a** was 83% (Table 1, entry 13).



Scheme 2. The synthetic design of 4-aryl-2,6-diamino-3,5-dicyanopyridine.

Furthermore, to demonstrate the scope and generality of this procedure for the synthesis of 2,6-diamino-3,5-dicyanopyridine **6**, a series of aromatic aldehydes **1a-o** were employed to react with **2** and **4** under the optimized conditions. As shown in Table 2, all the reactions underwent well to provide the desired 2,6-diamino-3,5-

Table 1
Optimization of reaction conditions.[a]



Entry	Solvent	Catalyst (equiv)	Time (h)	Temp (°C)	Yield (%)[b]
1	MeOH	NH_3 (1.0)	3	25	79
2	MeOH	NaOH (1.0)	20	25	35
3	MeOH	NaOMe (1.0)	20	25	27
4	MeOH	DBU (1.0)	48	25	Trace
5	MeOH	CH_3NH_2 (1.0)	20	25	5
6	MeOH	$(C_2H_5)_3N$ (1.0)	20	25	15
7	CH_2Cl_2	NH_3 (1.0)	10	25	20
8	CH_3CN	NH_3 (1.0)	10	25	23
9	THF	NH_3 (1.0)	10	25	35
10	EtOH	NH_3 (1.0)	3	25	72
11	H_2O	NH_3 (1.0)	3	25	46
12	Mixture[c]	NH_3 (1.0)	3	25	83
13	Mixture[c]	NH_3 (1.0)	3	40	85
14	Mixture[c]	NH_3 (1.0)	2	60	69
15	Mixture[c]	NH_3 (1.0)	2	80	42
16	Mixture[c]	NH_3 (1.0)	2	100	31

[a] Reaction conditions: benzaldehyde (10 mmol), malonoitrile (20 mmol), ammonia solution (20 mmol, 26–28 wt%).

[b] Isolated yields.

[c] $V_{MeOH}:V_{H_2O} = 6:1$.

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