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Pyrimidine-Core Extended π-Systems: General Synthesis and Interesting Fluorescent Properties

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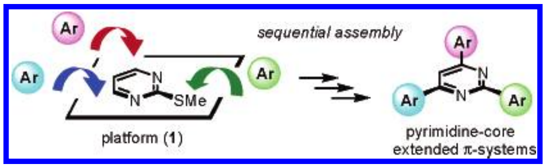
The introduction of a heteroaryl moiety into extended π-systems often brings about a number of interesting properties that are useful in the development of advanced electronic and photonic materials.[1] In particular, the high electron affinity of heteroaromatics has found many uses where electron transport is necessary. For example, extended π-systems based on heteroaromatic cores (units) have been utilized as electron-transport materials (or emitter materials) in organic electroluminescent devices.[2,3] Although pyrimidine is one of the least exploited core heteroaromatics in functional π-systems,[4] Wong and Wu have recently reported the use of such π-systems in organic electroluminescent devices.[5] Herein, we report on the sequential assembly of π-systems, such as aryl groups, onto the pyrimidine core (platform) as a useful method for the construction of pyrimidine-core extended π-systems.[6] We demonstrated the usefulness of 2-methylthiopyrimidine (**1**) as a platform in this strategy.



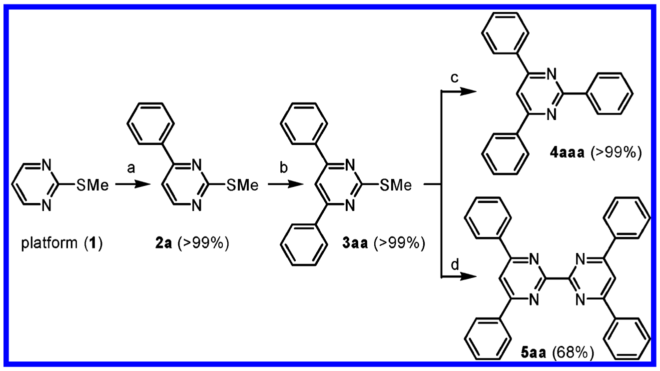
Representative π-assembling reactions based on **1** are shown in Scheme 1. The nucleophilic addition of PhLi to **1** occurred at 0 °C in tetrahydrofuran (THF) (at the 4-position). Quenching of the mixture with HOAc followed by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) resulted in the production of **2a** quantitatively.[7] The iterative reactions of **2a** with PhLi then gave **3aa** quantitatively. The resulting adduct **3aa** was further allowed to react with PhMgBr under the catalytic influence of $NiCl_2$(dppe) to afford the pyrimidine-core π-system **4aaa** quantitatively.[8] Furthermore, the treatment of **3aa** with $NiCl_2/PPh_3/Zn$ in dimethylformamide (DMF) resulted in a novel C−S homo-coupling reaction giving substituted 2,2′-bipyrimidine **5aa** in 68% yield.[9]

On the basis of these transformations, various electronically and structurally diverse aryl groups can be assembled onto the pyrimidine and 2,2′-bipyrimidine core in a programmable and diversity-oriented manner. The 2,4,6-triarylpyrimidines **4** prepared by the methods described in Scheme 1 are listed in Table 1, together with the yields of each step of the aryl group installation.

The photophysical study of these π-systems revealed that the installed aryl groups, in particular a p-$Me_2NC_6H_4$ group (**h**), influence absorption/emission maxima (λ_{abs} and λ_{em}) substantially.[10] For example, the $\lambda_{abs}/\lambda_{em}$ values of **4aah** (344 nm/495 nm), **4aha** (363 nm/444 nm), and **4jjh** (354 nm/539 nm) are significantly red-shifted from those of the parent **4aaa** (265 nm/381 nm). The cyclic voltammetry experiments showed that the reduction peak potential values (E_{pc}) of **4** are in a range of −2.20 to −2.63 V versus Ag/Ag^+, depending on the nature of the aryl groups on the pyrimidine core. For example, the introduction of electron-rich aryl groups such as p-$Me_2NC_6H_4$ group (**h**) increases the reduction potential as somewhat expected.[10]

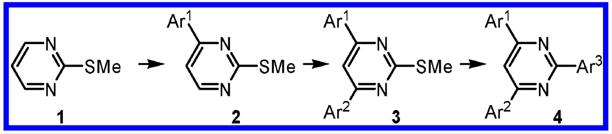
The power of this strategy becomes apparent when we utilize dilithium reagents (Li−Ar−Li) in place of monolithium reagents (Ar−Li) in the first and/or second π-assembling reactions. For example, when the first π-assembling reaction was performed with 2,7-dilithio-9,9-dioctylfluorene, the interesting fluorene-linked π-system **6nha** was prepared in good overall yield (eq 1). The π-system

Scheme 1[a]



[a] Reagents and conditions: (a) PhLi (1.1 equiv), THF, 0 °C, 2 h, then HOAc (1.1 equiv), room temperature, then DDQ (1.1 equiv), room temperature; (b) PhLi (1.7 equiv), THF, 0 °C, 2 h, then HOAc (1.1 equiv), room temperature, then DDQ (1.1 equiv), room temperature; (c) PhMgBr (1.5 equiv), $NiCl_2$ (dppe) (3 mol %), toluene, 60 °C, 24 h; (d) $NiCl_2$ (1.0 equiv), PPh_3 (4.0 equiv), Zn (1.5 equiv), DMF, 90 °C, 24 h.

Table 1. Synthesis of 2,4,6-Triarylpyrimidines **4**[a]



run	**2** (yield, %)	**3** (yield, %)	**4** (yield, %)
1	**2a** (>99)	**3aa** (>99)	**4aaa** (>99)
2			**4aab** (92)
3			**4aac** (85)
4			**4aad** (84)
5			**4aae** (90)
6			**4aah** (>99)
7			**4aai** (75)
8			**4aal** (>99)
9		**3ah** (64)	**4aha** (96)
10	**2j** (93)	**3ja** (64)	**4jaa** (97)
11		**3jh** (92)	**4jha** (96)
12			**4jhh** (>99)
13			**4jhj** (35)
14		**3jj** (84)	**4jjh** (95)
15	**2k** (68)	**3kk** (59)	**4kkg** (95)
16	**2l** (95)	**3ll** (63)	**4llg** (>99)
17	**2m** (85)	**3mm** (56)	**4mma** (>99)

[a] Aryl groups (π-units) are assigned as follows: C_6H_5 (**a**), o-$MeOC_6H_4$ (**b**), m-$MeOC_6H_4$ (**c**), p-$MeOC_6H_4$ (**d**), p-$PhOC_6H_4$ (**e**), p-MeC_6H_4 (**f**), p-BuC_6H_4 (**g**), p-$Me_2NC_6H_4$ (**h**), p-FC_6H_4 (**i**), p-$CF_3C_6H_4$ (**j**), 1-naphthyl (**k**), 2-naphthyl (**l**), 4-biphenyl (**m**).

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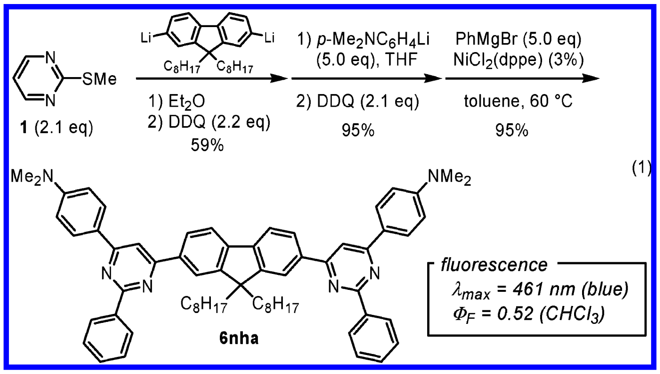
6nha exhibits strong blue fluorescence in $CHCl_3$ with emission maximum at 461 nm. The fluorescence quantum yield (Φ_F) was determined to be 0.52 with reference to 9,10-diphenylanthracene. The first reduction peak potential value was found to be -2.65 V versus Ag/Ag^+. Nevertheless, the discovery of a compound bearing both high fluorescence efficiency and a high electron-accepting property is of great interest.



During the course of our investigation on photophysical properties (UV/vis and fluorescence measurements) of pyrimidine-core extended π-systems, it was found that the introduction of a p-$Me_2NC_6H_4$ group (**h**) onto the pyrimidine ring substantially increases the fluorescence efficiency (Figure 1). For example, while the parent **4aaa** exhibits almost no fluorescence in solution, **4aha** was found to emit strong blue light upon irradiation ($\lambda_{max} = 444$ nm, $\Phi_F = 0.63$). Although a similar increase of fluorescence efficiency was also observed with **4aah**, the effect was much smaller ($\Phi_F = 0.05$) than that observed with **4aha**, indicating the importance of the attaching site of π-units on the photophysical properties.

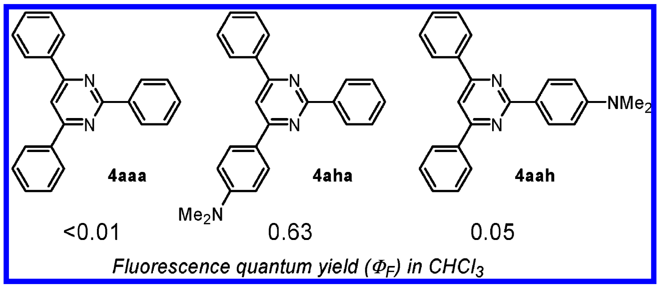


Figure 1. Effect of p-$Me_2NC_6H_4$ group in fluorescence efficiency.

More interestingly, it was found that 2,4,6-triarylpyrimidines with a p-$Me_2NC_6H_4$ group (**h**) exhibit solvatofluorochromism.[11] In particular, 2,4,6-triarylpyrimidines with an electron-releasing p-$Me_2NC_6H_4$ group (**h**) and electron-accepting p-$CF_3C_6H_4$ group (**j**) attached, such as **4jha**, **4jhh**, **4jhj**, and **4jjh**, exhibit strong positive solvatofluorochromism. The emissive behaviors and fluorescence spectra of representative **4jha** with various solvents are depicted in Figure 2. The decrease in the fluorescence energy with increasing solvent polarity corresponds to an increase in the dipole moment, indicating the charge-transfer character of the emitting state. Nevertheless, the realization of a wide range of wavelengths (400−584 nm) with reasonable fluorescence efficiency is notable. Its application as a fluorescent probe might be interesting.

In summary, we have developed a simple but powerful synthetic strategy that permits the assembly of π-systems onto a pyrimidine core in a programmable and diversity-oriented format. The successful discovery of a number of interesting fluorescent materials and properties (e.g., solvatofluorochromism) speaks well for the potential of our platform strategy in the development of functional organic materials.

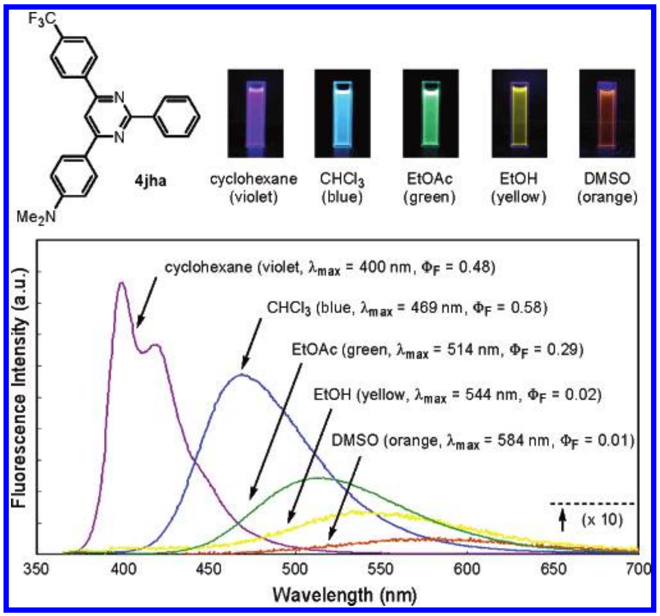


Figure 2. Emissive behaviors and fluorescence spectra of **4jha** with various solvents.

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Supporting Information Available: Experimental procedures and analytical and spectroscopic data of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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