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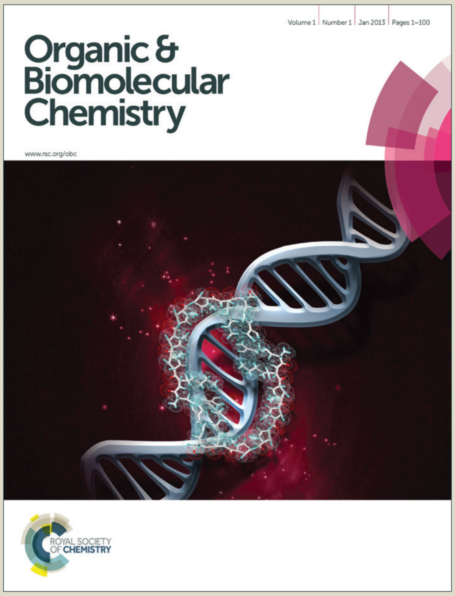

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Organic &
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COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Received 00th xxxx 2015
Accepted 00th xxxx 2015

DOI: 10.1039/x0xx00000x

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Cu-catalysed direct C–H (hetero)arylation of [1,2,4]triazolo[4,3-*a*]pyridine to construct deep-blue-emitting luminophores†

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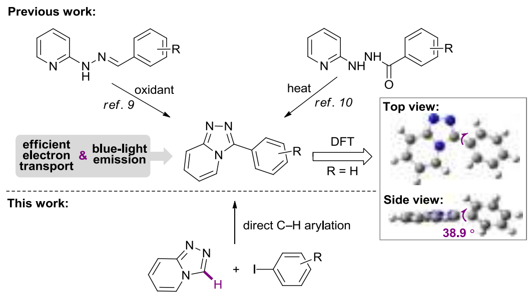
Cu-catalysed direct C–H (hetero)arylation of [1,2,4]triazolo[4,3-*a*]pyridine has been accomplished for the first time to streamline the synthesis of 3-aryl-[1,2,4]triazolo[4,3-*a*]pyridines for screening blue-emitting materials. On this basis, the photophysical properties of the resulting compounds were systematically investigated, most of which exhibited excellent deep-blue emission with moderate to high quantum yields, photostability, air stability and thermal stability.

Organic light-emitting diodes (OLEDs) have attracted considerable interest because of their potential applications in flat-panel displays and solid-state lighting.[1] Organic materials with red, green and blue-light emissions are usually required for the fabrication of full-colour displays and white-light lighting. Among the three primary colour light-emitting materials, high performance deep-blue emitters have been one of the most important prerequisites to promote the popularization of OLEDs.[2,3] Such emitters not only can effectively reduce the power consumption of OLEDs but also can be used to generate other emission colours through energy transfer.[2] However, only a limited number of deep-blue-emitting materials applied in OLED devices with sufficiently high efficiency, proper chromaticity and luminance have been reported.[3] Thus, it is highly desirable to develop new luminophores with deep-blue emission for OLED applications.

Organic functional molecules containing the electron-deficient triazole have frequently been used as the electron transport (ET) materials in OLEDs due to their efficient electron-transport and hole-blocking characteristics.[4] Recently, triazole skeletons have also been introduced into π-conjugated system to construct blue-emitting materials, which can combine the electron-transporting with light-emitting moiety into a single molecule and thus help to simplify device fabrication.[5] We conceived that the incorporation of pyridine could extend the π-conjugation and tune the molecular energy levels, which might offer an opportunity to discover new materials with high-performance blue-emissions. Therefore, [1,2,4]triazolo[4,3-*a*]pyridine, constituted by triazole and pyridine fusing together, was chosen as a core architecture for the development of new luminophores. Because non-substituted [1,2,4]triazolo[4,3-*a*]pyridine exhibits a short-wavelength emission located at the ultraviolet region,[6] it is reasonable to speculate that the introduction of an aryl group onto the triazole ring might trigger a red-shifted emission through the extension of π-conjugation and intramolecular charge transfer (ICT). Density functional theory (DFT) calculation shows that the HOMO of 3-phenyl-[1,2,4]triazolo[4,3-*a*]pyridine is delocalized over the whole molecule (Fig. S1, ESI†), supporting its effective π-conjugation. Meanwhile, the LUMO is mainly centered on the [1,2,4]triazolo[4,3-*a*]pyridine skeleton. These results implied that this type of dyes might exhibit ICT character.[7] Moreover, the benzene ring adopts a twisted conformation with a dihedral angle of 38.9° (Scheme 1), which can inhibit molecular aggregation and the excimer formation.[8]

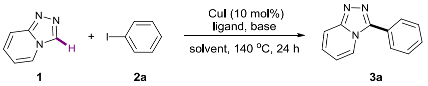


Scheme 1. Synthesis and DFT calculation of 3-aryl-[1,2,4]triazolo[4,3-*a*]pyridines.

The main methods to prepare 3-aryl-[1,2,4]triazolo[4,3-*a*]pyridines usually involve two types of annulation reactions by using 2-pyridylhydrazones or acylated 2-hydrazinopyridines as synthetic precursors (Scheme 1).[9,10] These methods generally suffer from some disadvantages with regard to direct handling of highly toxic or carcinogenic hydrazine reagents, substrate generality, stoichiometric amount of metal oxidants, or harsh reaction conditions. In addition, most of current synthetic methods involve tedious multi-step procedures to prepare a target molecule, which restricts the ability to quick build a structurally diverse chemical library. Direct C–H functionalisation as a kind of efficient synthetic method has been widely used in construction of bioactive molecules and functional materials.[11] From the viewpoint of synthetic simplicity, the direct C–H arylation of [1,2,4]triazolo[4,3-*a*]pyridine is undoubtedly one of the most ideal approaches to forge 3-aryl-[1,2,4]triazolo[4,3-*a*]pyridines. Herein, as a continuation of our interest in developing luminophores through direct C–H functionalisation,[12] we report the development of a facile and efficient approach to construct 3-aryl-[1,2,4]triazolo[4,3-*a*]pyridines through Cu-catalysed direct C–H (hetero)arylation process for screening high-performance blue-emitting materials (Scheme 1).

We initiated our exploration by examining the direct C–H arylation of [1,2,4]triazolo[4,3-*a*]pyridine (**1**) and iodobenzene (**2a**) as a model reaction (Table 1). Using CuI as a catalyst, we first surveyed a wide range of solvents, and found that DMSO was clearly the most effective (Table 1, entries 1-4). Next, some other parameters were investigated. After screening a variety of bases, K_2CO_3 was found to be the best choice (Table 1, entries 4-7). Pleasingly, when a phosphine ligand was added, the reaction could give the desired product **3a** in a satisfying yield (Table 1, entries 8-9). However, an attempt to lower the reaction temperature resulted in a sharp decrease of yield (Table 1, entry 10). Accordingly, the best result was obtained in DMSO at 140 °C for 24 h by using two equivalents of K_2CO_3 as the base in the presence of a catalyst system that was generated in situ from CuI (10 mol%) and PPh_3 (10 mol%), delivering **3a** in 94% yield. The structure of **3a** was confirmed by single-crystal X-ray diffraction (Fig. S2, ESI†).[13] The **3a** shows a dihedral angle of 37.0° between phenyl and triazole plane, similar to the DFT calculated result.

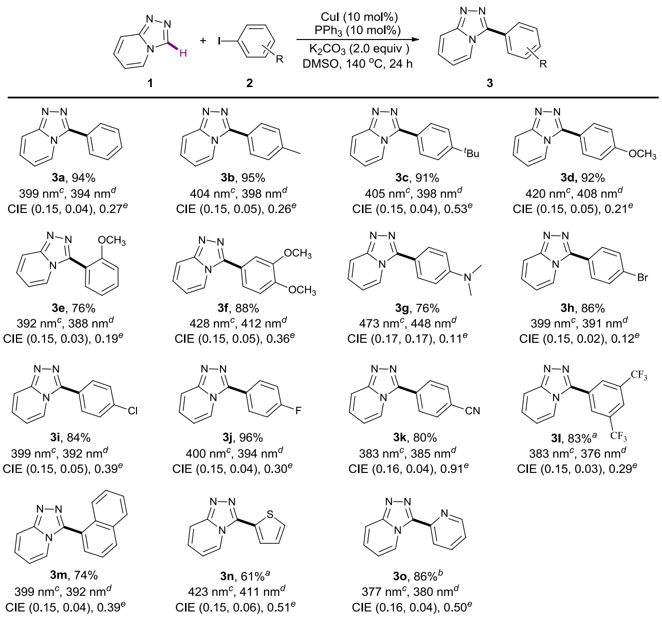
Table 1 Optimization of the reaction conditions[a]



Entry	Ligand	Base	Solvent	Yield (%)[b]
1	Phen	K_2CO_3	DMF	36
2	Phen	K_2CO_3	xylene	30
3	Phen	K_2CO_3	1,4-dioxane	32
4	Phen	K_2CO_3	DMSO	70
5	Phen	Na_2CO_3	DMSO	28
6	Phen	K_3PO_4	DMSO	59
7	Phen	Cs_2CO_3	DMSO	43
8[c]	--	K_2CO_3	DMSO	50
9	**PPh_3**	**K_2CO_3**	**DMSO**	**94**
10[d]	PPh_3	K_2CO_3	DMSO	55

[a] Reaction conditions: **1** (0.50 mmol), **2a** (0.75 mmol), CuI (10 mol%), ligand (10 mol%), base (2.0 equiv) and solvent (1.0 mL) at 140 °C for 24 h under N_2. [b] Isolated yield. [c] No ligand. [d] 120 °C. Phen = 1,10-phenanthroline. DMF = *N,N*-dimethyl formamide. DMSO = dimethyl sulfoxide.

With the optimized conditions in hand, the scope of the direct C–H (hetero)arylation was investigated, and the results were summarized in Scheme 2. Gratifyingly, whether phenyl iodides are electron-rich, electron-poor, or sterically bulky, all of them could afford the expected C3-arylated [1,2,4]triazolo[4,3-*a*]pyridine in good to excellent yields (up to 96%). The reaction condition could be compatible with various functional groups on the phenyl ring, such as alkyl, halogen (Br, Cl and F), nitrile, amine, and methoxy groups (Scheme 2, **3b**–**3l**), and many of which are very useful for further synthetic elaborations. Naphthyl iodide and heteroaryl iodide derivatives were also competent reactants in this reaction (Scheme 2, **3m**–**3o**).



Scheme 2. Direct C–H (hetero)arylation and corresponding photophysical data. Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), CuI (10 mol%), PPh_3 (10 mol%), and K_2CO_3 (2.0 equiv) in DMSO (1.0 mL) at 140 °C for 24 h. Isolated yield. [a] CuI (30 mol%) and PPh_3 (30 mol%). [b] 2-Bromopyridine (0.75 mmol). [c] Emission maximum in CH_2Cl_2 (10 μM). [d] Emission maximum in PS film (5 wt%). [e] CIE coordinate and absolute quantum yield in PS film (5 wt%).

After obtaining a variety of diverse products of the direct arylation, their photophysical properties were investigated and the data were summarized in Scheme 2. It was observed that all of the arylated products show similar emissions in the blue-light region, presumably because of the twisted configuration between the C3-aryl and the triazole plane. No matter introduction of an electron-donating or electron-withdrawing substituent onto the C3-aryl, there is little influence on the emissions. Product **3g** has the longest emission wavelength in all compounds, maybe because of the ICT effect from the dimethylaniline to [1,2,4]triazolo[4,3-*a*]pyridine. Very little overlap between the absorption and emission spectra are observed (Fig. S3, ESI†), which suggest that these triazolopyridine-based compounds may be advantageous for suppressing self-absorption. Noteworthily, all of compounds have good photostability, their fluorescence intensities showed negligible change under constant excitation for 1 hour. Taking **3k** as a representative example, its emission intensity remained stable even after 6 hours of light exposure (Fig. S4, ESI†).

Subsequently, their photophysical data in polystyrene (PS) film (5 wt%) were also explored. To our delight, all of doped films show bright blue-light emissions (Scheme 2 and Fig. 1). The emission maxima in PS film generally blue-shift a little compared with those in the CH_2Cl_2, perhaps due to the solvation effect.[14] Commission Internationale de L'Eclairage (CIE) colour coordinates of them were further investigated. As seen in Scheme 2, except for **3g**, all of compounds locate in deep-blue gamut ($CIE_x + CIE_y < 0.30$ and $CIE_y < 0.10$)[3] with little variation in the CIE coordinates. However, **3g** shows a sky-blue emission with CIE coordinates of (0.17, 0.17), as a result of the strongly charge transfer (CT).[15] Significantly, compound **3n** shows a particular blue emission with excellent CIE chromaticity coordinates of (0.15, 0.06), which is very close to the National Television System Committee (NTSC) blue standard of (0.14, 0.08).[16]

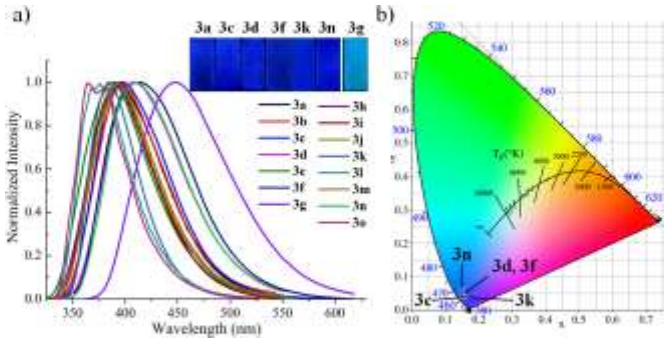


Fig. 1 (a) Fluorescent spectra of 3-aryl-[1,2,4]triazolo[4,3-*a*]pyridines in PS film (5 wt%). Insert: fluorescence images of selected compounds in PS film (5 wt%) under UV light (365 nm). (b) A plot of the CIE coordinates of **3c**, **3d**, **3f**, **3k** and **3n** on the CIE 1931 chromaticity chart.

Cyclic voltammetry (CV) experiments were performed to study the electrochemical properties (Fig. S5, ESI†). The HOMO and LUMO levels of **3c**, **3d**, **3f**, **3k** and **3n** vary from -5.66 to -6.00 eV and -2.21 to -2.63 eV, respectively (Table 2). All of compounds possess low-lying HOMO energy level, which make them sufficient for air stability.[17] Meanwhile, the electrochemical band gaps were approximate to the optical energy gaps estimated from the absorption edges.

Table 2 Photophysical, electrochemical and thermal properties of **3c**, **3d**, **3f**, **3k** and **3n**

Comp	λ_{onset} nm[a]	E_g^{opt} eV[b]	E_{on}^{ox} V	HOMO eV[c]	E_{on}^{red} V	LUMO eV[d]	E_g^{CV} eV	T_d °C[e]
3c	330	3.76	1.04	-5.84	-2.56	-2.24	3.60	250
3d	333	3.72	0.98	-5.78	-2.59	-2.21	3.57	273
3f	336	3.69	0.86	-5.66	-2.58	-2.22	3.44	285
3k	349	3.55	1.20	-6.00	-2.17	-2.63	3.37	295
3n	351	3.53	0.96	-5.76	-2.51	-2.29	3.47	250

[a] Estimated from the absorption band edge in CH_3CN (10 μM). [b] $E_g^{opt} = 1240/\lambda_{onset}$ eV. [c] HOMO = $-(4.8 + E_{on}^{ox})$ eV. [d] LUMO = $-(4.8 + E_{on}^{red})$ eV. [e] Detected by TGA analysis and heating rate = 10 °C/min.

The thermal properties of **3c**, **3d**, **3f**, **3k** and **3n** were gauged by thermogravimetric analysis (TGA, Fig. S6, ESI†). Thermal decomposition temperatures (T_d, corresponding to 5% weight loss) of them range from 250 °C to 295 °C (Table 2), indicating the thermal stability for OLED applications.

In summary, we have established an efficient and straightforward procedure for the synthesis of 3-aryl-[1,2,4]triazolo[4,3-*a*]pyridines through Cu-catalysed direct C–H (hetero)arylation process. The resulting compounds exhibit bright deep-blue emissions with moderate to high quantum yields, high photostability, good air stability and good thermal stability, which make them potential candidates for applications in high-performance OLEDs, or as models for further developing other triazolopyridine-based organic materials.

Acknowledgements

This work was supported by grants from 973 Program (2011CB808601), the National NSF of China (Nos. 21432005, 21372164, 21172155, 21272160 and 21321061) and Sichuan Provincial Foundation (2012JQ0002) for financial support. We thank the Comprehensive Training Platform of Specialized Laboratory, College of Chemistry, Sichuan University, for NMR measurements, HRMS measurements, and X-ray measurement.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c000000x

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13 CCDC 1032909 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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