Microwave-assisted synthesis and complexation of luminescent cyanobipyridyl-zinc(II) bis(thiolate) complexes with intrinsic and ancillary photophysical tunability†

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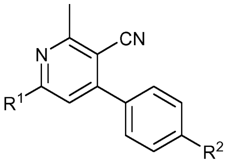
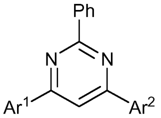
A series of cyanobipyridine-derived zinc(II) bis(thiolate) complexes are prepared rapidly and efficiently by a microwave-assisted cross-coupling/complexation sequence and display luminescence that can be modulated using intrinsic functionality and ancillary ligands.

Convenient protocols for synthesizing functionalized chromophores with tunable optical properties are highly desirable for delivering new materials for wide-ranging applications such as photovoltaics, OLEDs and fluorescence imaging microscopy.[1,2] Recently we described the synthesis of a new series of solvatochromic 3-cyanopyridine-derived chromophores **1** (Fig. 1) with visible absorption and charge transfer (CT)-based emission properties, significant Stokes shifts, excellent quantum yields and usable nanosecond fluorescent lifetimes.[3] Our route to this motif was both rapid and efficient and employed a novel microwave-assisted tandem oxidation/Bohlmann-Rahtz heteroannulation to establish the central tetrasubstituted pyridine. Furthermore, incorporated into this scaffold was capability for two-dimensional tunability through modification of substituents, and this was varied in order to modulate photophysical behaviour. Further application of this work provided a series of highly-fluorescent π-extended triarylpyrimidines **2** (Fig. 1) that display solvent-dependent emission wavelengths.[4] These reports demonstrate that the photophysical properties of chromophoric frameworks can be readily tuned *via* control of electronic properties by structural modification in order to develop materials with unusual optical properties.[5-7]



1 (13 examples)

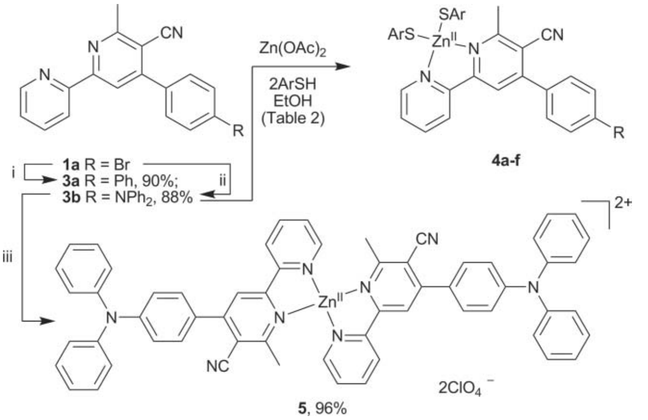


2 (14 examples)

Fig. 1 Electro-luminescent frameworks with tunable photophysical and solvatochromic properties prepared by microwave-assisted synthesis.

Central to our approach has been the use of controlled microwave dielectric heating in order to gain rapid access to compounds for study. Applications of microwave technology have received increasing attention in recent years,[8] in particular for transition metal-mediated processes.[9] In this manuscript we report on the photophysical properties of a series of new cyanobipyridines prepared and modified by microwave-assisted methods for rapid access to structural variants. The addition of a second pyridyl unit provides the basic chromophoric framework with an additional dimension for modulating luminescent behaviour, through complexation with a metal ion. Furthermore, simply by changing the ligands coordinating to the metal it was hoped that the photophysical properties of these novel chromophores could be further controlled.

The starting point for this study (Scheme 1) was cyanobipyridine **1a**, prepared by our previously reported method[3,10] in good yield. This versatile precursor contains a bromide substituent that it was envisaged could be transformed rapidly and efficiently by cross-coupling methods in order to provide good variation in electronic properties. Two different methods for bipyridine functionalization were investigated under microwave dielectric heating: a Pd-mediated Suzuki cross-coupling reaction or Cu-mediated *N*-arylation. Microwave irradiation of bromide **1a** and phenylboronic acid at 150 °C for 30 min in DMSO in the presence of $Pd(PPh_3)_4$ under basic conditions gave (biphenyl)bipyridine **3a**, whereas reaction with diphenylamine at 120 °C for 1 h in toluene using the pre-formed Cu(I) catalyst $Cu(neocup)(PPh_3)Br$[11] under basic conditions, according to our established procedure,[4] gave (aminophenyl)bipyridine **3b**, both reactions proceeding in excellent yield (Scheme 1).



Scheme 1 Synthesis of zinc bipyridine complexes **4a-f** and **5**. *Reagents & conditions*: (i) $PhB(OH)_2$, $Pd(PPh_3)_4$ (10 mol%), Na_2CO_3, DMSO, microwaves, 150 °C, 30 min; (iv) diphenylamine, $Cu(neocup)(PPh_3)Br$ (10 mol%), ^tBuOK, PhMe, microwaves, 120 °C, 1 h; (iii) $Zn(ClO_4)_2\cdot6H_2O$, CH_2Cl_2, SiC PHE, microwaves, 120 °C, 10 min.

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Table 1 Conditions for the synthesis of Zn^{II} complex **4a**

Entry	Conditions[a]	Yield%[b]
1	25 °C, 24 h	36
2	Conductive heating, reflux, 24 h	44
3	Microwaves, 120 °C, 10 min[c]	82
4	Microwaves, SiC passive heating element, 120 °C, 10 min	94

[a] Microwaves denotes microwave irradiation in a sealed tube at the given temperature, monitored by the in-built IR sensor, using a CEM Discover® single-mode microwave synthesizer by moderating the initial microwave power (150 W). [b] Isolated yield. [c] Set temperature; recorded temperature was actually lower (see Fig. 2).

The formation of cyanobipyridyl-zinc(II) bis(thiolate) complex **4a** was first investigated by stirring bipyridine **3a**, $Zn(OAc)_2$ and thiophenol (2 equiv) in EtOH at room temperature for 24 h (Scheme 2, Table 1) but surprisingly only proceeded in poor yield. Furthermore, the efficiency of this process was improved only a little by carrying out the complexation at reflux over a prolonged period (entry 2). The use of controlled microwave dielectric heating to promote the formation of metallo complexes has hitherto been reported only recently, for example in the synthesis of Ru^{II} coordination complexes,[12] despite long standing recognition of the benefits of microwave-assisted autoclave reactions for bipyridine complexation by Greene and Mingos.[13] Gratifyingly, under microwave dielectric heating at greatly elevated temperature (entry 3), Zn^{II} complex **4a** was formed in high yield without the need for further purification.

In order to investigate if this dramatic improvement in chemical yield was attributed to Arrhenius behaviour, or whether a specific microwave effect[14] was in evidence, the reaction was repeated under microwave irradiation in the presence of a SiC passive heating element (PHE)[15,16] (entry 4). Under these conditions, the thermal profile of the reaction improved (Fig. 2), an observation that we have made before in microwave-assisted tandem oxidation processes,[16] and Zn^{II} complex **4a** was formed in excellent yield. Although firm conclusions regarding rate accelerations under microwave dielectric heating would require much more detailed experimentation, we believe these findings are indicative of Arrhenius behaviour for this complexation reaction and not specific, or indeed non-thermal, microwave effects in contrary to other suggestions.

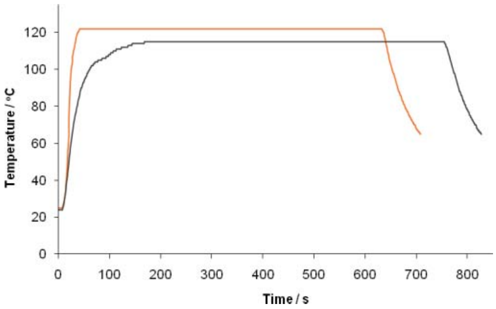

Fig. 2 Heating profile under microwave irradiation in the presence (orange) or absence (black) of a SiC passive heating element.

Table 2 Synthesis of Zn^{II} complexes **4a-f** under microwave dielectric heating and at reflux

Entry	3	4	R	Ar	Yield% [a] at reflux	Microwave Yield%[b]
1	**a**	**a**	Ph	Ph	44	94
2	**a**	**b**	Ph	4-$MeOC_6H_4$	52	97
3	**a**	**c**	Ph	2-naphthyl	50	96
4	**b**	**d**	NPh_2	Ph	54	96
5	**b**	**e**	NPh_2	4-$MeOC_6H_4$	48	95
6	**b**	**f**	NPh_2	2-naphthyl	56	98

[a] Isolated yield of **4a-f** after heating a solution of **3a,b**, the corresponding thiol (2 equiv) and $Zn(OAc)_2$ (1 equiv) in EtOH at reflux for 24 h; [b] Isolated yield of **4a-f** after microwave irradiation of a solution of **3a,b**, the corresponding thiol (2 equiv) and $Zn(OAc)_2$ (1 equiv) in EtOH using a SiC passive heating element in a sealed tube at 120 °C (measured by the in-built IR sensor) for 10 min with a CEM Discover® microwave synthesizer by moderation of the initial microwave power (150 W); all products exhibited satisfactory characterization data by IR, ^1H and ^{13}C NMR spectroscopy, and low and high resolution mass spectrometry.

A series of bipyridyl-zinc(II) bis(thiolate) complexes **4a-f** were prepared using this approach and compared with the zinc(II) bis(bipyridyl) perchlorate complex **5**, prepared in high yield by microwave-mediated complexation, in order to establish the role of the metal, intrinsic functionality and the ancillary ligands upon CT character. In so doing, the high efficiency of both microwave-assisted complexation procedures was established by comparison with conductive heating methods. Microwave irradiation of bipyridine **3a,b**, $Zn(OAc)_2$ (1 equiv) and the corresponding thiophenol (2 equiv) in EtOH at 120 °C in a sealed tube in the presence of a SiC passive heating element (Scheme 1) gave a series of complexes **4a-f** suitable for photophysical study in excellent (94-98%) yield (Table 2); far in excess of the chemical yield at reflux in EtOH after 24 h. Similarly, irradiation of bipyridine **3b** (2 equiv) and zinc perchlorate in CH_2Cl_2 at 120 °C gave complex **5** in excellent yield (96%) after 10 min whereas a known conductive heating method[17] was poorly efficient (42% yield after 24 h).

Electronic absorption spectra were obtained for each of the complexes in chloroform (10^{-6} M). Comparison with the free ligands **3a-b** revealed the presence of ligand-centred transitions together with an additional broadened low-energy shoulder at *ca.* 390 (**4a-c**) and *ca.* 485 nm (**4d-f**). In accordance with previous reports this transition was assigned to an inter-ligand thiolate-to-bipyridine charge transfer (LLCT),[18] further evidenced by a subtle wavelength dependence upon the electron donating ability of the coordinated thiolate.[19] For **4d-f** the LLCT band was red-shifted, presumably as a consequence of the greater dipolar CT character of the parent bipyridine (**3b**). Further confirmation was provided with the homoleptic complex **5**, which gave an absorption spectrum lacking the LLCT feature at *ca.* 490 nm.

The emission characteristics of the Zn(II) complexes (see Table 3) were probed in both solid and solution-states. Room temperature measurements on solid samples showed a featureless fluorescence band (< 1 ns in all cases) in the visible region, which was independent of excitation wavelength and was therefore attributed to emission from a LLCT excited state. However, in chloroform solution each of the complexes' emission profiles were dependent upon the wavelength of excitation: for **4a-c** two emission bands at *ca.* 400 and *ca.* 510 nm resulted from excitation at 330 and 400 nm respectively (Fig. 3 clearly shows the emission profile dependence of **4a** upon variable excitation wavelength). The corresponding excitation spectra showed that the longer wavelength emission was

Table 3 Absorption and photophysical properties of complexes **4a-f**

Entry	l**4**	λ_{abs} (logε)/nm[a]	λ_{em}/nm[b]	λ_{em}/nm[a] (τ/ns)	λ_{em}/nm[a] (τ/ns)	(ϕ)[a,g]
1	**a**	325 (4.37), 390 (4.03)	584	410[c] (2.7)	520[e] (1.6)	0.24
2	**b**	322 (4.40), 392 (3.96)	625	402[c] (2.5)	510[e] (2.6)	0.2
3	**c**	328 (4.32), 388 (4.06)	512	398[c] (1.6)	512[e] (7.2)	0.28
4	**d**	392 (4.18), 486 (3.86)	590	540[d] (3.9)	604[f] (6.5)	0.05
5	**e**	390 (4.20), 490 (3.78)	615	539[d] (3.1)	618[f] (7.6)	0.01
6	**f**	394 (4.14), 484 (3.90)	627	524[d] (6.9)	612[f] (< 1)	0.08

[a] aerated $CHCl_3$ solution; [b] solid; [c] $\lambda_{ex} = 320$ nm; [d] $\lambda_{ex} = 390$ nm; [e] $\lambda_{ex} = 390$ nm; [f] $\lambda_{ex} = 500$ nm; [g] obtained for LLCT emission.

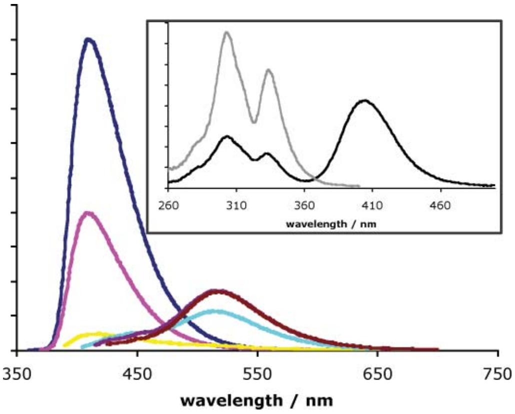

Fig. 3 Main: Emission profiles for **4a** in $CHCl_3$ ($\lambda_{ex} = 330$ (blue), 350 (pink), 370 (yellow), 390 (turquoise), 400 (purple) and 410 (brown) nm. Inset: excitation spectra for **4a** $\lambda_{em} = 410$ nm (grey) and 520 nm (black).

associated with a unique excitation peak at *ca.* 400 nm, consistent with the LLCT assignment in the corresponding absorption spectra. Similar observations were noted for compounds **4d-f**, although with notable red-shifts in all cases. Time-resolved luminescence lifetime measurements showed that each of the emission peaks were relatively short-lived (< 10 ns) and indicative of a fluorescence in each case, whilst the quantum yields of the low energy emissions are significantly reduced for **4d-f**.

Taken together with the data obtained for the corresponding free ligands **3a-b**, and the solid-state fluorescence (assigned to a LLCT emitting state), these results indicate that the longer wavelength emission in chloroform solution can again be attributed to the LLCT excited state, but that the shorter wavelength band probably arises from an intra-ligand charge transfer (ILCT) associated with the cyanobipyridine. In this context, the extent of restricted motion of the coordinated thiol can be invoked to explain disparities in single (LLCT) or dual emission.[20]

The solvatochromic behaviour of **4f** was probed and revealed that the emission in acetonitrile ($\lambda_{em} = 573$ nm) and DMSO ($\lambda_{em} = 593$ nm) was independent of excitation wavelength (390, 450 or 500 nm). A comparison with the free ligand **3b** ($\lambda_{em} =$ 576 nm (MeCN); 580 nm (DMSO)) suggests that in polar solvent the red-shifted emission of **4f** is likely to be dominated by (Zn(II)-perturbed) $IL_{(bpy)}CT$ character. This observation is consistent with our previous studies into solvatochromic cyanopyridines[3] and related reports in the literature into classical *N*,*N*-dimethylaminobenzonitrile (DMABN) species.[6]

In conclusion, a series of cyanobipyridine-derived Zn(II) bisthiolate complexes can be prepared rapidly and in high yield by the microwave-assisted complexation of cyanobipyridine **3a-b**, a thiophenol and $Zn(OAc)_2$ using a passive heating element. The complexes display LLCT fluorescence in the solid-state, but tunable dual emission in chloroform, arising from co-emissive excited states. In general, the luminescence from the complexes can be tuned through changes in bipyridine functionality and subtly modulated by changes in the ancillary thiolate co-ligands.

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