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5-Aryl-2,2′-bipyridines as tunable fluorophores

Dmitry N. Kozhevnikov,[a,b,*] Olga V. Shabunina,[b] Dmitry S. Kopchuk,[b]
Pavel A. Slepukhin[a] and Valery N. Kozhevnikov[a,b]

[a]*Institute of Organic Synthesis, Ural Branch of Russian Academy of Sciences, Kovalevskoy 22, Ekaterinburg 620219, Russia*
[b]*Ural State Technical University, Mira 19, Ekaterinburg 620002, Russia*

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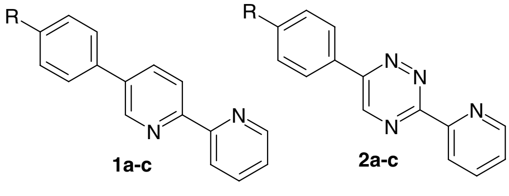
Abstract—Readily available 5-aryl-2,2′-bipyridines and their derivatives are a unique family of fine-tunable chromophores, where changes in the substitution patterns, solvation and coordination are translated into dramatic spectral changes. They exhibit sensitive and selective response to zinc ions with dramatic increases in emission intensity or significant red-shifts of emission maxima.

Luminescent organic/organometallic compounds have attracted much attention because of their potential applications in electroluminescent displays.[1–3] Luminescent chelate complexes have been shown to be particularly useful in electroluminescent (EL) displays because of their relatively high stability.[4,5] A critical element in designing and fabricating such materials is the control of their emission wavelength.[6] One of the approaches for controlling the emitted color of organic materials is to append fluorescent chromophores to a polymeric backbone or to blend such dyes into inert polymeric matrices.[7–9] Ideally, one would like to utilize one family of modular chromophores and tune their photophysical characteristics at will.[10]

Metal complexes of polypyridines are widely used luminophores. However, the parent 2,2′-bipyridine, 2,2′:6′,2″-terpyridine and 1,10-phenanthroline possess extremely low fluorescence quantum yields and undesirable short emission wavelengths, which can be explained by emission from the n–π^* excited state.[11,12] Introduction of conjugated electron-donor moieties, for example, pyrrolylethenyl,[13] phenylethynyl,[10] aminophenyl[14] or manisyl[15] leads to an increase in quantum yields and a shift of emission wavelength in the visible area. A distinguishing feature of such ligands is a sensitive response toward Zn^{2+} ions with a significant red-shift in emission. Here, we describe a novel series of highly fluorescent 2,2′-bipyridines. Tuning of the emission wavelength of any of the derivatives is possible by changing the nature of its substituents and it can be further modulated by protonation or metal ion coordination. Since the most intense electronic transition of the 2,2′-bipyridine skeleton is polarized along the 5,5′-positions,[16] it was shown[10] that increasing the conjugation along this axis provides highly fluorescent derivatives of 1,10-phenanthroline. The 5-position of bipyridines is considered the best for introduction of aromatic substituents, for example, 5-manisyl-2,2′-bipyridines have been previously shown to exhibit higher emission quantum yields compared with the 2- and 4-manisyl analogues.[15] Moreover, increasing polarization along the 5,5′-axis may lead to a significant red-shift of the emission maximum. Unsymmetrical arylbipyridines are attractive candidates for this purpose. In addition, aryl moieties at the β-position do not affect the coordination behavior of the ligand.



R = H (a), Me (b), OMe (c)

5-Aryl-2,2′-bipyridines **1a**–**c** were obtained according to a recently reported method that involves initial synthesis

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[*] Corresponding author. Tel.: +7 343 3623341; fax: +7 343 3741189; e-mail: dnk@ios.uran.ru

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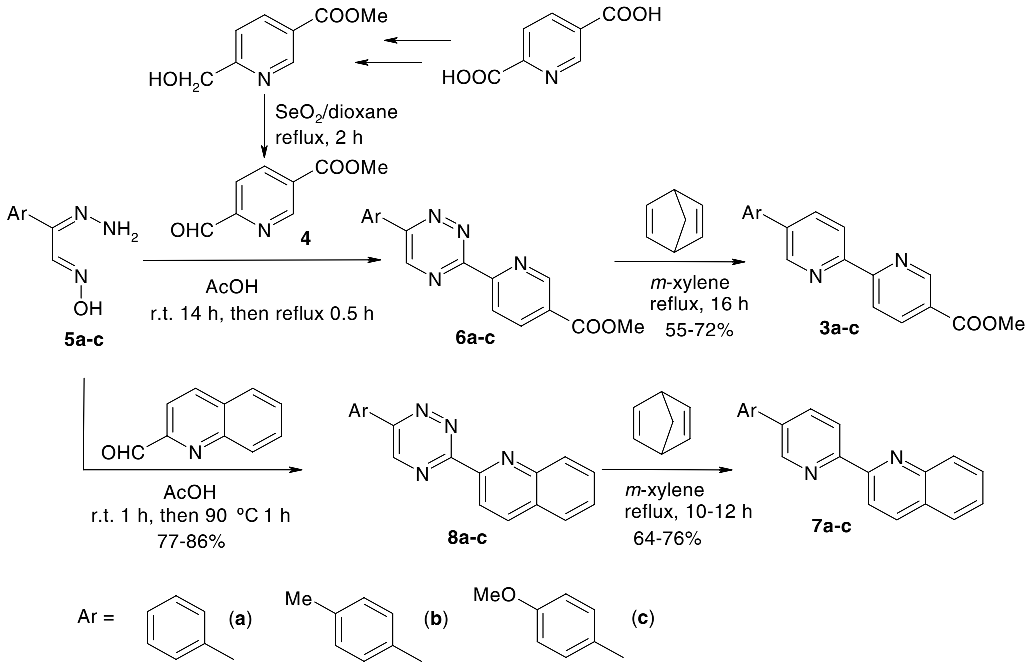
of 6-aryl-3-pyridyl-1,2,4-triazines **2a**–**c** and their conversion to substituted bipyridines **1** through an inverse electron demand Diels–Alder reaction with 2,5-norbornadiene (Scheme 1).[17]

Table 1 summarizes the photophysical data of 5-aryl-2,2′-bipyridines **1a-c** in ethanol at room temperature. The lowest energy absorbance maxima of the bipyridines **1a**–**c** in solutions is not affected by the nature of the aryl substituent or the solvent polarity. On the other hand, the aryl substituent has a significant influence on the emission characteristics (Table 1 and Fig. 1). Phenylbipyridine **1a** (R = H) possesses a very weak emission, which is slightly blue-shifted upon increasing solvent polarity. This indicates a greater contribution of the n–π^* excited states in fluorescence and explains the low emission quantum yield of **1a**, since the n–π^* excited state often decays through non-radiative pathways.

We observed that acidification of an ethanolic solution of **1a** (addition of excess CF_3COOH) led to a bathochromic shift in the longest wavelength absorption band. The fluorescent emission band underwent a 74 nm red-shift of emission maxima and some associated increase in integrated emission intensity. This data can be explained by stabilization of the intramolecular charge transfer (ICT) excited state which is expected to occur due to an increase in the electron deficient nature of the bipyridine upon protonation.

It is known that coordination to zinc(II) shifts the absorption bands of polypyridine units to the red.



Scheme 1.

Table 1. Photophysical data for arylbipyridines **1**, **3** and **7**

Compound	$\lambda_{\max}$ [nm][a]	λ_{em} [nm][b]	(Φ_F)[c]	$\lambda_{\max}(Zn^{2+})$ [nm][d]	$\lambda_{\text{em}}(Zn^{2+})$ [nm][e]	$\lambda_{\max}(H^+)$ [nm][f]	$\lambda_{\text{em}}(H^+)$ [nm][g]
1a	300	359	0.05	322	375	320	433
1b	303	363	0.38	326	397, 430$_{\text{sh.}}$	337	438
1c	312	399, 430$_{\text{sh.}}$	0.80	339	405$_{\text{sh.}}$, 442	350	525
3a	314	382	0.05	337	405, 426	315	385
3b	319	400, 428$_{\text{sh.}}$	0.39	339	436	322	404, 428
3c	329	440, 510$_{\text{sh.}}$	0.36	355	517	331	443, 510$_{\text{sh.}}$
7a	315$_{\text{sh.}}$, 325, 340$_{\text{sh.}}$	369	0.019	357	398, 430$_{\text{sh.}}$	362	455, 517$_{\text{sh.}}$
7b	317$_{\text{sh.}}$, 328, 341$_{\text{sh.}}$	382	0.12	362	435	366	440, 520
7c	318$_{\text{sh.}}$, 330, 343$_{\text{sh.}}$	432	0.62	365	517	378	517

[a] Absorption maxima in EtOH.

[b] Emission maxima in EtOH.

[c] Fluorescence quantum yields were measured using anthracene as the standard ($\Phi = 0.27$ in EtOH[8]).

[d] Absorption maxima in EtOH after addition of excess $Zn(ClO_4)_2$.

[e] Emission maxima in EtOH after addition of excess $Zn(ClO_4)_2$.

[f] Absorption maxima in EtOH after addition of excess CF_3COOH.

[g] Emission maxima in EtOH after addition of excess CF_3COOH.

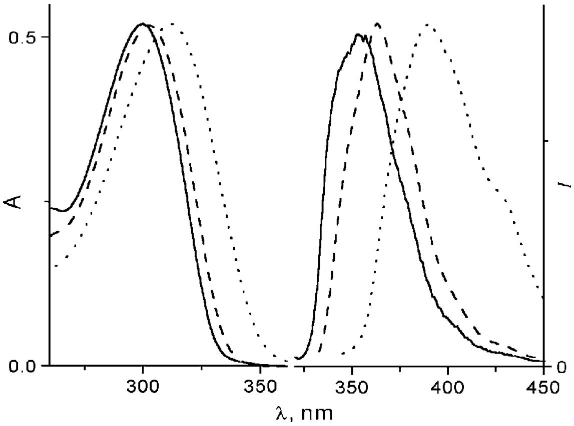


Figure 1. Normalized UV–vis absorbance and fluorescence spectra of **1a** (solid), **1b** (dash) and **1c** (dot) recorded in EtOH.

Titrating Zn^{2+} (as perchlorate or chloride) into a solution of **1a** in ethanol led to a bathochromic shift similar to that of the protonated ligand. However, in contrast to protonation, coordination to zinc resulted only in a small red-shift of the emission maxima of **1a**, but an extremely enhanced emission intensity (by a factor of 14, when excited at the isosbestic point (308 nm)). The emission maxima of **1a** was blue-shifted upon increasing the solvent polarity. This indicates that the emitting excited state is a π–π^* state, not an ICT excited state.

We isolated complex [Zn(**1a**)Cl_2] from the reaction of **1a** with $ZnCl_2$. Single crystals of [Zn(**1a**)Cl_2] suitable for X-ray diffraction were grown from acetonitrile.[18] The molecular structure of the complex [Zn(**1a**)Cl_2] is shown in Figure 2, and selected bond distances are given in the caption. The bipyridine fragment is essentially planar (torsion angle is 1.13°), while the torsion angle between the pyridine ring and the aromatic substituent is 29.26°. The Zn atom adopts a tetrahedral coordination geometry and the measured Zn–N(1)/(2) distances are 2.059 and 2.060 Å, and the Zn–Cl(1)/(2) distances are 2.194 and 2.218 Å. Complex face-to-face π–π stacking interactions between the phenylbipyridine ligands are also evident, the interplanar separations are in the range 3.4–3.7 Å, and the glide-related complexes are linked in a head-to-tail fashion to generate a supramolecular architecture of infinite chains. Inspection of the crystal packing shows that there are two types of stacks involving the same array of intermolecular forces but possessing π–π stacking interactions aligning along different directions, hence a herringbone-type pattern is created (see Supplementary data).

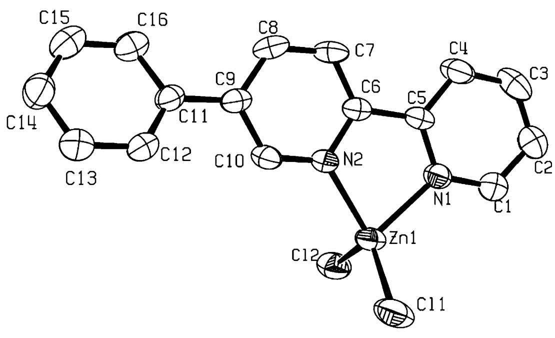


Figure 2. ORTEP view of [Zn(**1a**)Cl_2]. Selected bonds length, (Å): Zn(1)–N(1) 2.0593, Zn(1)–N(2) 2.0602, Zn(1)–Cl(1) 2.1944, Zn(1)–Cl(2) 2.2175.

Introduction of a weak electron-donor group such as methyl results in a significant change of the photophysical properties of **1b** (R = Me). While the absorption spectra and the emission maxima of **1b** are similar to those of **1a**, the emission quantum yield of **1b** is seven times as large as that of **1a**. The low dependence of the emission of **1b** on solvent polarity and the high emission intensity suggest that the emitting excited state of **1b** is a π–π^* state. Protonation of **1b** led to changes in the absorption and emission spectra similar to those of **1a**. However, addition of zinc ions to a solution of **1b** resulted in bright purple emission with a 34 nm red-shift, which is greater than that of **1a**. Moreover, the emission spectrum of the Zn(II) complex of **1b**, in polar solvents, has a shoulder on the long-wavelength side which can be attributed to the ICT state contribution, which is not very substantial.

Substituting phenylbipyridine with a methoxy group (**1c**, R = MeO) resulted in a 40 nm red-shift in the emission and an extremely enhanced fluorescence intensity ($\Phi_F = 0.80$) in ethanolic solution. The emission maxima of **1c** is more susceptible to solvent polarity than those of **1a**,**b**. The red-shift observed for **1c** upon increasing solvent polarity is indicative of stabilization of the ICT excited state. Protonation and Zn(II) coordination resulted in a large red-shift of the emission (Fig. 3). Addition of excess CF_3COOH to a solution of **1c** in EtOH caused yellow–green fluorescence with decreasing fluorescence intensity. A shift of approximately 45 nm was observed upon addition of Zn^{2+} ions to **1c** leading to a bright blue emission.

To overcome the shortcomings peculiar to arylbipyridines **1**, such as short-wavelength excitation and insufficient red-shift of emission, we decided to introduce an electron-withdrawing group (methoxycarbonyl) oppo-

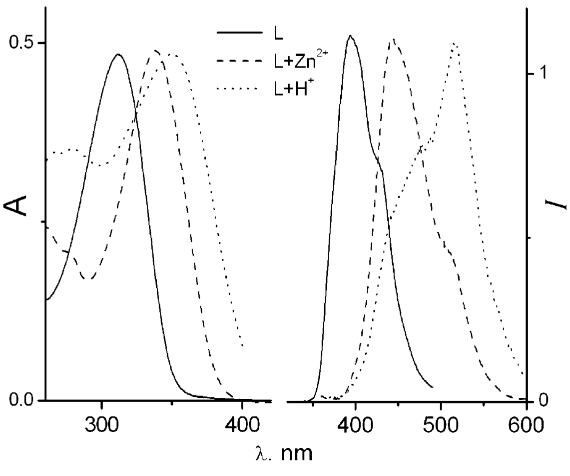


Figure 3. Normalized UV–vis absorbance and fluorescence spectra of **1c** (solid), **1c** + Zn^{2+} (dash) and **1c** + H^+ (dot) recorded in EtOH.

site to the aryl substituent. 5-Aryl-5′-methoxycarbonyl-2,2′-bipyridines **3a–c** were synthesized using the method described for bipyridines **1a–c** (Scheme 1). The key reagent in this case is 5-methoxycarbonylpyridine-2-carboxaldehyde **4** which was obtained from the 2,5-dicarboxylic acid through esterification, mono-reduction of the ester group at C-2 of the pyridine[19] and oxidation of the resulting 2-hydroxymethyl-5-methoxycarbonylpyridine with SeO_2. The reaction of hydrazones **5a–c** with aldehyde **4** resulted in 6-aryl-3-(5′-methoxycarbonyl-2-pyridyl)-1,2,4-triazines **6a–c**. Refluxing triazines **6a–c** with 2,5-norbornadiene in *m*-xylene gave target bipyridines **3a–c**. It should be noted that derivatives of 2,2′-bipyridine-5-carboxylic acid are important building-blocks for supramolecular chemistry.[20–23] The method described herein makes compounds of this type readily available with tunable structures.

Introduction of the ester group resulted in red-shifts of the absorption (13–17 nm) and emission (23–41 nm) maxima of bipyridinecarboxylates **3a–c** compared to those of **1a–c** (see Table 1 and Fig. 4). The absorption and emission spectra of **3a–c** exhibited the same dependence on the aryl substituents as arylbipyridines **1a–c**. Phenyl derivative **3a** possessed weak fluorescence ($\Phi_F = 0.05$), while tolyl and methoxyphenyl derivatives **3b**,**c** exhibited bright purple and blue fluorescence ($\Phi_F = 0.39$ and 0.36). Addition of Zn^{2+} to ethanolic solutions of esters **3a–c** caused changes in absorption and emission similar to those of **1a–c**, that is, a dramatic increase in the emission intensity of phenyl derivative **3a** (by a factor of 10) and a slight decrease in the fluorescence intensity of methoxyphenylbipyridine **3c**. However, coordination of esters **3a–c** to Zn(II) resulted in significantly higher red-shifts of the fluorescence maxima (23–77 nm) compared to those of bipyridines **1a–c** (15–43 nm), due to the electron-withdrawing ester group stabilizing the ICT state.

Unexpectedly, the photophysical properties of esters **3a–c** were insensitive to protonation. Addition of a large excess of CF_3COOH to solutions of **3a–c** had no influence on the absorption and emission maxima. At the same time, addition of Zn(II) to solutions of **3a–c** in EtOH, containing excess CF_3COOH, caused the same changes as observed for neutral ethanolic solutions. Such behavior can be explained by the decreasing basicity of the pyridine ring upon introduction of the electron-withdrawing methoxycarbonyl group. Thus, esters **3a–c** can be utilized as fluorescent probes for Zn(II) in acidic solutions.

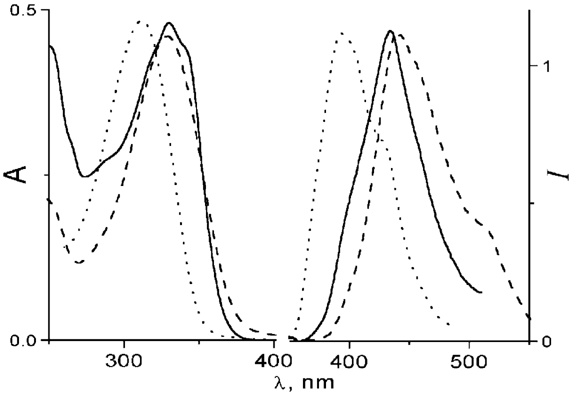


Figure 4. Normalized UV–vis absorbance and fluorescence spectra of **1c** (solid), **3c** (dash) and **7c** (dot) recorded in EtOH.

Extension of the conjugation in arylbipyridines by fusing an additional aromatic ring to one of the pyridines resulted in changes in the photophysical properties very similar to those caused by introduction of the ester group. 2-(5-Arylpyridin-2-yl)quinolines **7a–c** were obtained from 2-quinolinecarboxaldehyde and hydrazones **5a–c** (Scheme 1) through intermediate 3-quinolyl-1,2,4-triazines **8a–c**. As was expected, the absorption maxima of pyridylquinolines **7a–c** were red-shifted (20–25 nm) compared to those of **1a–c** (Table 1 and Fig. 4). Similar moderate red-shifts (10–35 nm) of the fluorescence maxima of **7a–c** occurred. A decrease in the emission quantum yields of pyridylquinolines **7a–c** compared to those of bipyridines **1a–c** was observed. However, the fluorescence intensity of **7a–c** was still strongly dependent on the aromatic substituents. Phenyl- and tolyl-substituted pyridylquinolines **7a**,**b** possess lower emission quantum yields ($\Phi_F = 0.019$ and 0.12, respectively), while **7c** (R = MeO) was intensely fluorescent chromophore ($\Phi_F = 0.62$) (Table 1). The weak emission of **7a**,**b** was slightly red-shifted upon increasing the solvent polarity: 8–12 nm when compared with the emission maxima in toluene and methanol. Obviously, **7a**,**b** emits from locally excited states: π–π^* and n–π^* excited states with considerable contribution of the latter, which was additionally confirmed by the low fluorescence intensity of **7a**,**b**. In contrast, a significant red-shift of the intense emission of **7c** in polar solvents (emission maximum is 375 nm in toluene, 396 nm in CH_2Cl_2 and 434 nm in methanol) indicated, that the ICT excited state is the main contributing factor in the emission of **7c**.

Addition of excess Zn^{2+} to ethanolic solutions of quinolines **7a–c** resulted in the expected bathochromic shift of the absorption maxima (30–35 nm). Zinc complexes of quinolines **7a–c** exhibit intense blue (**7a**,**b**) or yellow–green (**7c**) fluorescence (see Table 1). The longer red-shifts of the emissions of quinolines **7a–c** in comparison with pyridines **1a–c** can be explained by a larger contribution of the ICT excited state in the emission. Coordination of phenyl- and tolyl-quinolines **7a**,**b** to zinc dramatically increases the emission intensity, like pyridines **1a**,**b** by a factor of 25 for **1a** and 5 for **1b**. The emission intensity of methoxyphenylquinoline **7c** was slightly decreased upon addition of Zn^{2+}.

In conclusion, 5-aryl-2,2′-bipyridines and their derivatives are a unique family of fine-tunable chromophores, where changes in the substitution patterns, solvation, and coordination are translated into dramatic spectral changes. Unique selective responses allow new ligands to be considered as sensitive probes for zinc(II). The relatively simple synthesis and availability of numerous precursors make the preparation of other arylbipyridine-based chromophores with diverse photophysical properties facile.

Acknowledgements

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Supplementary data

Supplementary data containing experimental details can be found, in the online version, at doi:10.1016/j.tetlet.2006.07.111.

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18. Complex [Zn(**1a**)Cl_2]. A solution of bipyridine **1a** (50 mg, 0.15 mmol) in acetonitrile (30 mL) was added to a solution of $ZnCl_2$ (21 mg, 0.15 mmol) in acetonitrile (30 mL). The resulting colorless solution was kept for 23 days at rt. The resulting colorless crystals were filtered off. *Crystal data for* [Zn(**1a**)Cl_2] were measured with an *Xcalibur 3 CCD* (graphite monochromator, $MoK\backslash\alpha$): $C_{16}H_{12}Cl_2N_2Zn$, $FW = 368.55$, monoclinic, $a = 33.670(3)$, $b = 5.9039(2)$, $c = 16.0814(10)$ Å, $\alpha = 90.00°$, $\beta = 102.134(6)°$, $\gamma = 90.00°$, $V = 3125.3(3)$ Å^3, $T = 295(2)$ K, space group $C2/c$, $Z = 8$, 4826 reflections were used in all calculations. $R = 0.0361$. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 611928. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].
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