Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2017, **27**, 602–604

Mendeleev Communications

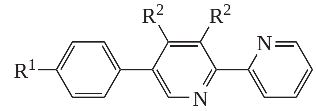
π-Extended fluorophores based on 5-aryl-2,2′-bipyridines: synthesis and photophysical studies

Olga V. Shabunina,[a] Daria Yu. Kapustina,[a] Alexey P. Krinochkin,[a] Grigory A. Kim,[a,b] Dmitry S. Kopchuk,*[a,b] Grigory V. Zyryanov,[a,b] Fengyu Li[c] and Oleg N. Chupakhin[a,b]

[a] *Ural Federal University, 620002 Ekaterinburg, Russian Federation*
[b] *I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 620990 Ekaterinburg, Russian Federation. Fax: +7 343 374 1189; e-mail: dkopchuk@mail.ru*
[c] *Institute of Chemistry, Chinese Academy of Sciences, 100190 Beijing, P.R. China*

DOI: 10.1016/j.mencom.2017.11.021

A straightforward and convenient synthesis of new fluorescent 5-aryl-2,2′-bipyridines with the extended conjugation system involves the ‘1,2,4-triazine’ methodology followed by Pd-catalyzed cross-coupling or Wittig reactions using 5-(4-bromophenyl)- or 5-(4-bromomethylphenyl)-2,2′-bipyridines as the starting materials. For these compounds, a pronounced bathochromic shift was observed in both absorption and emission spectra compared to previously reported 5-phenyl-2,2′-bipyridine. For the one of the products, adsorption and fluorescent titrations were fulfilled, fluorescent response on the addition of metal cations was examined.



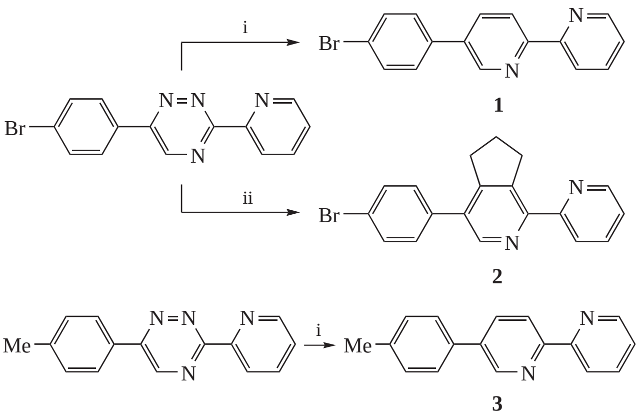
R^1 = Ph, PhC≡C, 5-dodecylthiophen-2-yl, *etc.*
R^2 = H, $R^2 + R^2 = (CH_2)_3$

Improved photophysical properties,
fluorescence response upon Zn^{2+} addition

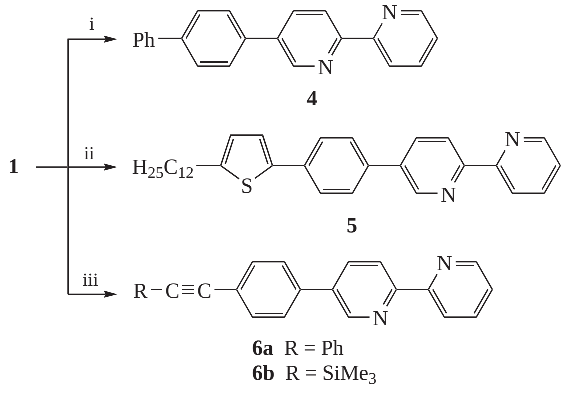
Recently, 2,2′-bipyridines have been used as the most common ligands for the transition metal cations.[1] In addition, the photophysical properties of 2,2′-bipyridines and their metal complexes became an object of a wide practical and theoretical interest.[2] The photophysical properties of 2,2′-bipyridine are very poor, since its emission and absorption maxima are located in short-wavelength region. To improve these properties, introduction of (hetero)aromatic substituents, especially those possessing the more conjugated aromatic systems, into the 2,2′-bipyridine core is needed. Previously, introduction of π-extended substituents (in particular, aromatic,[3,4] arylethynyl,[5] or arylvinyl[6] substituents) into the 2,2’-bipyridine core really caused pronounced bathochromic shift in both absorption and emission maxima. 2,2′-Bipyridines with an extended fluorophore system are used as chromophores for phosphorescent labels,[7] as chemosensors for the determination of metal cations,[8] as components for dye-sensitized solar cells,[9] as well as building blocks for some macroheterocycles.[10]

In our previous studies,[4,11] we reported on the improved photophysical properties of several 5-aryl-2,2′-bipyridines. Note that introduction of aromatic substituents into the β-position of the 2,2′-bipyridine ligand has no significant influence on its coordination properties. Herein, we consider the possibility for the extra tuning of photophysical properties of 2,2′-bipyridines by introducing various π-extended substituents into the β-position of 2,2′-bypyridine core.

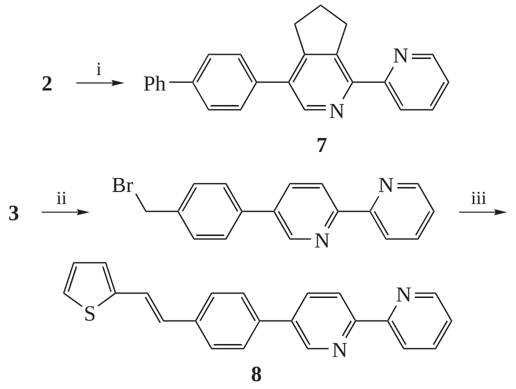
For the synthesis of starting 5-aryl-2,2′-bipyridines **1–3**, the advantageous previously reported[12–15] ‘1,2,4-triazine’ approach was applied (Scheme 1). The further transformation of substrates **1–3** is outlined in Schemes 2 and 3. To obtain compounds **4–7**, Suzuki, Stille or Sonogashira cross-coupling was used. Highly-



Scheme 1 *Reagents and conditions*: i, 2,5-norbornadiene, *o*-xylene, 143 °C, 24 h; ii, 1-morpholinocyclopentene, neat, 200 °C, 3 h, then MeCN, 20 °C, 1 h.



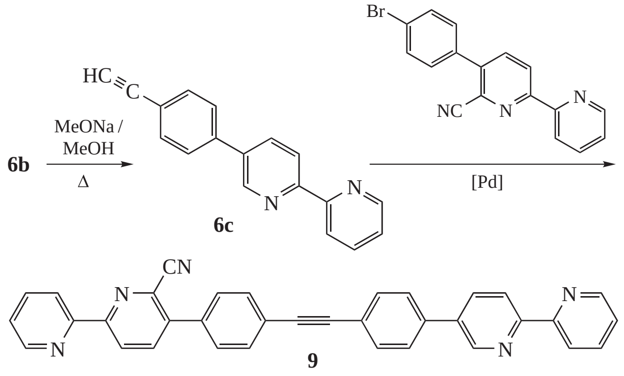
Scheme 2 *Reagents and conditions*: i, $PhB(OH)_2$, K_2CO_3, $PdCl_2(PPh_3)_2$, PPh_3, toluene–water, reflux, 8 h; ii, 2-tributylstannyl-5-dodecylthiophene, $Pd(PPh_3)_4$, DMF–THF (5 : 1), 100 °C, 2 h; iii, RC≡CH, $PdCl_2(PPh_3)_2$, PPh_3, CuI, LiBr, piperidine–THF (1 : 1), 80 °C, 7 h.



Scheme 3 *Reagents and conditions*: i, PhB(OH)$_2$, K$_2$CO$_3$, PdCl$_2$(PPh$_3$)$_2$, PPh$_3$, toluene–water, reflux, 20 h; ii, NBS, Bz$_2$O$_2$, CCl$_4$, reflux, 8 h; iii, PPh$_3$, benzene, reflux, 1 h, then thiophene-2-carbaldehyde, Bu^{t}OK, THF, 20 °C, 1 h.

conjugated compound **8** was prepared *via* the Wittig olefination at the key stage.

Compound **6b** bearing trimethylsilylethynyl group was used to achieve the greater expanded conjugation of the chromophore (Scheme 4). The base-catalyzed removal of trimethylsilyl group led to acetylene **6c**, whose Sonogashira cross-coupling with 5-(4-bromophenyl)-6-cyano-2,2′-bipyridine afforded the ditopic ligand **9**.



Scheme 4

The structure of products **4**–**9** was confirmed by the ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. In all the cases, a significant shift of the signals of protons of the C5-substituent in the 2,2′-bipyridine core as compared to the starting bipyridines of types **1**, **2** was detected. For example, in case of the Wittig reaction product **8**, the appearance of signals of two characteristic alkene protons as doublets with *J* 15.5 Hz (*trans*-configuration) as well as the characteristic signals of protons for the thiophene ring was observed. The ditopic ligand **9** is represented by the double set of the signals of 2,2′-bipyridine protons.

Table 1 Photophysical properties of 5-aryl-2,2′-bipyridines.

Compound	In MeCN			Φ^a	In MeCN with excess Zn(ClO$_4$)$_2$	
	λ_{abs}/nm	ε/dm^3 mol^{-1} cm^{-1}	λ_{em}/nm		λ_{abs}/nm	λ_{em}/nm
4	310	145600	380	0.86	334	473
5	337	160400	407	0.46	373	521
6a	335	202800	392	0.96	357	442
6c	308	146900	365	0.43	331	392
7	303	141000	371	0.36	324	470
8	352	90800	432	0.32	377	524
9	323	247000	373	0.76	346	442
Ph-bpy^b	298	71000	357	0.032	322	378

^{a}Fluorescence quantum yields were measured using anthracene as the standard (Φ = 0.27 in EtOH).[17] ^{b}5-Phenyl-2,2′-bipyridine.[4]

The comparison of the absorption spectra of 5-phenyl-2,2′-bipyridine (Ph-bpy) with new ligands (Table 1) clearly confirms that the increase in the conjugation of the 2,2′-bipyridine ligand causes the bathochromic shift of the absorption maxima along with the increase in the molar absorption coefficient. Most of bipyridines **4**–**9** demonstrated the bright fluorescence with quantum yields of 32–96%. The highest quantum yield value was observed for the compound **6a**, while the largest bathochromic shifts for both the absorption and emission maxima were revealed for compound **8**.

It was reported previously[4,5,16] that in organic solutions aryl-substituted 2,2′-bipyridines show a strong fluorescent response upon the addition of Zn^{2+} cations. Similarly, compounds **4**–**9** exhibited a pronounced fluorescence response on addition of Zn(ClO$_4$)$_2$ in acetonitrile solutions, therefore they can be used as indicators for Zn^{2+} cations. In all cases, the bathochromic shift of the emission maxima of compounds **4**–**9** was observed in the presence of Zn(ClO$_4$)$_2$. The maximum value of this shift was detected for (5-dodecylthienyl-2-yl)-containing 2,2′-pyridine **5** (see Table 1). Emission spectra of compounds **4**–**9** are presented in Figure 1.

For the most representative compound **4**, the absorption and fluorescence titrations by the solution of Zn(ClO$_4$)$_2$ in acetonitrile have been carried out, and the enhancement of the intensity of the fluorescence maxima for the resulting complex compared to the starting ligand was observed. A linear character of the dependence between the concentration of the added Zn(ClO$_4$)$_2$ and the intensity of the fluorescence of the proposed complex **4**·Zn^{2+} was revealed in the 0–0.6 molar equivalent range for both cases (Figure 2) (for the full set of absorption and fluorescence spectra, see Figures S1, S2 in Online Supplementary Materials).

Additionally, the fluorescence response of ligand **4** was studied towards other metal cations in acetonitrile. Thus, addition of

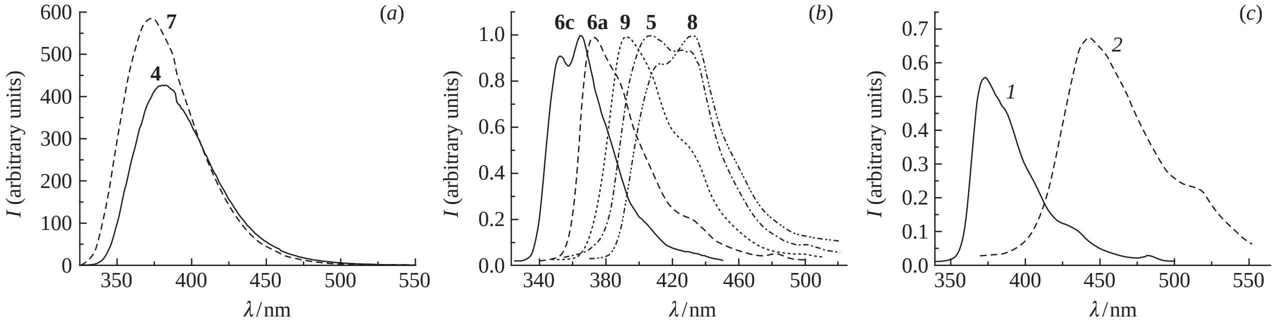


Figure 1 Fluorescence spectra in MeCN solution at room temperature (*a*), (*b*) compounds **4**–**9**, (*c*) compound **6b** (*1*) before and (*2*) after addition of excess Zn(ClO$_4$)$_2$.

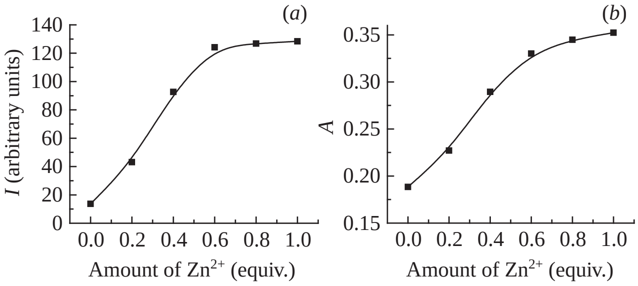


Figure 2 (*a*) Fluorescence (at 473 nm) and (*b*) absorption (at 333 nm) of **4** *vs*. amount of added Zn^{2+} (molar ratio plots).

$HgCl_2$ caused only slight quenching of the fluorescence intensity with no shifting of the fluorescence maxima, and the following addition of $Zn(ClO_4)_2$ led to the characteristic bathochromic shift in the fluorescence spectra of the resulting complex (Figure S3). The addition of CdI_2 caused bathochromic shift of the emission maxima, and the following addition of $Zn(ClO_4)_2$ did not affect the fluorescence spectra of the resulting complex (Figure S4). Finally, addition of $Cu(OAc)_2$ led to the dramatic quenching of the fluorescence intensity of the ligand **4** both in the presence and in the absence of $Zn(ClO_4)_2$ (Figure S5).

For compound **4**, no solvatochromism was found, fluorescence maxima in MeCN, MeOH and toluene were located at 381, 379 and 377 nm, respectively (Figure S6).

In summary, we have proposed straightforward and convenient way to customize the photophysical properties of 5-aryl-2,2′-bipyridine *via* further expanding its conjugation by means of cross-coupling and the Wittig reactions involving the aromatic substituent in the β-position of the 2,2′-bipyridine core. In all of the new ligands, a pronounced bathochromic shift of both the absorption and emission spectra was observed as compared to ‘naked’ 5-phenyl-2,2′-bipyridine. All new 2,2′-bipyridines demonstrated fluorescent response on the addition of zinc perchlorate. Compound **4**, whose adsorption and fluorescent titrations were fulfilled and fluorescent response on the addition of metal cations was studied, does not exhibit solvatochromism.

This work was supported by the Russian Science Foundation (grant no. 15-13-10033).

The article is dedicated to the memory of Academician Nikolay S. Zefirov (1935–2017).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.11.021.

References

1 (*a*) A. von Zelewsky, *Stereochemistry of Coordination Compounds*, Wiley, Chichester, 1996; (*b*) *Comprehensive Supramolecular Chemistry*, eds. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Voegtle, J.-M. Lehn, J.-P. Sauvage and M. W. Hosseini, Pergamon, Oxford, 1996, vol. 9; (*c*) C. Kaes, A. Katz and M. W. Hosseini, *Chem. Rev*., 2000, **100**, 3553; (*d*) R. D. Hancock, *Chem. Soc. Rev*., 2013, **42**, 1500; (*e*) I. F. Sakhapov, Z. N. Gafurov, V. M. Babaev, I. Kh. Rizvanov, A. B. Dobrynin, D. B. Krivolapov, Kh. R. Khayarov, O. G. Sinyashin and D. G. Yakhvarov, *Mendeleev Commun*., 2016, **26**, 131.

2 (*a*) S. E. Angell, Y. Zhang, C. W. Rogers, M. O. Wolf and W. E. Jones, Jr., *Inorg. Chem*., 2005, **44**, 7377; (*b*) J.-C. G. Bünzli, L. J. Charbonnière and R. F. Ziessel, *J. Chem. Soc., Dalton Trans*., 2000, 1917; (*c*) J.-L. Chen, G.-P. Gao, B.-S. Di, Y.-S. Luo, X.-H. Zeng, L. Qiu, L.-H. He, S.-J. Liu and H.-R. Wen, *J. Coord. Chem*., 2016, **69**, 2908; (*d*) M. Kovács, K. L. Ronayne, W. R. Browne, W. Henry, J. G. Vos, J. J. McGarvey and A. Horváth, *Photochem. Photobiol. Sci*., 2007, **6**, 444.

3 (*a*) J. C. Loren and J. S. Siegel, *Angew. Chem. Int. Ed*., 2001, **40**, 754; (*b*) F. Xiong, S.-Q. Wang, L.-M. He, S.-Y. Li, Q. Gan, G.-Q. Zhang, Y. Li and G.-Q. Yang, *Chin. J. Chem*., 2005, **23**, 811.

4 V. N. Kozhevnikov, O. V. Shabunina, D. S. Kopchuk, M. M. Ustinova, B. König and D. N. Kozhevnikov, *Tetrahedron*, 2008, **64**, 8963.

5 H. S. Joshi, R. Jamshidi and Y. Tor, *Angew. Chem. Int. Ed*., 1999, **38**, 2722.

6 (*a*) A. H. Younes, L. Zhang, R. J. Clark and L. Zhu, *J. Org. Chem*., 2009, **74**, 8761; (*b*) A. Ajayaghosh, P. Carol and S. Sreejith, *J. Am. Chem. Soc*., 2005, **127**, 14962.

7 A. M. Prokhorov, V. N. Kozhevnikov, D. S. Kopchuk, H. Bernard, N. Le Bris, R. Tripier, H. Handel, B. König and D. N. Kozhevnikov, *Tetrahedron*, 2011, **67**, 597.

8 (*a*) D. S. Kopchuk, A. M. Prokhorov, P. A. Slepukhin and D. N. Kozhevnikov, *Tetrahedron Lett*., 2012, **53**, 6265; (*b*) V. N. Kozhevnikov, O. V. Shabunina, A. R. Sharifullina, V. L. Rusinov and O. N. Chupakhin and B. König, *Mendeleev Commun*., 2005, **15**, 8.

9 F.-R. Dai, W.-J. Wu, Q.-W. Wang, H. Tian and W.-Y. Wong, *Dalton Trans*., 2011, **40**, 2314.

10 (*a*) J. R. Nitschke, S. Zürcher and T. Don Tilley, *J. Am. Chem. Soc*., 2000, **122**, 10345; (*b*) J. Sakamoto and A. D. Schlüter, *Eur. J. Org. Chem*., 2007, 2700.

11 (*a*) V. N. Kozhevnikov, D. N. Kozhevnikov, T. V. Nikitina, V. L. Rusinov, O. N. Chupakhin, M. Zabel and B. König, *J. Org. Chem*., 2003, **68**, 2882; (*b*) D. N. Kozhevnikov, O. V. Shabunina, D. S. Kopchuk, P. A. Slepukhin and V. N. Kozhevnikov, *Tetrahedron Lett*., 2006, **47**, 7025.

12 (*a*) G. R. Pabst, O. C. Pfüller and J. Sauer, *Tetrahedron*, 1999, **55**, 8045; (*b*) A. Rykowski, D. Branowska and J. Kielak, *Tetrahedron Lett*., 2000, **41**, 3657; (*c*) A. M. Prokhorov and D. N. Kozhevnikov, *Chem. Heterocycl. Compd*., 2012, **48**, 1153 (*Khim. Geterotsikl. Soedin*., 2012, **48**, 1237); (*d*) I. S. Kovalev, D. S. Kopchuk, A. F. Khasanov, G. V. Zyryanov, V. L. Rusinov and O. N. Chupakhin, *Mendeleev Commun*., 2014, **24**, 117; (*e*) A. F. Khasanov, D. S. Kopchuk, I. S. Kovalev, O. S. Taniya, G. V. Zyryanov, V. L. Rusinov and O. N. Chupakhin, *Mendeleev Commun*., 2015, **25**, 332.

13 (*a*) A. M. d’A. Rocha Gonsalves, T. M. V. D. Pinho e Melo and T. L. Gilchrist, *Tetrahedron*, 1992, **48**, 6821; (*b*) D. S. Kopchuk, I. L. Nikonov, G. V. Zyryanov, I. S. Kovalev, V. L. Rusinov and O. N. Chupakhin, *Chem. Heterocycl. Compd*., 2014, **50**, 907 (*Khim. Geterotsikl. Soedin*., 2014, **50**, 983).

14 (*a*) D. S. Kopchuk, A. F. Khasanov, I. S. Kovalev, G. A. Kim, I. L. Nikonov, G. V. Zyryanov, V. L. Rusinov and O. N. Chupakhin, *Chem. Heterocycl. Compd*., 2014, **50**, 864 (*Khim. Geterotsikl. Soedin*., 2014, **50**, 936); (*b*) J. Ławecka, E. Olender, P. Piszcz and A. Rykowski, *Tetrahedron Lett*., 2008, **49**, 723.

15 (*a*) A. P. Krinochkin, D. S. Kopchuk and D. N. Kozhevnikov, *Polyhedron*, 2015, **102**, 556; (*b*) D. S. Kopchuk, A. P. Krinochkin, D. N. Kozhevnikov and P. A. Slepukhin, *Polyhedron*, 2016, **118**, 30.

16 (*a*) S. Pawar, M. Akula, S. Labala, V. V. K. Venuganti, A. Bhattacharya and A. Nag, *ChemPlusChem*, 2016, **81**, 1339; (*b*) Z. Xu, J. Yoon and D. R. Spring, *Chem. Soc. Rev*., 2010, **39**, 1996; (*c*) C. Núñez, S. M. Santos, E. Oliveira, H. M. Santos, J. L. Capelo and C. Lodeiro, *ChemistryOpen*, 2014, **3**, 190.

17 W. R. Dawson and M. W. Windsor, *J. Phys. Chem*., 1968, **72**, 3251.

Received: 10th March 2017; Com. 17/5197