

1 **Synthesis and photophysics of new unsymmetrically substituted 5,5'-diaryl-2,2'-**
 2 **bypiridine-based “push-pull” fluorophores**

3 Ekaterina S. Starnovskaya,^a Dmitry S. Kopchuk,^{a,b} Albert F. Khasanov,^{a,b} Olga S. Tanya,^a
 4 Sougata Santra*,^a Kousik Giri,^c Matiur Rahman,^a Igor S. Kovalev,^a Grigory V. Zyryanov,^{a,b} Adinath
 5 Majee,^d and Valery N. Charushin^{a,b}

6 ^a Department of Organic and Biomolecular Chemistry, Chemical Engineering Institute, Ural Federal
 7 University, 19 Mira Str., Yekaterinburg, K-2, 620002, Russian Federation.

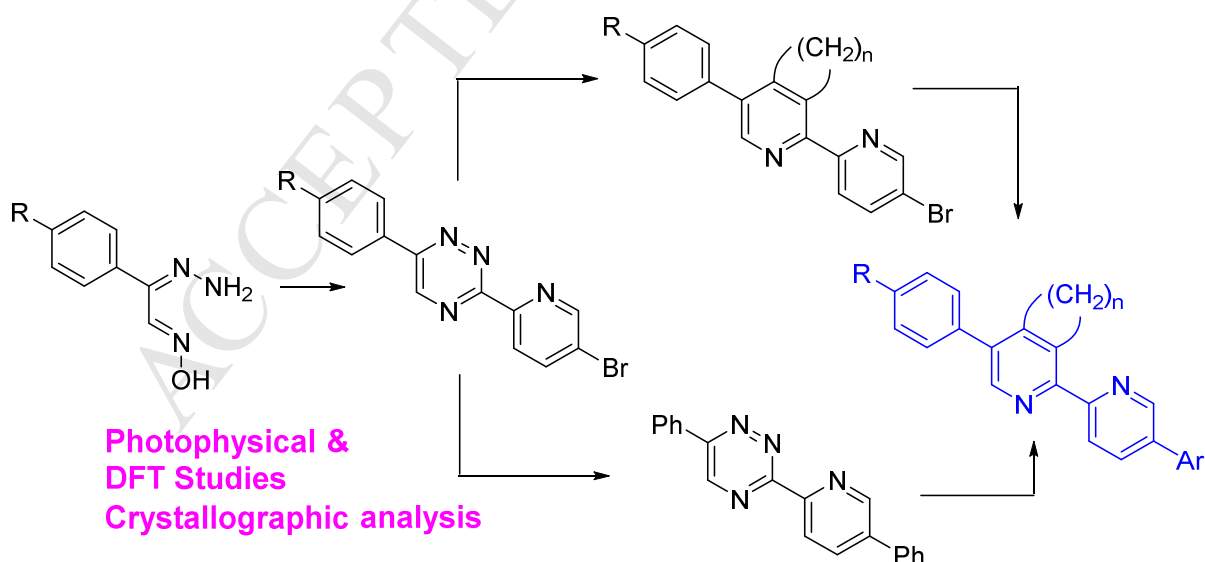
8 Email: sougatasantra85@gmail.com; ssantra@urfu.ru

9 ^b I. Ya. Postovskiy Institute of Organic Synthesis, Ural Division of the Russian Academy of
 10 Sciences, 22 S. Kovalevskoy Str., Yekaterinburg, 620219, Russian Federation

11 ^c Department of Computational Sciences, Central University of Punjab, City Campus, Mansa Road,
 12 Bathinda-151001, India

13 ^d Department of Chemistry, Visva-Bharati (A Central University) Santiniketan-731235, India

14



1 **Abstract:** New unsymmetrically substituted 5,5'-diaryl-2,2'-bipyridine “push-pull” fluorophores
2 were prepared in good yields *via* the “1,2,4-triazine method”/Suzuki coupling reaction sequence.
3 The obtained fluorophores contain the “push-pull” system with donor and acceptor moieties
4 arranged in a D- π -A- π -D fashion, and that provides both the prospective photophysical properties
5 and unique solvatochromic effects for the most representative compounds.

6 **Keywords:** 5,5'-diaryl-2,2'-bipyridine; “1,2,4-triazine method”; Suzuki cross-coupling; “push-pull”
7 fluorophores; photophysical studies; solvatochromism

8 **1. Introduction**

9 Currently 2,2'-bipyridines are the most commonly used ligands for both early and late
10 transition metal cations [1]. The photophysical properties of “naked” (unsubstituted) 2,2'-bipyridines
11 are very poor for the possible practical applications; therefore, the introduction of aromatic
12 substituents into the 2,2'-bipyridine moiety in many cases serves as a convenient tool for fine tuning
13 the photophysical properties, in particular, for adjusting the bathochromic shift of the absorption and
14 emission maxima [2-5]. Among aryl-substituted 2,2'-bipyridines, 5,5'-diaryl-2,2'-bipyridines hold
15 the specific place as in this case introduction of two different aromatic substituents can be used to
16 construct “push-pull” fluorophores of D- π -A types (especially donor (D) and acceptor (A) ones), [6],
17 similar to 5-arylvinylene-2,2'-bipyridine-based “push-pull” dyes [7] and/or Zn(II) indicators [7].
18 The last one requires the absence of substituents at the α -position of the 2,2'-bipyridine core to
19 provide the efficient chelation of Zn(II) and other metal cations [8]. Additionally, 5,5'-diaryl-2,2'-
20 bipyridines are applied as organic components of electroluminescent devices [9] and dye-sensitized
21 solar cells [9-13] and some of their metal complexes are used as catalysts [14].

22 Synthesis of 5,5'-diaryl-2,2'-bipyridines is usually performed by using various combinations
23 of cross-coupling reactions, starting from either 5,5'-dibromo-2,2'-bipyridine [15], or 2-

1 bromopyridine derivatives [16]. And rarely some other synthetic approaches have been proposed,
2 for example, cobalt-catalyzed [2+2+2] cycloaddition reactions of nitriles and α,ω -diynes [17] or
3 dimerization of 3-phenylpyridine in the presence of Ni(II) catalyst [18]. Additionally, some aryl
4 anneleted derivatives of 5,5'-diaryl-2,2'-bipyridines, such as 1,10-phenanthrolines, were obtained
5 from the heterocyclization of the phenanthroline moiety [19]. It should also be noted that most of the
6 literature references are devoted to the formation of symmetrically functionalized 5,5'-diaryl-2,2'-
7 bipyridines. Only in very few cases some unsymmetrically substituted 5,5'-diaryl-2,2'-bipyridines or
8 their anneleted analogues were obtained from consecutive cross-coupling of two bromine atoms in
9 the corresponding positions of 1,10-phenanthroline [20] or 2,2'-bipyridine [21]. Previously we
10 reported [22] a synthetic approach to such compounds *via* the "1,2,4-triazine" methodology, namely,
11 by means of sequential construction of two 1,2,4-triazine rings and followed by converting them
12 into pyridine ones. The main disadvantage of this method is a relatively large number of reaction
13 steps for obtaining the desired product.

14 In this manuscript we wish to report an alternative approach for the synthesis of
15 unsymmetrically substituted 5,5'-diaryl-2,2'-bipyridine fluorophores by using the combination of
16 two different methodologies: "1,2,4-triazine" methodology and followed by cross-coupling
17 reactions. To the best of our knowledge such combination was reported only in very few cases for
18 the preparation of substituted 2,2'-bipyridines and their analogs [23].

19 **2. Materials and methods**

20 *2.1 Chemicals and methods*

21 ^1H NMR spectra were determined on a Bruker Avance-400 spectrometer, 298 K, digital resolution \pm
22 0.01 ppm. Chemical shifts are expressed in parts per million (δ) and are referenced to
23 tetramethylsilane (TMS) as internal standard and the signals were reported as s (singlet), d (doublet),

1 t (triplet), m (multiplet) and coupling constants J were given in Hz. TLC was done on silica gel
2 coated glass slide (Merck, Silica gel G for TLC). Silica gel (60–120 mesh, SRL, India) was used for
3 column chromatography. Melting points were measured on the instrument Boetius. Mass-spectra
4 were recorded on MicroTOF-Q II (Bruker Daltonics), electrospray as a method of ionization.
5 Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 elemental analyzer. All
6 solvents were dried and distilled before use. Commercially available substrates were freshly distilled
7 before the reaction. Solvents, reagents and chemicals were purchased from Aldrich, Fluka, Merck,
8 SRL, Spectrochem and Process Chemicals. All reactions involving moisture sensitive reactants were
9 executed using oven dried glassware. Fluorescence spectra were measured on a Horiba-Fluoromax-4
10 spectrofluorometer. UV/Vis absorption spectra were recorded on a Shimadzu UV-2550 UV-Vis
11 spectrometer.

12 2.2 Synthesis of the compounds

13 2.2.1 Typical procedure for the synthesis of hydrazones 2

14 Corresponding acetophenone (0.5 mol) was added to the solution prepared by dissolving Na (11.5 g)
15 in EtOH (200 mL) at 10 °C. *Iso*-propylnitrite was added after 2 min, and the resulting mixture was
16 stirred at 10–15 °C for 2 h and kept at room temperature for overnight. The obtained precipitate of
17 the sodium salt of *iso*-nitrosoacetophenone was filtered off, dried in vacuo, and dissolved in water
18 (100–200 mL) at room temperature. Acetic acid (21 mL, 0.35 mol) was added to the solution, the
19 resulting mixture was cooled by adding of ice (50 g), thus the obtained crystals of the *iso*-
20 nitrosoacetophenone were filtered off, and dried under reduced pressure. The latter was dissolved in
21 a mixture of EtOH (100 mL) and hydrazine hydrate (25 mL, 0.5 mol) at 40–50 °C and the mixture
22 was kept for 1 h at room temperature. Water (300–500 mL) was added, obtained crystals were
23 filtered off and dried. The crude hydrazone was used directly in the next step.

24

1 2.2.2 General method for the synthesis of 1,2,4-triazines **3**

2 Corresponding hydrazone of isonitrosoacetophenone (**2**, 3 mmol) was dissolved in ethanol (25 mL),
3 the solution of 5-bromopicolinaldehyde (**1**, 555 mg, 3 mmol) in ethanol (25 mL) was added and the
4 resulting mixture was stored at room temperature for 10 h. Then ethanol was removed under
5 reduced pressure. Glacial acetic acid (25 mL) was added to the residue and the resulting mixture was
6 refluxed for 40 min. Solvent was removed under reduced pressure, the residue was triturated with
7 ethanol, the obtained precipitate was filtered off. The triazines **3** were used in the next step without
8 additional purification.

9 2.2.3 Typical procedure for the synthesis of 5-bromo-5'-phenyl-2,2'-bipyridine (**4a**)

10 Triazine **3a** (400 mg, 1.28 mmol) was suspended in *o*-xylene (40 mL), 2,5-norbornadiene (0.52 mL,
11 5.11 mmol) and the resulting mixture was refluxed for 9 h, then 2,5-norbornadiene (0.52 mL, 5.11
12 mmol) was added and the resulting mixture was refluxed for additional 9 h. Solvent was removed
13 under reduced pressure, the residue was purified by flash chromatography (DCM as eluent). The
14 analytical sample was obtained by recrystallization (ethanol).

15 2.2.4 General method for the synthesis of 1-(5-bromopyridin-2-yl)-4-aryl-6,7-dihydro-5H-
16 cyclopenta[*c*]pyridines **4b,c**

17 A mixture of corresponding triazine **3** (2 mmol) and 1-morpholinocyclopentene (1.6 mL, 10 mmol)
18 was stirred at 200 °C under argon atmosphere for 2 h. Then an additional portion of 1-
19 morpholinocyclopentene (0.8 mL, 5 mmol) was added and the resulting mixture was stirred under
20 the same conditions for 1 h. Products were then purified by column chromatography (DCM as
21 eluent).

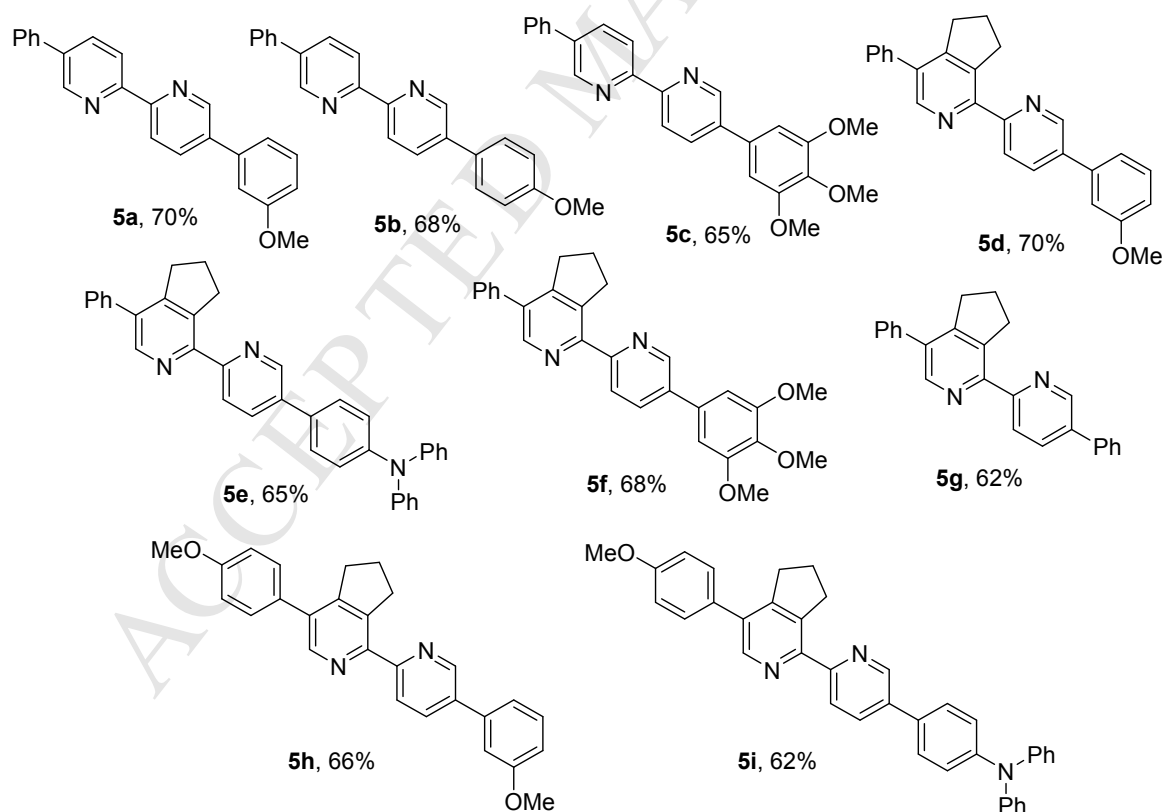
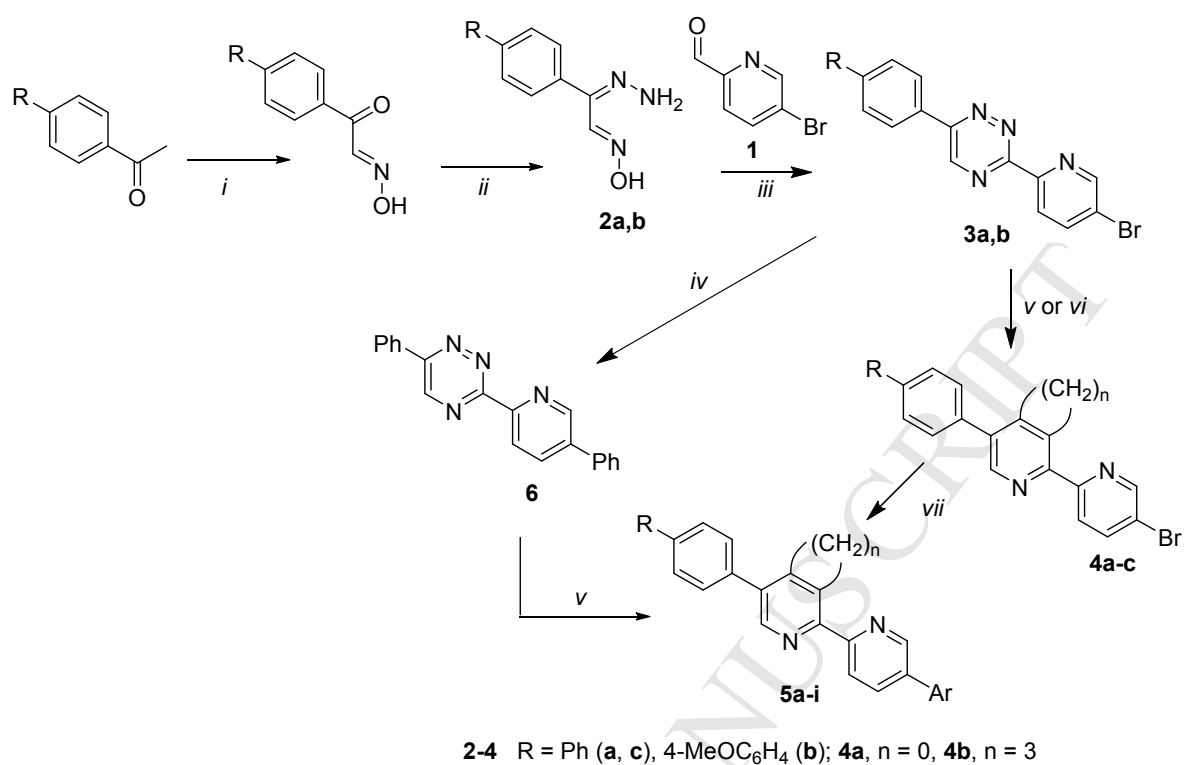
22 2.2.5 General method for the synthesis of 5,5'-diaryl-2,2'-bipyridines **5**

1 The corresponding 5-bromobipyridine (0.3 mmol) was dissolved in toluene (15 mL). The
2 corresponding boronic acid (0.33 mmol), bis(triphenylphosphine)palladium dichloride (6.3 mg,
3 0.009 mmol), triphenylphosphine (3.9 mg, 0.015 mmol), aqueous solution of K₂CO₃ (415 mg, 3
4 mmol, 15 mL) and ethanol (10 mL) were added. The resulting mixture was stirred under reflux
5 under argon atmosphere for 15 h. The organic phase was washed with aqueous solutions of KOH
6 and ammonium chloride and dried with anhydrous sodium sulfate. The solvents was removed under
7 removed pressure, the residue was triturated by ethanol. The obtained precipitate was filtered off,
8 washed with ethanol and dried. The analytical samples were obtained by recrystallization (ethanol).

9 **3. Results and discussion**

10 *3.1 Synthesis of the fluorophores 5a-i*

11 Commercially available 5-bromopyridine-2-carbaldehyde **1** was used as a starting
12 compound. Thus, following the slightly modified procedure [2] the condensation reaction between **1**
13 and isoazoanitroso-acetophenone hydrazones **2** followed by aromatization in boiling acetic acid
14 afforded 1,2,4-triazines **3**. A further *aza*-Diels-Alder reaction between **3** and dienophiles, such as
15 2,5-norbornadiene and 1-morpholinocyclopentene, yielded 2,2'-bipyridines **4**. The further
16 functionalization was carried out by means of the Suzuki cross-coupling. As a result, compounds **5**
17 were obtained in good yields, including ones reported before [17] as well as some new derivatives,
18 including ones, which are hardly accessible by previously described approaches starting from the
19 corresponding acetophenone derivatives.



1

2 **Scheme 1.** Synthesis of 5,5'-diaryl-2,2'-bipyridines **5a-i**. Reagents and conditions: *i*) Na in ethanol,3 10 °C, *iso*-propyl nitrite, 2 h, then at rt, overnight, water/acetic acid; *ii*) EtOH, NH₂NH₂·H₂O, 40–50

1 °C, then water; *iii*) ethanol, rt, 10 h, then glacial acetic acid, reflux, 40 min; *iv*) phenylboronic acid,
2 Pd(PPh₃)₂Cl₂, PPh₃, Cs₂CO₃, toluene/ethanol/water (3:2:3), reflux, 25 h; *v*) 1-
3 morpholinocyclopentene, 200 °C, 3 h; *vii*) 2,5-norbornadiene, *o*-xylene, reflux, 18 h; *vii*)
4 corresponding arylboronic acid, Pd(PPh₃)₂Cl₂, PPh₃, K₂CO₃, toluene/ethanol/water (3:2:3), reflux,
5 15 h.

6 We have also tried an alternative approach, namely using the Suzuki reaction of the 1,2,4-
7 triazine **3** and followed by *aza*-Diels-Alder reaction. However, in this case the yields of the Suzuki
8 reaction depend on the nature of the base used. In particular, in the presence of potassium or sodium
9 carbonate, the reaction did not actually proceed, while the use of tetrabutylammonium hydroxide led
10 to afford mainly the bromo-free product, namely 3-(2-pyridyl)-6-phenyl-1,2,4-triazine based on the
11 spectral data [2]. Finally, 1,2,4-triazines **6** were obtained in the presence of cesium carbonate after
12 25 h. We also demonstrated the synthetic routes towards bipyridines **5g** with higher yield by means
13 of one-pot procedure, which includes the Suzuki cross-coupling and 1-morpholinocyclohexane-
14 mediated *aza*-Diels-Alder reaction sequence.

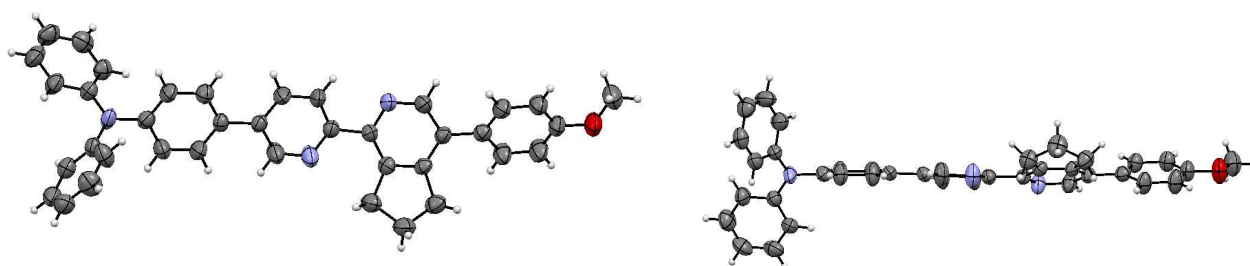
15 The structures of the obtained compounds were confirmed based on the ¹H- and ¹³C NMR
16 spectroscopy, mass spectrometry and elemental analysis. For one of the key compound, namely **5i**,
17 the single crystal X-ray diffraction studies were performed¹ (Fig. 1) [24].

¹ The XRD analysis for the single crystals of C₃₈H₃₁N₃O was accomplished on a Xcalibur 3 diffractometer on standard procedure (MoK irradiation, graphite monochromator, ω-scans with 1° step). The crystal was kept at 295(2) K during data collection. Using SHELXTL [25], the structure was solved with the XS structure solution program using by Direct Method and refined with the XL refinement package using Least Squares minimization. All non-hydrogen atoms were refined in anisotropic approximation; H-atoms were added in the calculated position and refined in isotropic

1 According to the XRD data, this compound is crystallized in the centrosymmetric space
2 group. The general view of the molecule is presented in the Fig. 1. The tetra(het)arene moiety is
3 non-planar with dihedral angle 37.4° between 4-MeOPh and pyridine rings. The main bond
4 distances and angles are typical for the conjugated π -system. The N-atom of the NAr_3 -group has sp^2 -
5 configuration. It can be noted that the C-N distances in the triphenylamino moiety increases from
6 1.391 \AA to 1.430 \AA with increasing dihedral angle between plane of N-atom and plane of arenes
7 (Fig. S1-S3, Supplementary Information). Additionally, according to Fig. S1 (Supplementary
8 Information) in the crystal the molecules of **5i** forms the “double-decker-like” *J*-aggregates in a
9 head-to-tail mode with a $\sim 3.8 \text{ \AA}$ distance between two nearest cyclopentan-annexed pyridine rings,
10 thus suggesting the strong π - π -interactions between them.

11 Based on the result of XRD studies it can be seen that in the fluorophore **5i** has a non-planar
12 structure with both 4-MeOPh and NPh_2 donor-moieties which are twisted with respect to 2,2'-
13 bipyridine acceptor moiety, and that possibly hampers the electronic conjugation in a whole donor-
14 π -acceptor system in a ground state. It may suggest that the photoexcitation of **5i** will cause the
15 excited-state relaxation *via* the rotation of the both 4-MeOPh and NPh_2 donor-moieties around the
16 single bonds.

approximation in the “riding” model. **Crystal Data.** $\text{C}_{38}\text{H}_{31}\text{N}_3\text{O}$, $M = 545.66$, monoclinic, space
group $\text{P2}_1/\text{c}$, $a = 16.783(2) \text{ \AA}$, $b = 10.0214(11) \text{ \AA}$, $c = 18.4238(15) \text{ \AA}$, $\beta = 113.928(11)^\circ$, $V =$
 $2832.4(5) \text{ \AA}^3$, $T = 295(2) \text{ K}$, $Z = 4$, $\mu(\text{Mo K}\alpha) = 0.077 \text{ mm}^{-1}$. On the angles $2.94 < \Theta < 26.38^\circ$ 15792
reflections were measured, 5687 unique ($R_{\text{int}} = 0.0529$) which were used in all calculations.
Completeness to $\Theta = 26.38^\circ$ 98.3 %. The final $R_1 = 0.0424$, $wR_2 = 0.0404$ [$I > 2\sigma(I)$], $R_1 = 0.1618$,
 $wR_2 = 0.0444$ (all data), $\text{GooF} = 0.993$. Largest diff. peak/hole 0.153 and $-0.150 \text{ e}\text{\AA}^{-3}$.

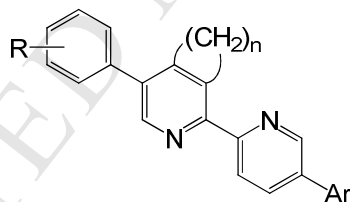


1 **Fig. 1.** Front view (left) and side view (right) of the single X-ray structure (ORTEP) of compound **5i**

2 *3.2 Photophysical studies of the obtained fluorophores*

3 Next aiming to study the influence of the structure of the fluorophores on their photophysical
 4 behavior we studied the photophysical properties of the new 5,5'-diaryl-2,2'-bipyridines as well as
 5 some previously reported ones. The results are collected in Table. 1 and the absorption and emission
 6 spectra are presented in Fig. 2.

7 **Table 1.** Photophysical properties of new bipyridines **5** and some previously reported analogues



8

#/Ref.	R	n	Ar	$\lambda_{\text{abs}}^{\text{a}}$, nm	$\lambda_{\text{em}}^{\text{b}}$, nm	Φ^{c} , %
[2]	H	0	H	298	357	3.2 ^d
5a	H	0	3-MeOC₆H₄	318	373	84
5b	H	0	4-MeOC₆H₄	224, 303, 370	521	31.6
[2]	H	0	COOMe	312	380	4.5 ^d
5c	H	0	3,4,5- tri(MeO)C₆H₂	323	470	94
5d	H	3	3-MeOC₆H₄	314	358sh, 370	21.7
5e	H	3	4-(Ph₂N)C₆H₄	274_{sh}, 299, 359	508	60

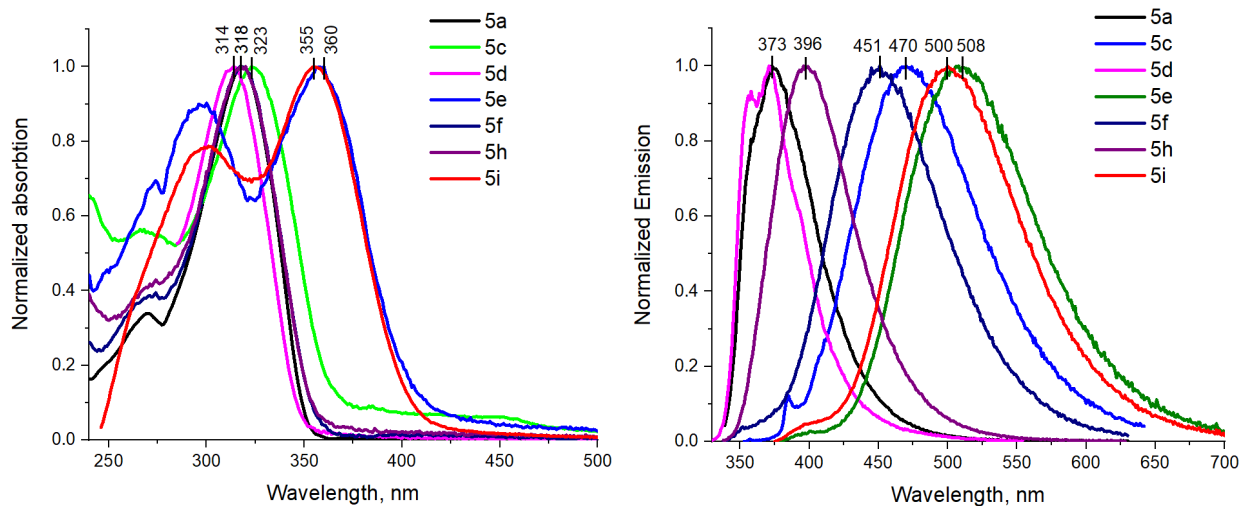
5f	H	3	3,4,5- tri(MeO)C₆H₂	318	451	89
5g	H	3	Ph	216, 251, 278, 340	422	62.7
[2]	4-MeO	0	H	309	399	89 ^d
[2]	4-MeO	0	COOMe	326	438, 510 _{sh.}	49 ^d
5h	4-MeO	3	3-MeOC₆H₄	319	396	95.6
5i	4-MeO	3	4-(Ph₂N)C₆H₄	301, 355	500	60.5
[17]	4-MeO	3	Ph	231, 289, 351	506	30.5
[26]	2,6-(Me) ₂ -4- MeOC ₆ H ₂	0	2,6-(Me) ₂ -4- MeOC ₆ H ₂	296	408	87
[19]	2,6-(Me) ₂ -4- MeOC ₆ H ₂	0	H	286	410	78

1

2 ^a Absorption maxima at room temperature; ^b fluorescence maxima at room temperature; ^c fluorescence
3 quantum yields were measured in degassed CH₃CN solution using quinine sulfate as standard [27]

4 Based on the collected data, the influence of the introduced functional groups on the
5 photophysical properties of new 2,2'-bipyridines was estimated. In particular, a hypsochromic shift
6 of the both absorption and emission maxima is observed when a 3-methoxyphenyl moiety is
7 introduced into the 2,2'-bipyridine core instead of a phenyl one. For example, for the compound **5d**,
8 a hypsochromic shift of the absorption maximum of 26 nm was observed compare to its Ph-
9 substituted analog, while the hypsochromic shift of the emission maximum of 29 nm was observed.
10 The only explanation of such behavior is the possible steric hindrances caused by the 3-OMe
11 substituent in the aromatic ring to prevent the excited-state relaxation *via* rotation, which leads to the
12 occurrence of the higher energy peaks in both the emission and absorption spectra [28]. Except the

1 compound **5d** high values of fluorescence quantum yields (up to 95.6%) were observed for all the
 2 bipyridines **5**.



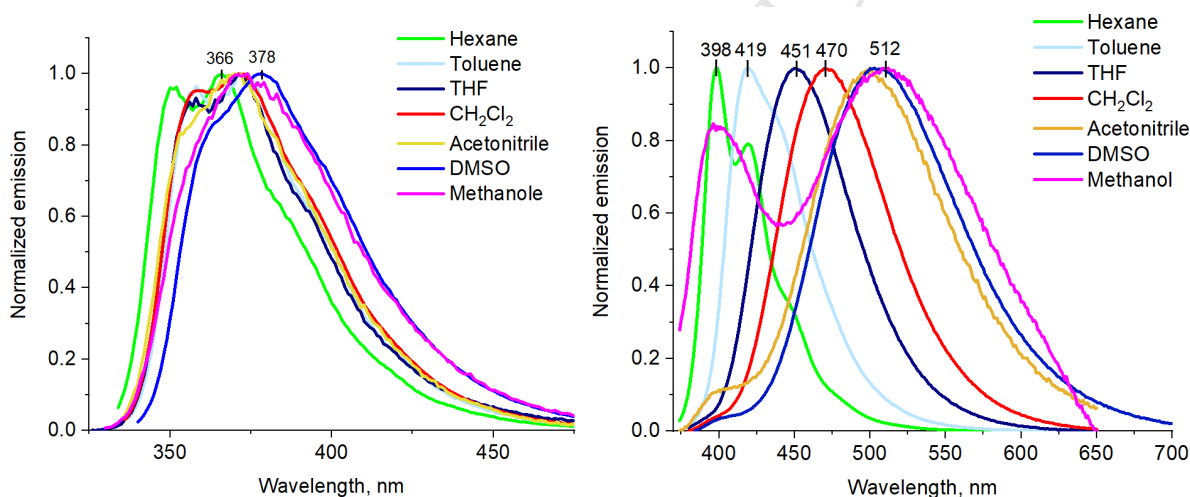
3

4 **Fig. 2.** Normalized absorption (left) and emission (right) spectra for the compounds **5a-i**

5 For the 3,4,5-trimethoxyphenyl substituted compound **5f** the introduction of extra OMe-
 6 moieties into the 5-aryl-substituent in the 2,2'-bipyridine core caused the bathochromic shift of the
 7 emission maxima by 29 nm compared to the 5-phenyl substituted 2,2'-bipyridine. For the non-
 8 annealed compound **5c** even higher value of 38 nm was observed. It should also be noted that both
 9 the compounds exhibited very high fluorescence quantum yield values of 89% (**5c**) and 94% (**5f**).

10 Even greater bathochromic shift was achieved upon the introduction of the most electron
 11 donating 4-diphenylamino moiety into the 5-aryl substituent of 2,2'-bipyridine. Both the 5'-Ph-
 12 substituted compound **5e** and 5'-(4-MeOPh)-substituted compound **5i** exhibited bathochromic shifts
 13 of the emission maxima from 500 to 508 nm, which is by 86 nm higher compared to the 5-phenyl
 14 substituted 2,2'-bipyridine, while the observed fluorescence quantum yields values were around
 15 60%, which is lower than the values observed for the 3,4,5-trimethoxyphenyl-substituted 2,2'-
 16 bipyridines. The lowering of the quantum yields could be explained by a strong charge transfer in
 17 chromophores **5e**, **5i** which leads to a fast nonradiative decay.

1 As it was mentioned above, substituted 2,2'-bipyridines are commonly used as “push-pull”
 2 fluorophores [7], photosynthesizers for the solar cells [10-13] and as components for NLO-devices
 3 [29]. In order to study the possible influence of the nature of the substituents in the 2,2'-bipyridine
 4 core of compounds **5** on their ability to serve as “push-pull” chromophores the photophysical
 5 properties in various solvents were investigated. According to the literature [7] the main feature of
 6 such compounds is a pronounced solvatochromism, which results from the dipole moment change
 7 during the photoexcitation-induced intramolecular charge transfer (ICT) between the electron-donor
 8 and electron-acceptor fragments of push-pull fluorophores in various solvents.



9

10 **Fig. 3.** Normalized emission spectra of compound **5d** (left) and **5i** (right) in solvents of various
 11 polarity

12 Therefore, as a next step we have investigated photophysical properties of two the most
 13 representative fluorophores, namely containing the 4-diphenylamino moiety compound **5i** and 3-
 14 methoxyphenyl-substituted compound **5d**. Based on the collected fluorescence spectra (Fig. 3) it can
 15 be seen that the fluorophore **5i** demonstrates a very efficient charge separation in the excited state
 16 which can be stabilized in the most polar solvent, namely methanol, and compare to hexane a strong
 17 bathochromic shift of 135 nm was observed. Additionally, in methanol the dual fluorescence is

1 observed with high energy band corresponding to localized excited (LE) state (398 nm) and a low
 2 energy band due to the ICT process (512 nm) (Fig. 3, right). Based on the X-ray data of the
 3 compound **5i** (Fig.1) the main reasons for the efficient ICT process is the planarity of the molecule
 4 due to its flat geometry. Compound **5d** demonstrates a very weak dependence on the polarity of the
 5 solvents used, and, thus charge separation is less efficient as compared to compound **5i**. Only in
 6 methanol a bathochromic shift of 20 nm (Fig. 3, left) was observed.

7 The UV/Vis spectra of compounds **5d**, **5f** and **5i** in various solvents demonstrated the lower
 8 sensitivity of ICT bands to the change in solvent polarity, thus suggesting the nonpolar nature of the
 9 ground states of compounds **5d**, **5f** and **5i** (Fig. S6-S8, Supplementary Information). This indicates
 10 that the primarily excited Franck–Condon (FC) state is not the fluorescence-emitting state. Thus, the
 11 absorption spectra of compounds **5d**, **5f** and **5i** (Fig. S6-S8, Supplementary Information) remain
 12 almost the same in all solvents, indicating that the dipole moment of the both molecules keeps
 13 unchanged during transition from ground state to FC state. In the fluorescence spectra the obvious
 14 bathochromic shift for the **5i** (Fig 3), in comparison to **5d**, with increasing the polarity of solvents
 15 indicates that the fluorescence state has larger dipole moment than the ground state, which again
 16 suggests that the fluorescence state is an intramolecular charge-transfer (ICT) state. Additionally,
 17 this suggests that there is a big change of the dipole moment of the molecule while changing from
 18 the primarily excited FC state to the radiative ICT state [30].

19 As a next step, similarly to our previous studies [31], we used a Lippert-Mataga equation
 20 [29–32] to calculate the difference between the ground and excited states of the electric dipole
 21 moments of fluorophores **5d** and **5i** (Eq. 1), depending on the Stokes shift of the fluorophore in the
 22 emission and absorption spectra.

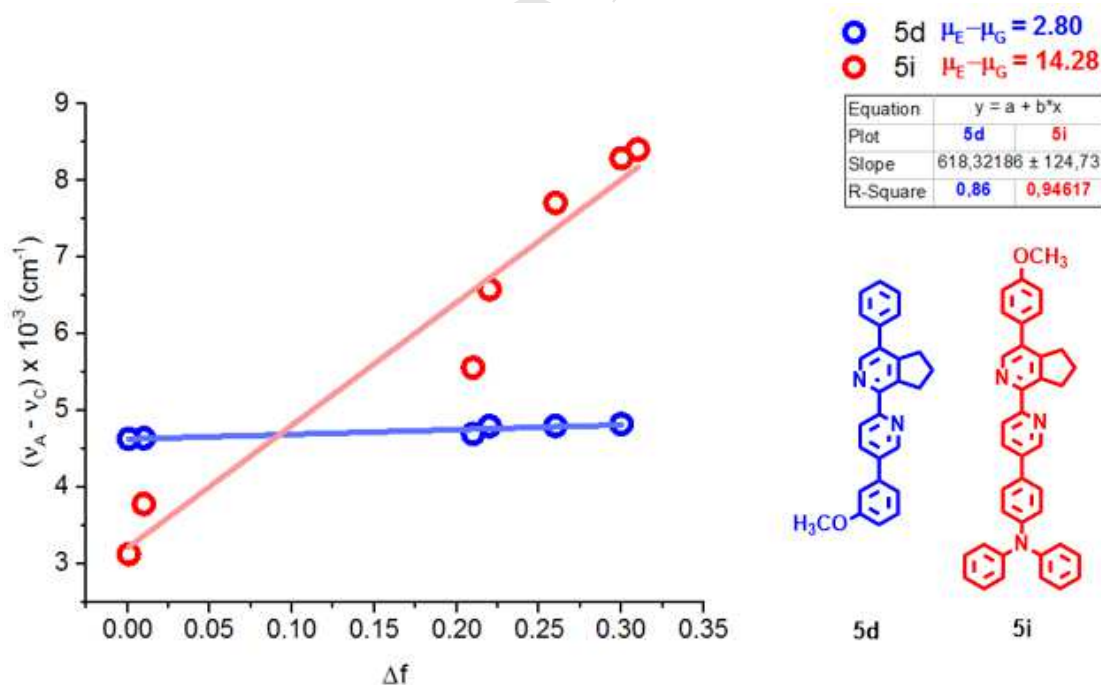
$$23 \quad \nu_A - \nu_F = \frac{2}{hc} \left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \frac{(\mu_E - \mu_G)^2}{a^3}$$

1 **Equation 1.** Lippert- Mataga equation; where ν_A and ν_F – the wavenumbers (cm^{-1}) of the absorption
 2 and emission, respectively; $h = 6.6256 \times 10^{-27}$ – the Planck's constant, $c = 2.9979 \times 10^{10}$ cm/s - the
 3 speed of light; a - the radius of the cavity in which the fluorophore resides; ε - Relative permittivity
 4 of the solvent; n - Refractive index of the solvent

5 The results of the calculations are represented in the Lippert–Mataga plot of fluorophores **5d**
 6 and **5i** in various solvents (Fig. 4). It can be seen that despite of the linearity of the plots the charge
 7 separation is more efficient for the compound **5i** and depends on the polarity of the solvents (the
 8 orientation polarizability Δf (Equation 2) of the solvent).

$$9 \quad \Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

10 **Equation 2.** The orientation polarizability of solvents; where ε = Relative permittivity of the
 11 solvent, n = Refractive index of the solvent



1 3.3 DFT Studies

2 For the better understanding the details of electronic transition of the present reported
3 chromophores, theoretical calculations were performed by using density functional theory (DFT) as
4 implemented in the Gaussian 09 suite of programs [36]. Systems were optimized using M06-2X/6-
5 31G(d) for geometries then single point calculations were carried out using HF/6-311+G(d,p) for
6 HOMO-LUMO gap or energies, all the calculations were in gas phase. Based on the both DFT
7 studies results (Table 2, Table S4-S5, Supplementary Information) and X-ray data (Fig. 1) it was
8 confirmed that for the most promising “push-pull” fluorophores (**5e** and **5i**), namely NPh₂-
9 substituted compounds, in a ground state the conjugation is hampered due to the rotation of the
10 NPh₂ moiety around the single bond. Most probably, upon the photoexcitation the excited-state
11 relaxation *via* rotation of the NPh₂ substituent occurs. According to HOMO-LUMO distribution
12 pictures (Table S5, Supplementary Information) for the fluorophores **5e** and **5i** in a gas phase the
13 HOMO mainly resides on the NPh₃ donor moieties in both molecules. Thus, the extent of electron
14 density transfer from HOMO to LUMO is very large, which is in agreement with its very strong ICT
15 process. For the other fluorophores such as **5d** and **5f** with weaker OMe donors (Table S5,
16 Supplementary Information), the HOMO is extended into the 2,2'-bipyridine core. Thus, the extent
17 of electron density transfer is less, resulting in a weaker ICT. Additionally, the calculated HOMO-
18 LUMO band gap value (Table 2) was the lowest for the fluorophores **5e** and **5i**, while the HOMO
19 energy values were the highest and resulting subsequent red-shifts for the both fluorophores in the
20 fluorescence maxima.

Table 2. HOMO-LUMO Energy levels for fluorophores **5a-5i** in a gas phase ^a

Fluorophores	HOMO energy, eV (a.u.)	LUMO energy, eV (a.u.)	Gap (eV)
5a	-7.80 (-0.28643)	1.43 (0.05268)	9.23

5b	-7.62 (-0.27981)	1.49 (0.05487)	9.11
5c	-7.75 (-0.28484)	1.40 (0.05146)	9.15
5d	-7.70 (-0.28374)	1.57 (0.05755)	9.29
5e	-7.09 (-0.26049)	1.51 (0.05559)	8.60
5f	-7.68 (-0.28208)	1.55 (0.05696)	9.23
5g	-7.74 (-0.28430)	1.54 (0.05662)	9.28
5h	-7.55 (-0.27754)	1.62 (0.05961)	9.17
5i	-7.06 (-0.25930)	1.52 (0.05600)	8.58

^a Systems were optimized using M06-2X/6-31G(d) for geometries then single point calculations were carried out using HF/6-311+G(d,p) for HOMO-LUMO gap or energies, all the calculations were in gas phase. 1 a.u. = 27.2116 eV.

1 **4. Conclusion**

2 In conclusion, an efficient synthetic approach towards 5,5'-diaryl-2,2'-bipyridine-based
 3 fluorophores was reported by the combination of the “1,2,4-triazine methodology” and the Suzuki
 4 cross-coupling reactions. The current approach makes it possible to obtain 2,2'-bipyridines,
 5 substituted with various aryl substituents, as well as with a cyclopentene moiety anneled to one of
 6 the pyridine rings. These 2,2'-bipyridines are extremely inaccessible by using the common synthetic
 7 approaches. The structure of the compound was confirmed, and the structure of one of the key
 8 products was confirmed based on the single crystal X-ray analysis. The photophysical studies of the
 9 present reported fluorophores were investigated and the influence of the nature of the aryl
 10 substituents in the 2,2'-bipyridine core on both the photophysical properties and on the
 11 intermolecular charge transfer was demonstrated.

12 **Acknowledgements**

1 This work was supported by the Russian Science Foundation (Grant # 16-43-02020) and the Council
2 for grants of the President of the Russian Federation (grant no. MK-644.2017.3). A. Majee
3 acknowledges financial support from the DST-RSF Major Research Project (Ref. No.
4 INT/RUS/RSF/P-08).

5 **Conflict of Interest**

6 The authors declare no conflict of interest.

7 **References**

- 8 [1] (a) von Zelewsky A. Stereochemistry of Coordination Compounds, Chichester: Wiley, 1996; (b)
9 Comprehensive Supramolecular Chemistry. Atwood JL, Davies JED, MacNicol DD, Voegtle F,
10 editors. Oxford: Pergamon; 1996, p.9, p.213; (c) Kaes C, Katz A, Hosseini MW. Bipyridine:
11 The most widely used ligand. A review of molecules comprising at least two 2,2'-bipyridine
12 units. Chem Rev 2000;100:3553-3590. (d) Hancock RD. The pyridyl group in ligand design for
13 selective metal ion complexation and sensing. Chem Soc Rev 2013;42:1500-1524.
- 14 [2] Kozhevnikov VN, Shabunina OV, Kopchuk DS, Ustinova MM, König B, Kozhevnikov DN.
15 Facile synthesis of 6-aryl-3-pyridyl-1,2,4-triazines as a key step toward highly fluorescent 5-
16 substituted bipyridines and their Zn(II) and Ru(II) complexes. Tetrahedron 2008;64:8963-8973.
- 17 [3] (a) Xiong F, Wang SQ, He LM, Li SY, Gan Q, Zhang GQ, Li Y, Yang GQ. Different
18 photophysical properties of aryl-bipyridine linked pyrene and anthracene. Chin J Chem
19 2005;23:811-815. (b) Younes AH, Zhang L, Clark RJ, Zhu L. Fluorescence of 5-arylvinyl-5'-
20 methyl-2,2'-bipyridyl ligands and their zinc complexes. J Org Chem 2009;74:8761-8772.
- 21 [4] Kopchuk DS, Chepchugov NV, Kim GA, Zyryanov GV, Kovalev IS, Rusinov VL, Chupakhin
22 ON. Preparation of 5,6'-diaryl-2,2'-bipyridines using a 1,2,4-triazine methodology. Russ Chem
23 Bull 2015;64:897-900.

- 1 [5] Harriman A. Photophysics of 2,2'-bipyridyl. *J Photochem* 1978;8:205-209.
- 2 [6] Sun Y, Wang S. Extending π -conjugation of triarylborons with a 2,2-bpy core: impact of
3 donor–acceptor geometry on luminescence, anion sensing, and metal ion binding. *Inorg Chem*
4 2010;49:4394–4404.
- 5 [7] Zhu L, Younes AH, Yuan Z, Clark RJ. 5-Arylvinylene-2,2'-bipyridyls: Bright “push–pull” dyes
6 as components in fluorescent indicators for zinc ions. *J Photochem Photobiol A: Chem*
7 2015;311:1–15.
- 8 [8] Constable EC, Housecroft CE, Neuburger M, Rösel PJ, Schaffner S. Diversification of ligand
9 families through ferriox–neocuproin metal-binding domain manipulation. *Dalton Trans*
10 2009;4918–4927.
- 11 [9] EP2241568A1.
- 12 [10] Dai FR, Wu WJ, Wang QW, Tian H, Wong WY. Heteroleptic ruthenium complexes containing
13 uncommon 5,5'-disubstituted-2,2'-bipyridine chromophores for dye-sensitized solar cells.
14 *Dalton Trans* 2011;40:2314–2323.
- 15 [11] Kalyanasundaram K. Photophysics, photochemistry and solar energy conversion with
16 tris(bipyridyl) ruthenium(II) and its analogues. *Coord Chem Rev* 1982;46:159–244.
- 17 [12] O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal
18 TiO₂ films. *Nature* 1991;353:737–740.
- 19 [13] Nazeeruddin MK, Kay A, Rodicio I, Humphry-Baker R, Muller E, Liska P, Vlachopoulos N,
20 Grätzel M. Conversion of light to electricity by cis-X₂Bis(2,2'-bipyridyl-4,4'-dicarboxylate)
21 ruthenium(II) charge-transfer sensitizers (X = Cl-, Br-, I-, CN-, and SCN-) on nanocrystalline
22 TiO₂ electrodes, *J Am Chem Soc* 1993;115:6382–6390.

- 1 [14] Zhang T, Manna K, Lin W. Metal-organic frameworks stabilize solution-inaccessible cobalt
2 catalysts for highly efficient broad-scope organic transformations. *J Am Chem Soc*
3 2016;138:3241–3249.
- 4 [15] (a) Nie HJ, Shao JY, Wu J, Yao J, Zhong YW. *Organometallics* 2012;31:6952-6959, (b) Briggs
5 BN, Durola F, McMillin DR, Sauvage JP. Luminescence studies of copper(I)-containing
6 [2]pseudorotaxanes. *Can J Chem* 2011; 89:98-103.
- 7 [16] (a) Ladouceur S, Fortin D, Zysman-Colman E. Role of substitution on the photophysical
8 properties of 5,5'-diaryl-2,2'-bipyridine (bpy*) in $[\text{Ir}(\text{ppy})_2(\text{bpy}^*)]\text{PF}_6$ complexes: a combined
9 experimental and theoretical study. *Inorg Chem* 2010;49:5625-5641. (b) Henze O, Lehmann U,
10 Schlueter AD. Synthesis of 5,5'-disubstituted 2,2'-bipyridines for modular chemistry. *Synthesis*
11 1999;683-687.
- 12 [17] (a) Goswami A, Ohtaki K, Kase K, Ito T, Okamoto S. Synthesis of substituted 2,2'-bipyridines
13 and 2,2':6',2''-terpyridines by cobalt-catalyzed cycloaddition reactions of nitriles and α,ω -diynes
14 with exclusive regioselectivity. *Adv Synth Catal* 2008;350:143-152. (b) Sugiyama Yk,
15 Okamoto S. Regioselective syntheses of substituted pyridines and 2,2'-bipyridines by cobalt-
16 catalyzed [2+2+2] cycloaddition of α,ω -diynes with nitriles. *Synthesis* 2011;2247–2254.
- 17 [18] Donohoe RJ, Tait CD, Dearmond MK, Wertz DW. A spectroscopic study of some substituted
18 tris(diimine) complexes of ruthenium(II) and their reduction products. *Spectrochimica Acta*
19 1986;42A:233-240.
- 20 [19] Schmittel M, Ammon H. A Short Synthetic Route to 4,7-Dihalogenated 1,10-Phenanthrolines
21 with Additional Groups in 3,8-Position: Soluble Precursors for Macrocyclic
22 Oligophenanthrolines. *Eur J Org Chem* 1998;785-792.
- 23 [20] (a) Voignier J, Frey J, Kraus T, Buděšínský M, Cvačka J, Heitz V, Sauvage JP.
24 Transition-metal-complexed cyclic [3]- and [4]pseudorotaxanes containing rigid

- 1 ring-and-filament conjugates: synthesis and solution studies. *Chem Eur J* 2011;17:5404-5414.
- 2 (b) Champin B, Sartor V, Sauvage JP. A phen-terpy conjugate whose chelate coordination axes
3 are orthogonal to one another and its zinc complex. *New J Chem* 2006;30:22–25.
- 4 [21] You YC, Tzeng MC, Lai CC, Chiu SH. Using oppositely charged ions to operate a three-station
5 [2]rotaxane in two different switching modes. *Org Lett* 2012;14:1046–1049.
- 6 [22] Krinochkin AP, Kopchuk DS, Chepchugov NV, Kim GA, Kovalev IS, Rahman M, Zyryanov
7 GV, Majee A, Rusinov VL, Chupakhin ON. An efficient synthetic approach towards new 5,5'-
8 diaryl-2,2'-bipyridine-based fluorophores. *Chin Chem Lett* 2017; 28:1099-1103.
- 9 [23] (a) Sauer J, Heldmann DK, Pabst GR. From 1,2,4-triazines and tributyl(ethynyl)tin to
10 stannylated bi- and terpyridines: the cycloaddition pathway. *Eur J Org Chem* 1999;313-321. (b)
11 Shabunina OV, Kapustina DY, Krinochkin AP, Kim GA, Kopchuk DS, Zyryanov GV, Li F,
12 Chupakhin ON. π -Extended fluorophores based on 5-aryl-2,2'-bipyridines: synthesis and
13 photophysical studies. *Mendeleev Commun* 2017;27:602-604. (c) Kopchuk DS, Khasanov AF,
14 Kovalev IS, Zyryanov GV, Kim GA, Nikonov IL, Rusinov VL, Chupakhin ON. The extension
15 of conjugated system in pyridyl-substituted monoazatriphenylenes for the tuning of
16 photophysical properties. *Chem Heterocyclic Comp* 2014;50:871-879.
- 17 [24] Cambridge Crystallographic Data Centre number is CCDC 1841343.
- 18 [25] Sheldrick GM. A short history of SHELX. *Acta Cryst* 2008; A64: 112-122.
- 19 [26] Loren JC, Siegel JS. Synthesis and fluorescence properties of manisyl-substituted terpyridine,
20 bipyridine, and phenanthroline. *Angew Chem Int Ed* 2001;40:754-757.
- 21 [27] Lakowicz JR. *Principles of Fluorescence Spectroscopy* - Springer. 3. Auflage. Springer, ISBN
22 978-0-387-31278-1, doi:10.1007/978-0-387-46312-4.

- 1 [28] Stewart DJ, Dalton MJ, Long SL, Kannan R, Yu Z, Cooper TM, Haley JE, Tan L-S. Steric
2 hindrance inhibits excited-state relaxation and lowers the extent of intramolecular charge
3 transfer in two-photon absorbing dyes. *Phys Chem Chem Phys* 2016;18:5587-5596.
- 4 [29] Le Bouder T, Maury O, Bondon A, Costuas K, Amouyal E, Ledoux I, Zyss J, Le Bozec H.
5 Synthesis, photophysical and nonlinear optical properties of macromolecular architectures
6 featuring octupolar tris(bipyridine) ruthenium(II) moieties: evidence for a supramolecular self-
7 ordering in a dendritic structure. *J Am Chem Soc* 2003;125:12284-12299.
- 8 [30] He X, Liu Y, Du X, Yang Y, Xu B, Tian W, Ma Y. Excited-state relaxation processes of DPA-
9 DSB: Investigation of the reason for high fluorescence quantum yield of symmetric D- π -D
10 molecule. *Chem Phys Lett* 2011;501:296-299.
- 11 [31] Kopchuk DS, Krinochkin AP, Starnovskaya ES, Shtaitz YK, Khasanov AF, Taniya OS,
12 Santra S, Zyryanov GV, Majee A, Rusinov VL, Chupakhin ON. 6-Arylamino-2,2'-bipyridine
13 "push-pull" fluorophores: solvent-free synthesis and photophysical studies. *ChemistrySelect*
14 2018;3:4141-4146.
- 15 [32] Lippert E. Spektroskopische Bestimmung des Dipolmomentes aromatischer Verbindungen im
16 ersten angeregten Singulettzustand. In: *Z. Electrochem.* Band 61, 957, S. 962.
- 17 [33] Mataga N, Kaifu Y, Koizumi M. Solvent effects upon fluorescence spectra and the
18 dipolemoments of excited molecules. *Bull Chem Soc Jpn* 1956;29:465-470.
- 19 [34] Kawski A. On the estimation of excited-state dipole moments from solvatochromic shifts of
20 absorption and fluorescence spectra. *Z Naturforsch* 2002;57a:255-262.
- 21 [35] Rabek JF. *Progress in Photochemistry and Photophysics, Volume V.* In: CRC Press. 2016.
- 22 [36] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G,
23 Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov
24 AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J,

1 Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr JA, Peralta JE,
2 Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R,
3 Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N,
4 Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R,
5 Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL,
6 Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD,
7 Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ. Gaussian 09, Revision ABCD.0123,
8 Gaussian, Inc., Wallingford CT, 2009.

- Synthesis of unsymmetrically substituted 5,5'-diaryl-2,2'-bipyridine fluorophores.
- "1,2,4-Triazine" methodology and cross-coupling reactions were done.
- Photophysical studies of the present reported fluorophores were investigated.
- Single crystal X-ray diffraction studies were performed.

ACCEPTED MANUSCRIPT