**ORIGINAL ARTICLE**

# 5-Aryl-6-arylthio-2,2′-bipyridine and 6-Arylthio-2,5-diarylpyridine Fluorophores: Pot, Atom, Step Economic (PASE) Synthesis and Photophysical Studies

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## Abstract

A PASE (pot, step, atom, economic) synthetic approach to 5-aryl-6-arylthio-2,2′-bipyridine and 6-arylthio-2,5-diarylpyridine ligands/fluorophores has been reported via $S_NH$ in 6-aryl-5$H$-1,2,4-triazines/*aza*-Diels-Alder reaction sequence. In this article, the "1,2,4-triazine" methodology was successfully used for the synthesis of C6-thiophenol-substituted (2,2′-bi)pyridines as it is well known that thio-substituted (bi)pyridines and their *aza*-analogs are of wide practical interest. The photophysical properties of the obtained compounds are studied and compared with those reported earlier for 6-substituted 2,2′-bipyridines. The influence of the nature of substituents in the 6-arylthio(bi)pyridine core on the photophysical properties is discussed. It was observed that the new compounds exhibited promising photophysical properties and could be considered as potential push-pull fluorophores. In addition, they demonstrated greater Stokes shift values compared to the previously described 6-$H$, 6-arylamino and 6-pentafluoro-2,2′-bipyridines and higher fluorescence quantum yields values compare to pentafluorophenyl-substituted 2,2′-bipyridines. Depending on a nature of (bi)pyridine fluorophore LE (locally excited) and/or ICT (intramolecular charge transfer) state were prevailing in emission spectra.

## Introduction

2,2′-Bipyridines are perhaps the earliest [1, 2] and most common ligands [3–5]. Their fragments are part of bioactive compounds [6] including antitumor ones [7], as well as they are promising fluorophores [8–10]. To ensure acceptable photophysical properties, namely, long-wavelength absorption and emission maxima, the presence of an extended π-system in such bipyridines is important.

The main object of this work is arylthio-functionalized derivatives of 5-aryl-2,2′-bipyridines which showed promising photophysical properties [11]. It was demonstrated that the photophysical properties of these fluorophores can be tuned by means of synthetic modification. In particular, C5-aromatic substituents can be modified by means of the introduction of various functionalities, including halogen atoms, phenylethynyl moieties or extra aromatic rings, including annelated ones [6]. The edge pyridine ring of the bipyridine core could also be modified by the introduction of (het)aromatic residues or annelation of aromatic rings [12–14]. Modification of the central pyridine ring may also be carried out. In particular, the possibilities of introducing various fragments, such as arenes, phenylethynes [15] as well as the annelation of extra aromatic rings [11] were reported. Additionally, we have demonstrated a possibility of the modification of the central pyridine via so called "1,2,4-triazine methodology" by means of the pre-modification of 1,2,4-triazine precursors by introducing the residues of anilines [16–18], aliphatic alcohols [19], and pentafluorobenzene

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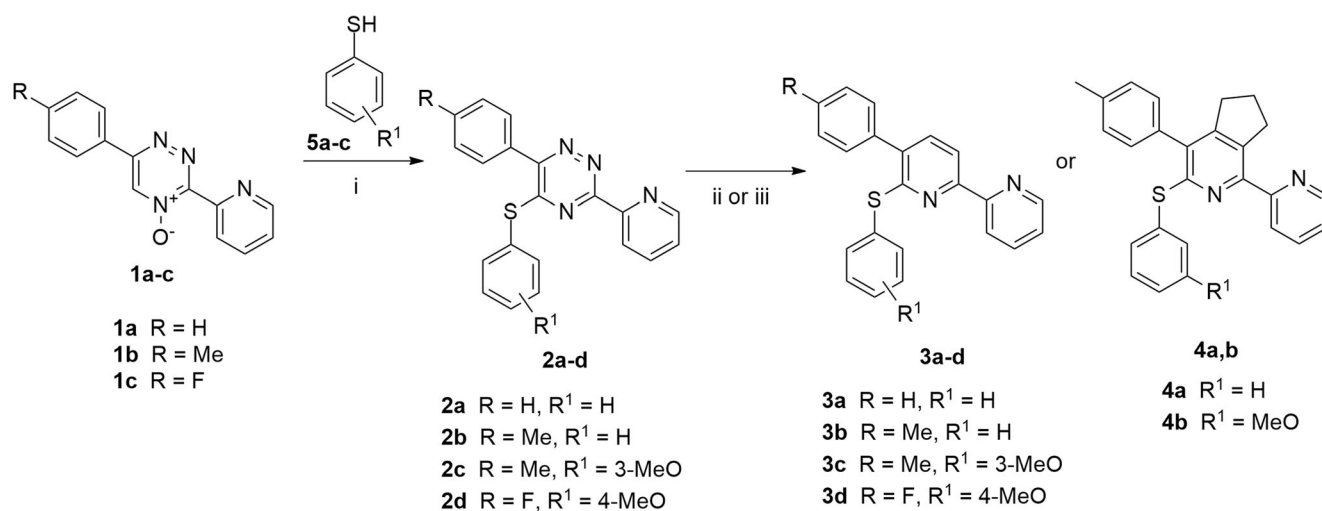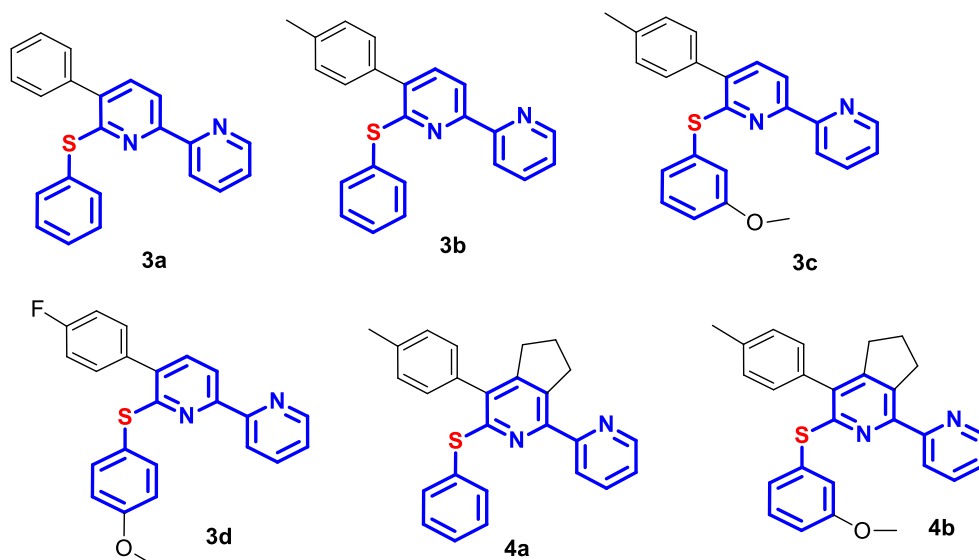
**Scheme 1** Reagents and conditions: i) **5a-c** (R$^1$ = H (**a**), 3-OMe (**b**), 4-OMe (**c**)) THF, CF$_3$COOH, reflux, 30 min, then BzCl, reflux, 30 min; ii) 2,5-norbornadiene, 1,2-dichlorobenzene, 215 °C, 20 h; iv) 1-morpholinocyclopentene, neat, reflux, 20 h.

[20] into the C5 position and the following *aza*-Diels-Alder reaction to afford the C6-substituted 2,2′-bipyridines. In this article, in continuation our research, we wish to report a convenient synthetic approach towards 5-aryl-6-arylthio-2,2′-bipyridine and 6-arylthio-2,5-diarylpyridine fluorophores as well as the studies of photophysical properties of these compounds.

Thio-substituted (bi)pyridines and their *aza*-analogs are of wide practical interest. For instance thiopyrimidines were reported as GluR5 antagonists [21]. 3-(Perfluoro)arylthio-4,4′-bipyridines were proposed as chalcogen and π-hole donors for the stereoselective HPLC separation purposes [22]. C6-Alkylthio-2,2′-bipyridines were reported as ligands for Cu(II) complexes for light-emitting electrochemical cells [23].

A relatively limited number of synthetic approaches to thio-substituted (bi)pyridines has been reported to date. Namely, the heterocyclization reaction under microwave irradiation can be used [24]. The *ipso*-substitution of halogen atom in the (bi)pyridine core by the thiophenol residue was also reported, in particular, bromine atom in a pressure vessel conditions [21], the substitution of bromine atom in the presence of sodium hydride [23] or chlorine atom in the presence of alkali [25]. In addition, the Pd-catalyzed cross-coupling between 6-bromobipyridine and thiophenol was reported [26]. Finally, thio(het)arene-substituted-2,2′-bipyridines were obtained via 1,2,4-triazine precursors by the *ipso*-substitution of chlorine atom(s) by thio(het)arene residues and followed by *aza*-Diels-Alder reaction sequence [27–29].

**Fig. 1** Chemical structures of fluorophores **3a-d**, **4a-b**
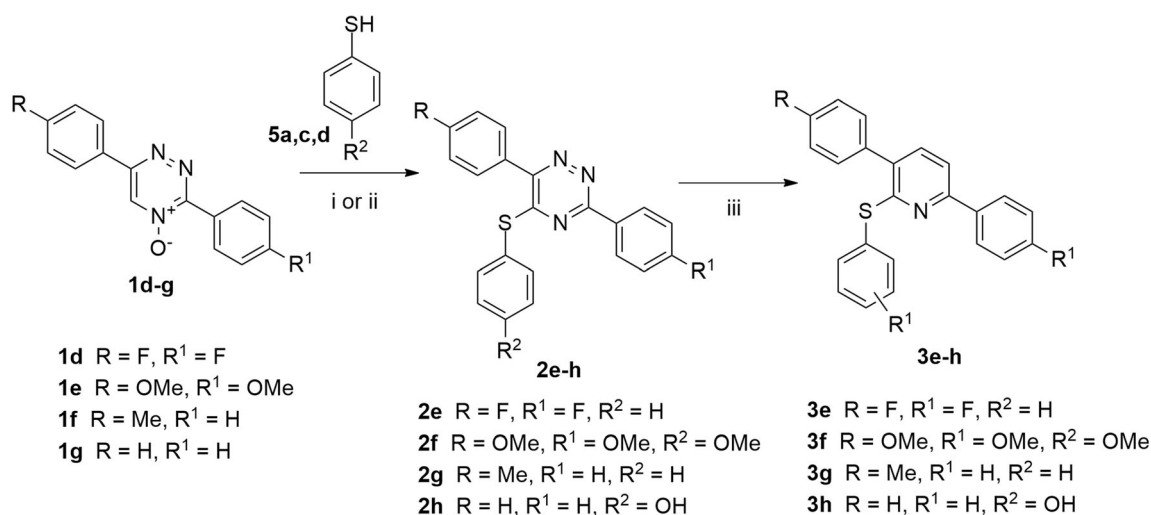
**Scheme 2** Reagents and conditions: i) **5a, c** ($R^2$ = H (**a**), OMe (**c**)) THF, $CF_3COOH$, reflux, 30 min, then BzCl, reflux, 30 min; ii) **5a, d** ($R^2$ = H (**a**), OH (**d**)), acetone, $CF_3COOH$, reflux, 5 min, then BzCl, reflux, 10 min; iii) 2,5-norbornadiene, 1,2-dichlorobenzene, 215 °C, 20 h.

In terms of the above reported "1,2,4-triazine" methodology, it is worthy to mention a more convenient approach for obtaining multifunctionalized 2,2′-bipyridines via the nucleophilic substitution of hydrogen atom ($S_NH$-reaction) in 1,2,4-triazines and *aza*-Diels-Alder reaction sequence. Such methodology has previously been successfully used for the synthesis of (bi)pyridines substituted with residues of carboranes [30], acetylenes [31], polynuclear aromatic hydrocarbons [32], coumarins [33], pentafluorobenzene [20], C-H active compounds [34], alcohols [19] and even hydroxyl-group as a way to obtain 2,2′-bipyridin-6-ones [35]. In this article, the "1,2,4-triazine" methodology was successfully used for the synthesis of C6-thiophenol-substituted (2,2′-bi)pyridines.

## Results and Discussion

To synthesize the 5-arylthio-3-(2-pyridyl)-1,2,4-triazines the previously reported [36] procedure was initially used via the deoxygenative nucleophilic substitution of hydrogen in 5-*H*-1,2,4-triazine-4-oxides. However, in case of 3-(2-pyridyl)-1,2,4-triazine-4-oxides **1a-c** the following method was followed: namely by a short-time refluxing in acetone in the presence of benzoyl chloride which led to the formation of a mixture of products, probably, due to the reaction of thiophenol both as S- and C-nucleophile. While the same reaction in THF instead of acetone resulted in the formation of the target products **2a-c** in up to 78% yields. The same conditions were used for obtaining 5-arylthio-3-(4-fluorophenyl)-1,2,4-triazine **2d**, and for obtaining compounds **2e-h** the previously described [36] conditions were successfully used.

Further *aza*-Diels-Alder reaction between the compounds **2** and 2,5-norbornadiene in 1,2-dichlorobenzene in a pressure vessel was carried out as described earlier [37–39] which afforded the target 2,2′-bipyridines **3a-d** in 75–82% yields (Scheme 1, Fig. 1). Cyclopentene-fused bipyridines **4a-b** were prepared via the solvent-free reaction [40] between the corresponding 1,2,4-triazines **2** and 1-morpholinocyclopentene under neat conditions. The purification of the obtained products was performed by means of flash chromatography.

In a similar way thiophenol-substituted pyridines **3e-h** were obtained for studying their photophysical properties with
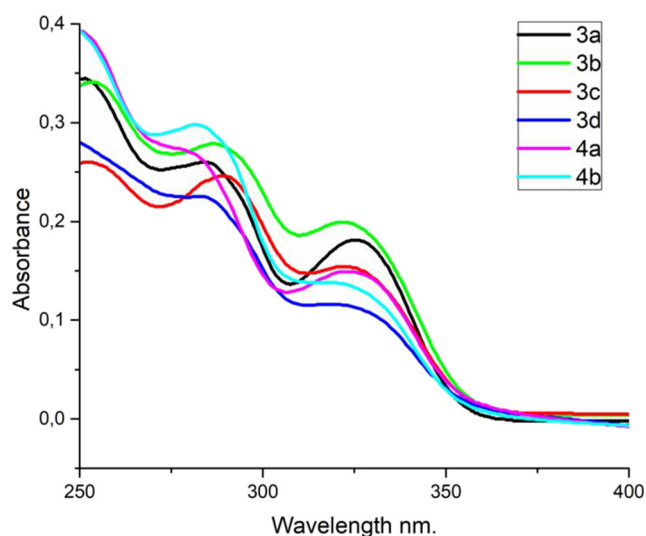


**Fig. 2** Absorption spectra ($2 \times 10^{-5}$ M) of the fluorophores **3–4** in acetonitrile
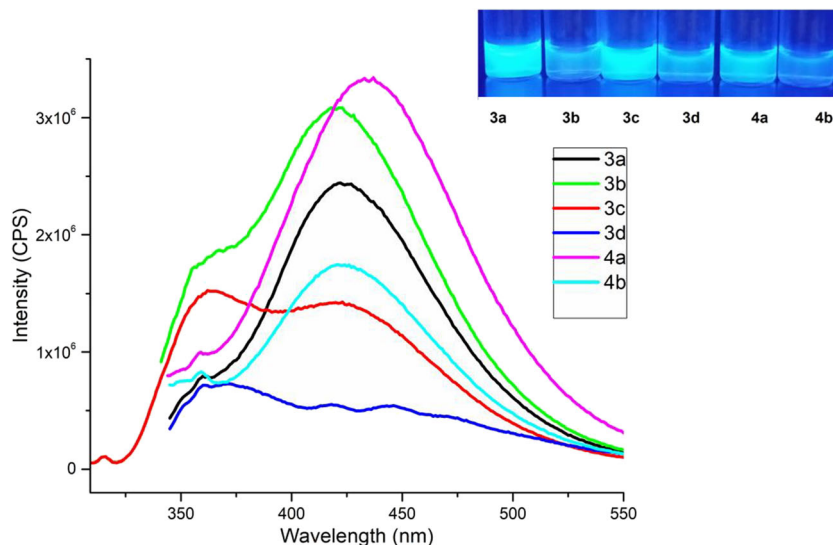
respect to thiophenol-substituted bipyridines **3a-d**, **4a-b** (Scheme 2).

## Photophysical Properties

### UV-*vis* and Photoluminescence (PL) Properties

Spectroscopic measurements for the new fluorophores **3–4** were performed in acetonitrile as an aprotic solvent with an average value of the orientational polarizability ($\Delta f = 0.3$). This eliminates the possibility of additional distortion of the results due to protonation. In addition, this reduces the possibility of a bathochromic shift of the absorption and emission maxima (since fluorophores **3–4** as polar compounds) to exhibit a high sensitivity to the polarity of the solvent. Indeed, it is known that upon increasing the solvent polarity the effect of

reducing the energy of the excited state is enhanced. That leads radiation at lower energies or, in other words, in a longer wavelength region of a spectra [41]. Absolute quantum yields were measured using the integrating sphere of a Horiba-Fluoromax-4 spectrofluorimeter in $CH_3CN$ and acetonitrile.

The non-normalized absorption and emission spectra of ligands **3–4** are shown in Fig. 2, 3 to carry out a comparative analysis of the results.

All absorption spectra are similar and contain two broad absorption bands in the near UV region with $\lambda_{max} \sim 280$ nm and $\lambda_{max} \sim 325$ nm, which corresponds to $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ electronic transitions. Characteristic emission spectra of the ligands **3c** and **3d** are well structured and contain two bands related to both the locally excited (LE) state ($\lambda_{max} = 372$ nm (**3d**), $\lambda_{max} = 364$ nm (**3c**)) and the ICT state ($\lambda_{max} = 443$ nm (**3d**), $\lambda_{max} = 420$ nm (**3c**)). In this case, the Stokes shift values
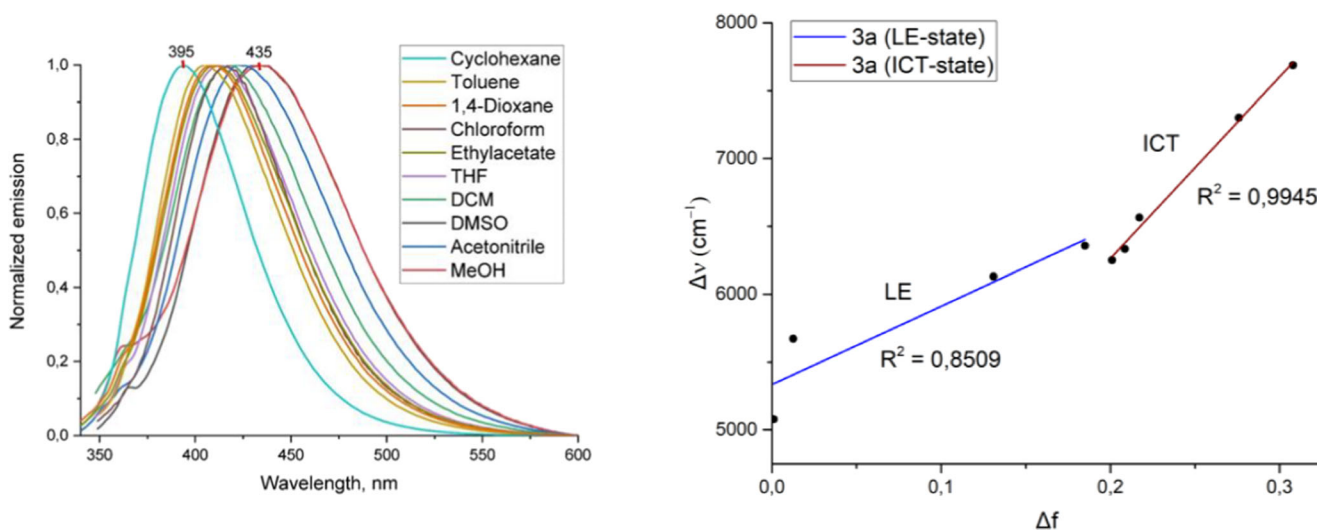


**Fig. 4** Emission spectra (left) of the fluorophore **3a** throughout the range of various solvents and Lippert-Mataga plot (right) with two different excitation states (LE-state and ICT-state for **3a**)
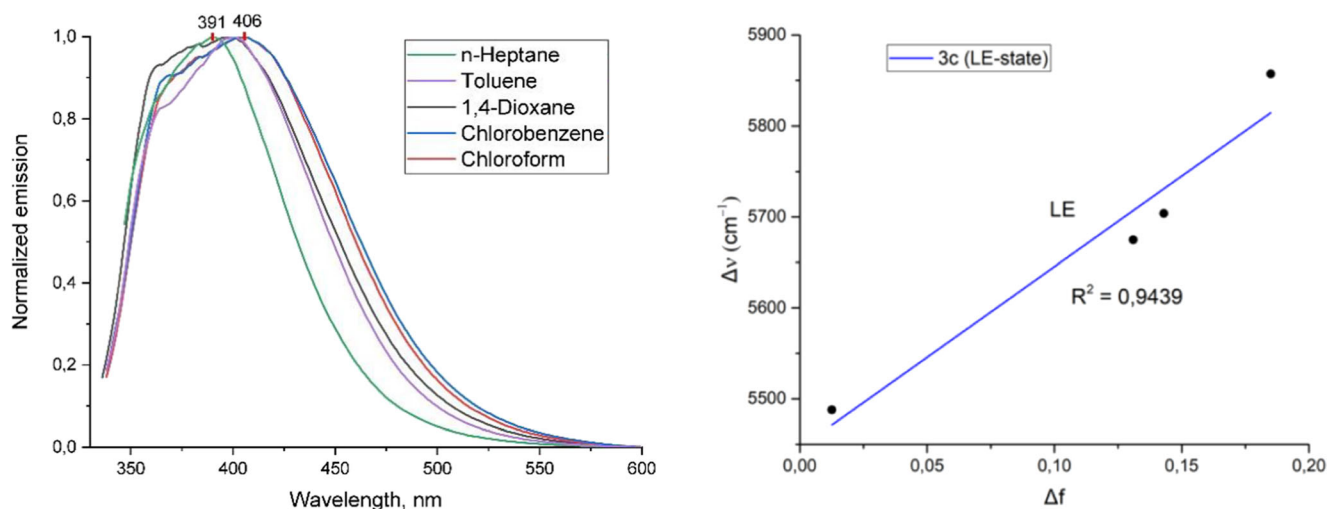
**Fig. 5** Emission spectra (left) of the fluorophore **3c** only in the non- and low-polarity regions ($\Delta f < 0,2$) and Lippert-Mataga plot (right) with one excitation state (LE-state)

are in the range of 40–50 nm, which leads to the conclusion that the state of fluorophores **3c** and **3d** predominates in a LE state (the group of the LE state). At the same time, for compounds **4a**, **4b**, **3a** and **3b**, the emission spectra are presented as by a continuous unstructured band with a maximum wavelength of 420–440 nm and with an average Stokes shift of about 100 nm. Such characteristics make it possible to attribute them to the group with the predominant intramolecular charge transfer (ICT state group).

As for the fluorescence quantum yields for the compounds **3–4**, their values were up to 10.6%, and the maximum value was observed for the compound **4a**. Moreover, the introduction of a cyclopentene fragment mostly does not affect the fluorescence quantum yield values. Thus, a comparison of the quantum yields for the related compounds **4a** and **3b**, as well as **4b** and **3c** shows no significant difference.

It turned out that the introduction of a condensed cyclopentene fragment into the central pyridine ring in compounds **4** affected the $\pi$-conjugation indirectly, i.e., the absorption maxima remained unchanged. But the molar extinction coefficient decreased, while the lifetime of the excited state increased on average by 2.5–3 times. For example, for compound **4a** $\varepsilon_M = 7500$ $M^{-1}$ $cm^{-1}$, $\tau = 7.2$ ns, while for compound **3b** $\varepsilon_M = 9900$ $M^{-1}$ $cm^{-1}$, $\tau = 2.7$ ns.

## LE-State Vs ICT-State for Fluorophores; Solvatochromic Properties

To clarify the nature of intramolecular charge transfer in the excited state and the solvent effect on the fluorescent behavior of chromophores, the study of the general effect of solvents for several fluorophores **3–4** was carried out (Table 2).
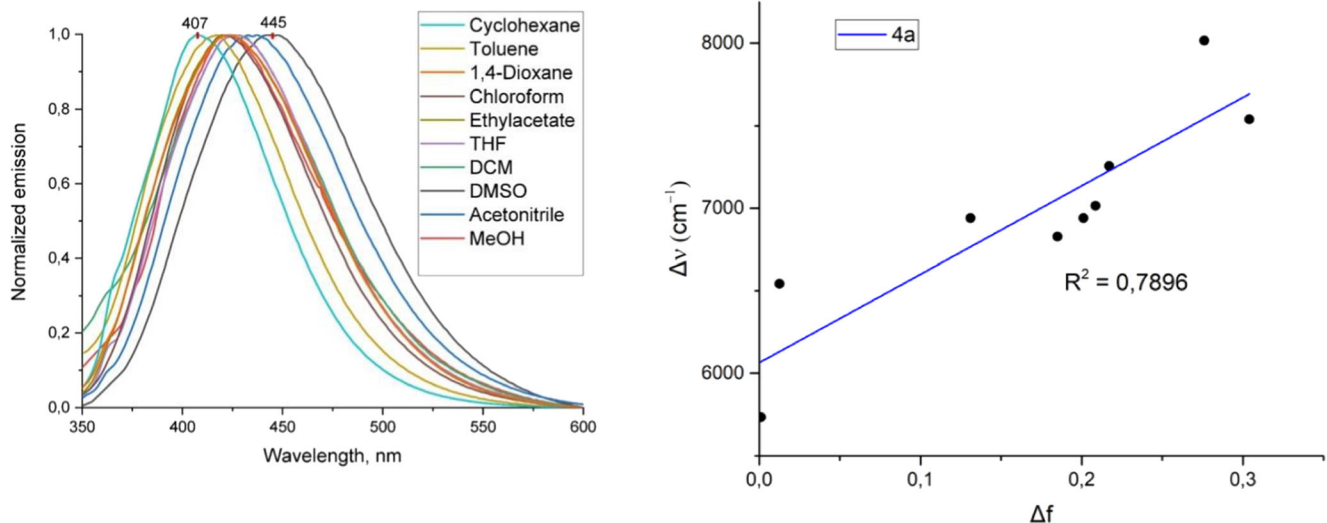


**Fig. 6** Emission spectra (left) of the fluorophore **4a** in various solvents and Lippert-Mataga plot (right)

**Table 1** The photophysical properties of new fluorophores **3a-d** and **4a-b** and previously reported 5-aryl-2,2′-bipyridines. [a] Absorption spectra were measured at rt. in $CH_3CN$ in a range from 220 to 350 nm; [b] Emission spectra were measured at rt. in $CH_3CN$; [c] Photoluminescence lifetimes ($\tau$) of fluorophores were measured at rt. in $CH_3CN$; [d] Chi squared ($\chi^2$) values obtained from fitting of the emission decays ($\lambda_{ex} = 310$ nm) at $\lambda_{em, \, max}$ nm; [e] Absolute quantum yields were measured in the Integrating Sphere by using the Horiba-Fluoromax-4 at rt. in $CH_3CN$.
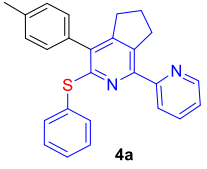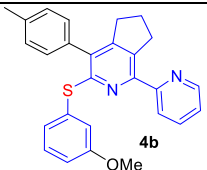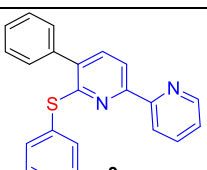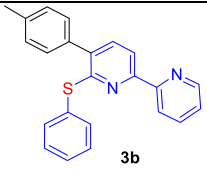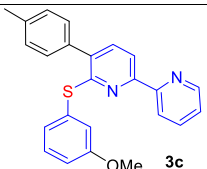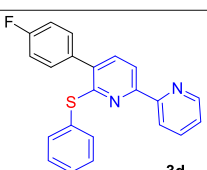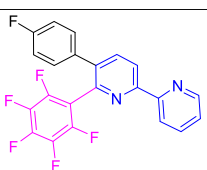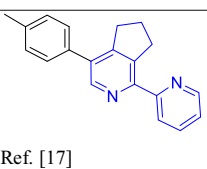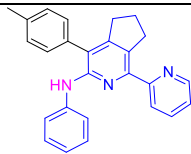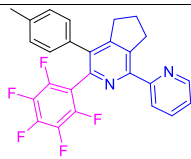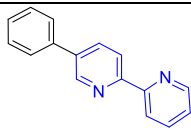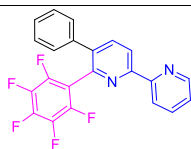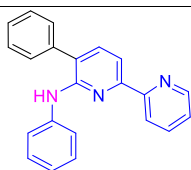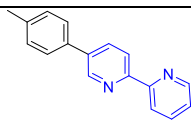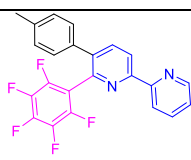
| Entry | Fluorophores | $\lambda_{abs \, max}$[a], nm | $\lambda_{em \, max}$[b], nm | $\varepsilon_M$ (at $\lambda_{abs \, max}$, $10^4$ $M^{-1}$ $cm^{-1}$) | Stokes shift, nm | $\tau$[c], ns | $\chi^{2 \, d}$ | $\Phi_f$, (%)[e] ($\lambda_{ex}$, nm) |
|---|---|---|---|---|---|---|---|---|
| 1 |  **4a** | 250, 324 | 434 | 0,75 | 110 | 7,2 | 1,14 | 10.6 (324 nm) |
| 2 |  **4b** | 223, 281, 325 | 424 | 0,68 | 99 | 5,4 | 1,14 | 4.9 (325 nm) |
| 3 |  **3a** | 251, 285, 325 | 423 | 0,91 | 98 | 2,9 | 1,10 | 4.9 (325 nm) |
| 4 |  **3b** | 253, 286, 321 | 421 | 0,99 | 100 | 2,7 | 1,00 | 8.0 (321 nm) |
| 5 |  **3c** | 225, 253, 289, 323 | 364, 420 | 0,77 | 41 | 2,7 | 1,05 | 9.1 (323 nm) |
| 6 |  **3d** | 232, 285, 325 | 372, 418, 443 | 0,58 | 47 | 2,0 | 1,11 | 2.3 (325 nm) |
| 7 |  Ref. [39] | 233, 292 | 302, 310, 316, 361, 379, 399 | | 10 | | | 2.0 |
| 8 |  Ref. [17] | 300 | 351 | | 51 | | | 5.4 |

**Table 1** (continued)

| 9 | | 295, 356 | 445 | | 89 | | 48.3 |
|---|---|---|---|---|---|---|---|
| | Ref. [17] | | | | | | |
| 10 | | 290 | 312, 319, 366, 384, 404 | | 22 | | <0.1 |
| | Ref. [20] | | | | | | |
| 11 | | 298 | 357 | | 59 | | 3.2 |
| | Ref. [11] | | | | | | |
| 12 | | 292 | 303, 310, 318, 359, 377, 396 | | 11 | | 1.0 |
| | Ref. [20] | | | | | | |
| 13 | | 358 | 454 | | 96 | | 42,0 |
| | Ref. [17] | | | | | | |
| 14 | | 302 | 360 | | 58 | | 17,0 |
| | Ref. [11] | | | | | | |
| 15 | | 293 | 304, 312, 319, 363, 382, 402 | | 11 | | 2,8 |
| | Ref. [20] | | | | | | |

In this case, a number of solvents was selected, and the value of the orientation polarizability $\Delta f$ of the subsequent solvent in the series differed from the previous one by no more than 0.05 units. The largest Stokes shifts of 117 nm for compound **4a** were observed in highly polar aprotic solvent DMF and of 114 nm for the compound **4b** in a protic solvent methanol. Solvatochromic shift of more than 100 nm usually originates from the redistribution of internal charge transfer in the excited state and a change in the difference between the dipole moments in the ground and excited states of the fluorophore [41]. In order to prove this fact mathematically, the dependence of the Stokes shift values in $cm^{-1}$ versus the orientation polarizability of solvents were plotted in accordance with the Lippert-Mataga equation.

It turned out that, for fluorophores **3a** and **3b**, the Lippert-Mataga plots do not obey a linear relationship over the whole range of solvent polarity, and each plot is represented by two independent approximating lines, which indicates the existence of two different excited states (Fig. 4).

**Table 2** Spectroscopic data of fluorophores **3–4**

| 3a | $\lambda_{abs\ max}$, nm | $\lambda_{em\ max}$, nm | Stokes shift, cm$^{-1}$ |
|---|---|---|---|
| Cyclohexane | 244, 287, 329 | 395 | 5079 |
| Toluene | 330 | 406 | 5672 |
| 1,4-Dioxane | 289, 327 | 409 | 6131 |
| Chloroform | 285, 329 | 416 | 6357 |
| Ethylacetate | 284, 237 | 411 | 6250 |
| THF | 240, 286, 328 | 414 | 6333 |
| DCM | 253, 286, 328 | 418 | 6564 |
| DMSO | 286, 329 | 433 | 7300 |
| Acetonitrile | 255, 276, 325 | 423 | 7128 |
| MeOH | 256, 326 | 435 | 7686 |
| **3b** | $\lambda_{abs\ max}$, nm | $\lambda_{em\ max}$, nm | Stokes shift, cm$^{-1}$ |
| Cyclohexane | 245, 288, 330 | 394 | 4922 |
| Toluene | 330 | 402 | 5427 |
| 1,4-Dioxane | 289, 327 | 407 | 6011 |
| Chloroform | 289, 329 | 414 | 6240 |
| Ethylacetate | 286, 325 | 407 | 6199 |
| THF | 225, 288, 328 | 409 | 6038 |
| DCM | 242, 288, 327 | 413 | 6368 |
| DMSO | 289, 328 | 428 | 7123 |
| Acetonitrile | 274, 326 | 421 | 6922 |
| MeOH | 253, 286, 326 | 370 (sh), 427 | 7256 |
| **3c** | $\lambda_{abs\ max}$, nm | $\lambda_{em\ max}$, nm | Stokes shift, cm$^{-1}$ |
| n-Heptane | 327 | 391 | 5005 |
| Toluene | 328 | 400 | 5488 |
| 1,4-Dioxane | 291, 326 | 400 | 5674 |
| Chlorobenzene | 329 | 405 | 5704 |
| Chloroform | 292, 328 | 406 | 5857 |
| **3d** | $\lambda_{abs\ max}$, nm | $\lambda_{em\ max}$, nm | Stokes shift, cm$^{-1}$ |
| n-Heptane | 320 | 352 | 2841 |
| Toluene | 323 | 358 | 3027 |
| 1,4-Dioxane | 289, 323 | 363 | 3411 |
| Chlorobenzene | 321 | 363 | 3604 |
| Chloroform | 286, 327 | 373 | 3771 |
| **4a** | $\lambda_{abs\ max}$, nm | $\lambda_{em\ max}$, nm | Stokes shift, cm$^{-1}$ |
| Cyclohexane | 253, 286, 330 | 407 | 5733 |
| Toluene | 327 | 416 | 6543 |
| 1,4-Dioxane | 284, 327 | 423 | 6940 |
| Chloroform | 327 | 421 | 6828 |
| Ethyl acetate | 327 | 423 | 6940 |
| THF | 241, 273, 328 | 426 | 7014 |
| DCM | 242, 326 | 427 | 7256 |
| DMSO | 259, 328 | 445 | 8016 |
| Acetonitrile | 274, 327 | 434 | 7540 |
| MeOH | 274, 322 | 424 | 7471 |
| **4b** | $\lambda_{abs\ max}$, nm | $\lambda_{em\ max}$, nm | Stokes shift, cm$^{-1}$ |
| Cyclohexane | 221, 253, 286, 331 | 400 | 5211 |
| Toluene | 327 | 406 | 5950 |
| 1,4-Dioxane | 284, 325 | 412 | 6497 |
| Chloroform | 284, 325 | 417 | 6788 |

**Table 2** (continued)
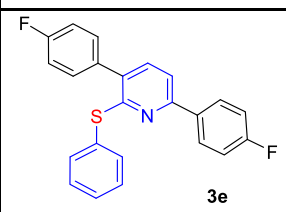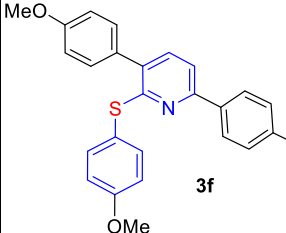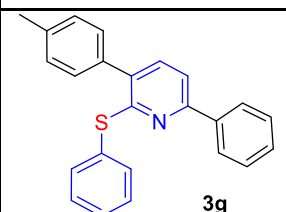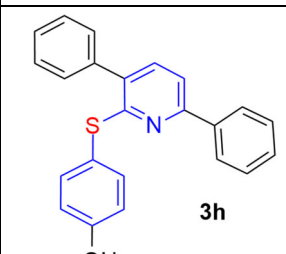
| 3a | $\lambda_{abs\ max}$, nm | $\lambda_{em\ max}$, nm | Stokes shift, cm$^{-1}$ |
|---|---|---|---|
| Ethyl acetate | 282, 324 | 413 | 6651 |
| THF | 225, 281, 329 | 415 | 6299 |
| DCM | 228, 283, 324 | 418 | 6941 |
| DMSO | 284, 325 | 433 | 7675 |
| Acetonitrile | 250, 282, 324 | 424 | 7280 |
| MeOH | 279, 314 | 428 | 8483 |

The transition dipole moment ($\Delta\mu$) for the compound **3a** was calculated from the slope of the Lippert-Mataga plot and amounted to 8.6D in the region of low and medium polar solvents ($\Delta f < 0.2$) and 13.0D in the region of polar solvents ($\Delta f > 0.2$). Approximately similar values were obtained for **3b** (8.9D and 12.1D). Thus, high magnitude of the dipole moment ($\Delta\mu > 10$ D, at $R^2 > 0.95$) for the fluorophores **3a**-**3b** in the region of highly polar solvents indicate a clear predominance of the ICT-state. In this case, the nonlinear relationship between the Stokes shift values and the solvent

**Table 3.** Photophysical characteristics of 2,5-diaryl-6-arylthio-pyridines **3e-h**. [a] Absorption spectra were measured at rt. in $CH_3CN$ in a range from 220 to 350 nm; [b] Emission spectra were measured at rt. in $CH_3CN$; [c] Absolute quantum yields were measured in the Integrating Sphere by using the Horiba-Fluoromax-4 at rt. in $CH_3CN$.

| Entry | Fluorophores | $\lambda_{abs\ max}$[a], nm | $\lambda_{em\ max}$[b], nm | $\Phi_f$, (%)[c] |
|---|---|---|---|---|
| 1 |  **3e** | 255, 321 | 400 | 2.3 |
| 2 |  **3f** | 280, 329 | 420 | 1.0 |
| 3 |  **3g** | 254, 324 | 407 | 2.0 |
| 4 |  **3h** | 253, 322 | 458 | 0.1 |
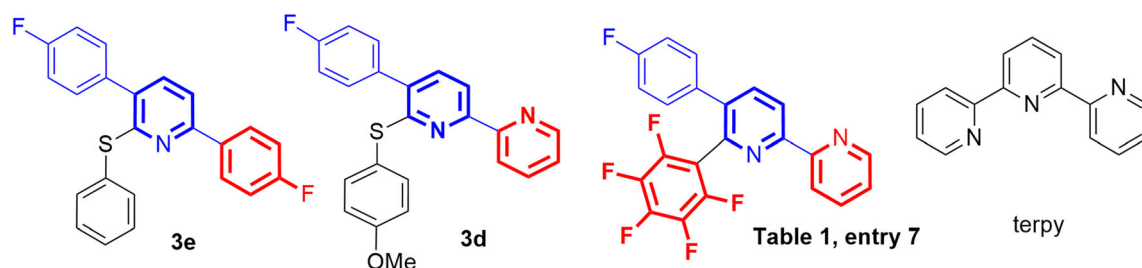
**Fig. 7** A number of 4-fluorophenyl-substituted pyridines and 5-(4-fluorophenyl) substituted bipyridines and terpy

polarity may indicate an additional intercrossed excited state of these fluorophores. [42]

On the contrary, the solvatochromic shift of the emission maxima for the compounds **3c** and **3d** was observed only in the non- and low-polarity regions. The high degree of the approximation of both Lippert-Mataga plots ($R^2 > 0.95$) made it possible to determine the difference in dipole moments, which was 4.9D and 7.2D, respectively, which can clearly be attributed to the prevailing LE-state (Fig. 5) and also see the Supplementary Information for compound **3d**.

Despite the regular solvatochromic shift on going from nonpolar cyclohexane to strongly polar DMF, for the compounds **4a** and **4b**, the permanent dipole moments were 8.3D and 9.7D, respectively, taking into account the low second order approximation reliability ($R^2 \sim 0.8$). At the same time, it was not possible to separate two sections with high approximations in the Lippert-Matag plots. Thus, for the compounds **4a** and **4b**, the low linear relationship between the Stokes shift values and the solvent polarity, along with low values of transition dipole moment ($\Delta\mu < 10D$), may indicate a large contribution of both the LE-state in the solvents of low polarity and the ICT-state in the solvents of high polarity due to the hampered π-conjugation caused by the presence of pyridine-fused cyclopentane fragments (Fig. 6).

We have compared the photophysical properties of new fluorophores with some of their analogs of the 5-aryl-2,2′-bipyridine series having different substituents at position C6. Thus, the introduction of the arylthio group at the position of C6 changes dramatically its photophysical properties of the designed fluorophore in the direction of enhancing "push-pull" properties compared to 6-unsubstituted analogues with or without cyclopentane fragment (Table 1, entry 8) (Table 1, entries 11 and 14). At the same time, the degree of π-conjugation increased significantly, which led to a significant bathochromic shift of the absorption and emission spectra, an increase in the Stokes shift by 1.5–2 times, and also an increase, in some cases, the fluorescence quantum yields. Based on all above, one can conclude that in new chromophores the ICT state is prevailing.

A comparison of the new compounds **3** and **4** with their arylamine-substituted analogs (Table 1, entries 9 and 13) showed that the replacement of the aniline residue with a thiophenol fragment in some cases causes an increase in the Stokes shift, for example, from 89 to 110 nm (entries 1 and 9). At the same time, due to the heavy-atom effect which increases the rate of intersystem crossing [43] the new fluorophores **3** and **4** have lower fluorescence quantum yield values compare to 6-arylamino-substituted 2,2′-bipyridines (2–10% vs up to 48%).

Compare to pentafluorophenyl-substituted 2,2′-bipyridines (Table 1, entries 10, 12, and 15) compounds **3–4** exhibited much higher fluorescence. Thus, the fluorescence quantum yields values for pentafluorophenyl-substituted 2,2′-bipyridines were not exceeding 1%, while for the compounds **3–4** the quantum yield value was observed as high as 10%. The Stokes shift values for pentafluorophenyl-substituted 2,2′-bipyridines were also, as a rule, noticeably lower.

Along with N^N ligands, a photophysical studies of thiophenol-substituted C^N ligands **3e-h** were carried out (Scheme 2, Table 3). These compounds demonstrated fluorescence quantum yields values as low as 2.3%, and this is less than the above mentioned N^N ligands **4a-b, 3a-d**. 4-Fluorophenyl-substituted pyridines and 5-(4-fluorophenyl) substituted bipyridines are of particular interest as isoelectronic analogs (Fig. 7).

It is worthy to mention that recently a detailed analysis of the energies of intermolecular interactions and supramolecular architectures of pyridine and fluorobenzene/pentafluorobenzene was carried out [44]. It was shown that the pyridine type nitrogen atom and fluorine atoms as substituents in the aromatic ring induce a molecular arrangement of one type in the solid state which manifested the isotypic transformation principle. It was logical that the replacement of the fluorophenyl group in compound **3e** with the 2-pyridyl group in fluorophore **3d** did not actually lead to noticeable changes in the photophysical properties of the ligands. On the other hand, the photophysical properties of 6-thiophenol-substituted pyridines were also differ from fluorophenyl-substituted C^N and N^N ligands, including 6-pentafluorophenyl-substituted 2,2′-bipyridine (Table 1, entry 7), whose photophysical properties are very similar to 2,2′:6,2″-terpyridine analogue (terpy).

In conclusion, we have reported a PASE approach to 6-arylthio-2,5-diarylpyridines and 5-aryl-6-arylthio-2,2′-bipyridines, including cyclopentene-fused bipyridines. New compounds exhibited promising photophysical properties

and could be considered as potential push-pull fluorophores. In particular, they demonstrated greater Stokes shift values compared to the previously described 6-*H*, 6-arylamino and 6-pentafluoro-2,2′-bipyridines and higher fluorescence quantum yields values compare to pentafluorophenyl-substituted 2,2′-bipyridines. Depending on a nature of (bi)pyridine fluorophore LE and/or ICT state were prevailing in emission spectra.

## Declarations

**Ethics Approval**    Not applicable.

**Consent to Participate**    Not applicable.

**Consent for Publication**    Not applicable.

**Conflict of Interest/Competing Interests**    The authors declare that they have no conflict of interests.

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