(*E*)-6-(2-Arylvinyl)-2,2′-bipyridines: a convenient synthesis and fluorescent properties*

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A convenient two-step synthesis of 6-(2-arylvinyl)-substituted 2,2′-bipyridines *via* S_N^H functionalization of 5-unsubstituted 1,2,4-triazines with subsequent aza-Diels—Alder reaction was proposed. The fluorescent properties of the obtained 2,2′-bipyridines were studied.

Key words: 6-(2-arylvinyl)-2,2′-bipyridines; nucleophilic substitution of hydrogen, aza-Diels—Alder reaction, 1,2,4-triazines, fluorescent properties.

6-(2-Arylvinyl)-2,2′-bipyridines and their derivatives are of practical interest as promising push-pull fluorophores,**[1]** materials for nonlinear optics,**[2]** as well as inhibitors of proliferation of eukaryotic tumor cells.**[3]** Most often, these compounds are ligands for the formation of various complexes with promising photophysical properties, in particular, complexes based on Cu^I,**[4,5]** Zn^{II},**[6,7]** Ru^{II},**[8]** and Al^{III},**[9]** which are used as components of LEDs and sensitizers for photocatalytic reactions.

The main approach to 6-arylvinyl-2,2′-bipyridines and their derivatives consists in the condensation of aromatic aldehydes with methyl-substituted heterocycles,**[10,11]** the synthesis of which, often as a multi-step process, is usually an obligatory issue. In this respect, the possibility of direct introduction of arylvinyl residues using the S_N^H methodology looks very attractive. This method was earlier used to obtain 6-aryl-5-arylvinyl-3-(2-pyridyl)-1,2,4-triazines,**[12]** which are of particular interest as synthetic precursors of 2,2′-bipyridines. A similar methodology is widely used for the synthesis of various bipyridines.**[13—17]**

In the present work, we show a possibility of obtaining α-arylvinyl-substituted 2,2′-bipyridines using the direct C—H functionalization of 5-*H*-1,2,4-triazines and the subsequent aza-Diels—Alder reaction.

Results and Discussion

The starting 6-phenyl-5-*H*-1,2,4-triazine (**1**) was obtained according to the procedure published earlier**[18]** (Scheme 1). The direct functionalization was carried out by interaction with lithium salts of the corresponding arylacetylenes obtained *in situ*. The yields of compounds **2a,b** correspond to previously reported values, which are close to quantitative.**[12]** In the case of pyrene derivative **2c**, the yield was 40%. Further synthesis of 6-arylvinyl-2,2′-bipyridines **3a—c** was carried out using the aza-Diels—Alder reaction between 1,2,4-triazines **2a—c** and 2,5-norbornadiene upon reflux in *o*-xylene for 18 h. The yields of target products **3a—c** were 55—65%. The structures of compounds **2c** and **3a—c** were confirmed by ^1H NMR spectroscopy, mass spectrometry, and elemental analysis.

We studied the photophysical properties of 2,2′-bipyridines **3a—c** and unsubstituted pyrene in acetonitrile solutions. It was found that compounds **3a,b** exhibit very weak fluorescence. They are characterized by the short-wave emission maxima at 380 and 363 nm and low quantum yields of 3.1 and 0.6%, respectively. Meanwhile, compound **3c** has more promising photophysical properties. It exhibits green fluorescence (λ_{fl} = 494 nm) with 34.0% quantum yield (Table 1). Note that the photophysical properties of compound **3c** differ significantly from the properties of individual components of this fluorophore. In particular, a bathochromic shift of the fluorescence maximum is observed for compound **3c** in comparison with unsubstituted 5-phenyl-2,2′-bipyridine**[18,19]** and pyrene**[20—23]** (by 137 and 102 nm, respectively), as well as an increase in the quantum yield measured in acetonitrile, more than by 30% (see Table 1). Thus, in the case of compound **3c**, the photophysical properties of the entire chromophore system are improved due to the conjugation of pyrene and 5-phenyl-2,2′-bipyridine fragments.

In conclusion, we described a convenient method for the synthesis of 6-(2-arylvinyl)-substituted 2,2′-bipyrid-

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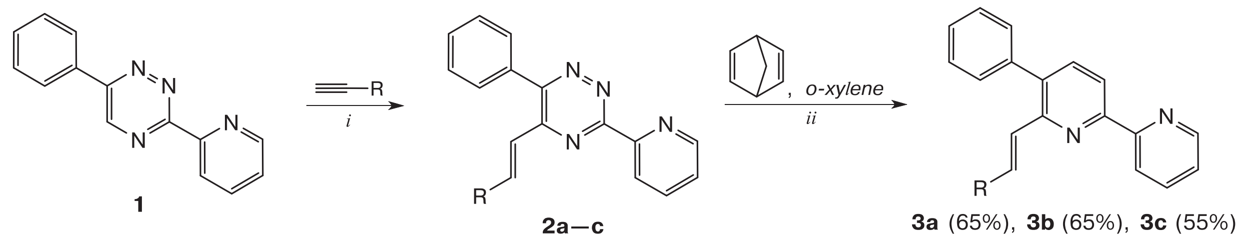
Scheme 1



R = Ph (**a**), 4-MeO-C_6H_4 (**b**), pyren-1-yl (**c**)

Reagents and conditions: *i.* 1) Bu^nLi, THF/toluene, –78 °C; 2) 20 °C, 12 h; *ii.* 144 °C, 18 h.

Table 1. Photophysical data of 6-arylvinyl-2,2′-bipyridines **3**, as well as unsubstituted 5-phenyl-2,2′-bipyridine and pyrene at room temperature

Compound	R	$\lambda_{abs}{}^a$/nm	$\lambda_{lum}{}^b$/nm	Φ^c (%)
3a	Ph	250_{sh}, 288, 325_{sh}	350_{sh}, 380	3.1
3b	4-MeOPh	224, 290, 341_{sh}	354, 363	0.6
3c	Pyren-1-yl	279, 347, 376	435, 460, 494_{sh}	34.0
Unsubstituted 5-phenyl-2,2′-bipyridine	—	298	357	3.2[18]
Pyrene	—	240, 262, 272, 306, 319, 334	371, 392	2.2

[a] Absorption maximum in acetonitrile.

[b] Emission maximum in acetonitrile.

[c] Absolute quantum yields were measured in acetonitrile solutions.[24]

ines using the strategy of direct CH-functionalization in 5*H*-1,2,4-triazines and the subsequent aza-Diels—Alder reaction between the obtained 5-arylvinyl-1,2,4-triazine and 2,5-norbornadiene. It was shown that the introduction of a 2-(pyren-1-yl)vinyl fragment into the bipyridine fluorophore improves the photophysical properties of the entire chromophore system.

Experimental

^{1}H NMR spectra were recorded on a Bruker-Avance II spectrometer (400.13 MHz) with TMS as an internal standard. Reaction progress and purity of the products were monitored by TLC on Sigma-Aldrich 91835 plates. The products were purified by column chromatography on silica gel (Sigma—Aldrich, 230—400 mesh). Electrospray ionization mass spectra were recorded on a Bruker Daltonics MicrOTOF-Q II spectrometer. Elemental analysis was performed at the Institute of Organic Synthesis of the Ural Branch of the Russian Academy of Sciences on an automatic PE 2400, series II CHN-analyzer (Perkin Elmer). Absorption UV spectra were recorded on a Lambda 45 spectrophotometer (Perkin Elmer). Luminescence spectra were recorded using Fluoromax-4 (Horiba) spectrofluorimeter. The absolute quantum yields were measured on a Fluoromax-4 spectrofluorimeter (Horiba) according to the method described previously.[24]

The starting 6-phenyl-5-*H*-1,2,4-triazine (**1**),[18] (*E*)-6-phenyl-3-(2-pyridyl)-5-styryl-1,2,4-triazine (**2a**), (*E*)-5-(4-methoxystyryl)-6-phenyl-3-(2-pyridyl)-1,2,4-triazine (**2b**),[12] and 1-ethynylpyrene[25] were synthesized according to the described procedures, other starting compounds and materials were purchased from commercial sources («Sigma—Aldrich»).

(*E*)-6-Phenyl-5-[2-(pyren-1-yl)vinyl]-3-(pyridin-2-yl)-1,2,4-triazine (2c) was synthesized according to the published procedure for similar compounds.[12] 1-Ethynylpyrene (452 mg, 2 mmol) was dissolved in anhydrous THF (4 mL) in a Schlenk flask in an argon atmosphere and cooled to –78 °C, followed by the addition of a solution of Bu^nLi in hexane (2.5 mol L^{-1}, 0.8 mL). The resulting mixture was stirred for 5 min at –78 °C, then a solution of 6-phenyl-5*H*-1,2,4-triazine (**1**) (375 mg, 1.6 mmol) in anhydrous toluene (35 mL) was added. The reaction mixture was stirred for 12 h at 20 °C, followed by the sequential addition of methanol (10 mL) and water (10 mL). The product was extracted with dichloromethane (3×25 mL). The extract was dried with anhydrous sodium sulfate. The solvents were evaporated under reduced pressure. The products were isolated from the residue by column chromatography (silica gel, eluent ethyl acetate—dichloromethane, 4 : 1; R_f 0.4). The yield was 40% (295 mg). Yellow crystals. M.p. 147—149 °C. ^{1}H NMR ($CDCl_3$), δ: 7.51—7.57 (m, 2 H, H(5) (py), ArCHC$\underline{H}$); 7.60—7.66 (m, 3 H, Ph); 7.89—7.93 (m, 2 H, Ph); 7.98—8.09 (m, 3 H, H(4) (py), pyrene); 8.11—8.15 (m, 2 H, pyrene); 8.20—8.27 (m, 4 H, pyrene); 8.64 (d, 1 H, pyrene, ^3J = 9.2 Hz); 8.80 (d, 1 H, H(3) (py), ^3J = 8.0 Hz); 9.00 (d, 1 H, H(6) (py), ^3J = 4.8 Hz); 9.56 (d, 1 H, ArC$\underline{H}$CH, ^3J = 15.2 Hz). MS (ESI), *m/z*: 461.18 $[M + H]^+$. Found (%): C, 83.32; H, 4.59; N, 12.25. $C_{32}H_{20}N_4$. Calculated (%): C, 83.46; H, 4.38; N, 12.17.

Synthesis of arylvinyl-substituted 2,2′-bipyridines 3a—c (general procedure). 2,5-Norbornadiene (184 mg, 0.2 mL, 2 mmol) was added to a solution of the corresponding 1,2,4-triazine **2**

(0.25 mmol) in *o*-xylene (25 mL). The reaction mixture was refluxed for 18 h in an argon atmosphere, introducing an additional portion of 2,5-norbornadiene (184 mg, 0.2 mL, 2 mmol) every 6 h. Then the solvent was evaporated under reduced pressure, the residue was purified by column chromatography (eluent ethyl acetate). Analytically pure samples were obtained by recrystallization from acetonitrile.

(*E*)-5-Phenyl-6-styryl-2,2′-bipyridine (3a). The yield was 65% (54 mg). Colorless crystals. R_f 0.5. ^{1}H NMR ($CDCl_3$), δ: 7.27—7.37 (m, 6 H, Ph, PhCHC$\underline{H}$); 7.43—7.53 (m, 6 H, Ph, H(5′)); 7.75 (d, 1 H, H(3), $^3J = 8.0$ Hz); 7.89 (ddd, 1 H, H(4′), $^3J = 7.6$ Hz, $^3J = 7.6$ Hz, $^4J = 2.0$ Hz); 8.03 (d, 1 H, PhC$\underline{H}$CH, $^3J = 15.6$ Hz); 8.36 (d, 1 H, H(4), $^3J = 8.0$ Hz); 8.64—8.73 (m, 2 H, H(3′), H(6′)). MS (ESI), *m/z*: 334.42 $[M + H]^+$. Found (%): C, 86.11; H, 5.38; N, 8.69. $C_{24}H_{18}N_2$. Calculated (%): C, 86.2; H, 5.43; N, 8.38.

(*E*)-6-(4-Methoxystyryl)-5-phenyl-2,2′-bipyridine (3b). The yield was 65% (59 mg). Colorless crystals. R_f 0.7. ^{1}H NMR ($CDCl_3$), δ: 3.80 (s, 3 H, MeO); 6.79 (m, 2 H, 4-$MeOC_6H_4$); 7.17 (d, 1 H, ArCHC$\underline{H}$, $^3J = 15.6$ Hz); 7.38 (m, 1 H, H(5′)); 7.44—7.55 (m, 7 H, Ph, 4-$MeOC_6H_4$); 7.73 (d, 1 H, H(3), $^3J = 8.0$ Hz); 7.89 (ddd, 1 H, H(4′), $^3J = 7.8$ Hz, $^3J = 7.8$ Hz, $^4J = 2.0$ Hz); 7.99 (d, 1 H, ArC$\underline{H}$CH, $^3J = 15.6$ Hz); 8.34 (d, 1 H, H(4), $^3J = 8.0$ Hz); 8.65—8.74 (m, 2 H, H(3′), H(6′)). MS (ESI), *m/z*: 364.45 $[M + H]^+$. Found (%): C, 82.45; H, 5.61; N, 7.26. $C_{25}H_{20}N_2O$. Calculated (%): C, 82.39; H, 5.53; N, 7.69.

(*E*)-5-Phenyl-6-[2-(pyren-1-yl)vinyl]-2,2′-bipyridine (3c). The yield was 55% (74 mg). Colorless crystals. ^{1}H NMR ($CDCl_3$), δ: 7.36—7.41 (m, 1 H, H(5′)); 7.49—7.56 (m, 6 H, Ph, ArCHC$\underline{H}$); 7.82 (d, 1 H, H(3), $^3J = 8.0$ Hz); 7.96 (ddd, 1 H, H(4′), $^3J = 7.6$ Hz, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz); 7.99—8.06 (m, 3 H, pyrene); 8.09—8.12 (m, 2 H, pyrene); 8.16—8.23 (m, 3 H, pyrene); 8.44 (d, 1 H, H(4), $^3J = 8.0$ Hz); 8.65 (d, 1 H, pyrene, $^3J = 9.2$ Hz); 8.75 (m, 1 H, H(6′)); 8.82 (m, 1 H, H(3′)); 9.15 (d, 1 H, ArC$\underline{H}$CH, $^3J = 15.2$ Hz). MS (ESI), *m/z*: 459.19 $[M + H]^+$. Found (%): C, 89.18; H, 4.77; N, 6.02. $C_{34}H_{22}N_2$. Calculated (%): C, 89.06; H, 4.84; N, 6.11.

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The authors declare no competing interests.

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