New monomers for (bi)pyridine-containing polymers

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Abstract. Convenient methods for the synthesis of three monomers based on functionalized (bi)pyridines with using “1,2,4-triazine” methodology have been developed.

Keywords: monomers; 1,2,4-triazines; (bi)pyridines; inverse demand Diels-Alder reaction


Introduction

(2,2′-Bi)pyridine containing polymers are of interest from the point of view of creating OLED [1, 2] for redox catalytic reactions [3], as electrolyte membrane fuel cell application [4] or anode materials components [5]. In this regard, the development of convenient methods for the synthesis of compounds with the (poly)pyridine fragment and suitable for using as monomers, is an actual purpose. In this article we propose the convenient methods for the synthesis of three potential monomers of the (bi)pyridine series.

Experimental part

\textsuperscript{1}H NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 MHz), the internal standard was SiMe\textsubscript{4}. Mass-spectra (ionization type — electrospray) were recorded on a MicrOTOF-Q II instrument from Bruker Daltonics (Bremen, Germany). Elemental analysis was performed on a Perkin Elmer PE 2400 II CHN analyzer. The starting 4-bromophenylhydrazone was obtained according to the described method [11].

General procedure for the synthesis of 1,2,4-triazines

Hydrazone was solved in ethanol (30 ml) and solution of the corresponding carbaldehyde in ethanol (25 ml) was added. The resulting mixture was kept at room temperature for 12 h. The precipitate was filtered off, washed with ethanol and dried. Then the obtained intermediate was suspended in acetic acid (30 ml) and mixture was heated to reflux two times. Solvent was removed under reduced pressure.
Ethanol (30 ml) was added to the residue; the resulting crystals of 3 were filtered off, washed with ethanol and dried. The crude triazines were used directly in the next step without additional purification.

6-(4-Bromophenyl)-3-(5-bromopyridin-2-yl)-1,2,4-triazine (3a). Yield 630 mg (1.60 mmol, 64%). NMR $^1$H (DMSO- $d_6$, δ ppm): 7.75–7.79 (m, 2H, C$_6$H$_4$Br), 8.23 (dd, 1H, $^3$J 8.4 Hz, $^4$J 2.4 Hz, H-4(py)), 8.25–8.29 (m, 2H, C$_6$H$_4$Br), 8.49 (d, 1H, $^3$J 8.4 Hz, H-5(py)), 8.89 (d, 1H, $^4$J 2.4 Hz, H-6(py)), 9.52 (s, 1H, H-5). ESI–MS, m/z: 390.92 (M+H)$^+$.  

6-Bromo-2-(6-(4-bromophenyl)-1,2,4-triazin-3-yl)quinoline (3b). Yield 800 mg (1.80 mmol, 72%). NMR $^1$H (DMSO- $d_6$, δ ppm): 7.77–7.83 (m, 2H, C$_6$H$_4$Br), 7.92 (dd, 1H, $^3$J 8.0 Hz, $^4$J 2.0 Hz, H-7(qui)), 8.15–8.20 (m, 2H, H-5,8(qui)), 8.30–8.35 (m, 2H, C$_6$H$_4$Br), 8.56 and 8.70 (both d, 1H, $^3$J 8.4 Hz, H-3 and H-4 (qui)), 9.61 (s, 1H, H-5). ESI–MS, m/z: 440.94 (M+H)$^+$.  

3-(4-Bromophenyl)-6-(thiophen-2-yl)-1,2,4-triazine (7). A mixture of 349 mg (1.7 mmol) of 2-bromo-1-(thiophen-2-yl)ethanone 5, 732 mg (3.4 mmol) of hydrazide 6 and 25 mL of DMF was heated at 120 °C under argon for 10 h. The solvent was distilled off under reduced pressure, the residue was treated with ethanol, and the precipitate was filtered off. The crude triazine was used directly in the next step without additional purification. Yield 343 mg (1.08 mmol, 63%). NMR $^1$H (DMSO- $d_6$, δ ppm): 7.27 (dd, 1H, $^3$J 5.2 Hz, 3.8 Hz, H-4(thio)), 7.70–7.76 (m, 2H, C$_6$H$_4$Br), 7.27 (dd, 1H, $^3$J 5.2 Hz, $^4$J 0.8 Hz, H-5 (thio)), 8.10 (dd, 1H, $^3$J 3.8 Hz, $^4$J 0.8 Hz, H-3(thio)), 8.37–8.42 (m, 2H, C$_6$H$_4$Br), 9.43 (s, 1H, H-5).  

A general procedure for the synthesis of (bi)pyridines 4 and 8  

The mixture of corresponding 1,2,4-triazine 3 or 7 (0.8 mmol) and 1-morpholinocyclo-pentene (0.64 ml, 4.0 mmol) was stirred at 200 °C for 2 h under argon atmosphere. Then, the additional portion of 1-morpholinocyclopentene (0.32 ml, 2.0 mmol) was added and the resulting mixture was stirred for additional 1 h at the same conditions. The reaction mass was cooled to room temperature. The products were purified by flash chromatography (DCM as eluent) and then by recrystallization (ethanol).

4-(4-Bromophenyl)-1-(5-bromopyridin-2-yl)-6,7-dihydro-5$H$-cyclopenta[c]pyridine (4a). Yield 270 mg (0.63 mmol, 78%). NMR $^1$H (DMSO- $d_6$, δ ppm): 2.08 (m, 2H, CH$_2$-6), 3.04 (t, 2H, J 7.6 Hz, CH$_2$-7), 3.46 (t, 2H, J 7.6 Hz, CH$_2$-5), 7.48–7.54 (m, 2H, C$_6$H$_4$Br), 7.64–7.70 (m, 2H, C$_6$H$_4$Br), 8.11 (dd, 1H, J 8.4 Hz, J 1.6 Hz, H-4'), 8.30 (d, 1H, J 8.4 Hz, H-5'), 8.47 (s, 1H, H-3), 8.75 (d, 1H, J 1.6 Hz, H-6'). ESI–MS, m/z: 428.96 (M+H)$^+$. Found, %: C 53.19, H 3.39, N 6.40. C$_{19}$H$_{14}$Br$_2$N$_2$. Calculated, %: C 53.05, H 3.28, N 6.51.

6-Bromo-2-(4-(4-bromophenyl)-6,7-dihydro-5$H$-cyclopenta[c]pyridin-1-yl)quinoline (4b). Yield 290 mg (0.60 mmol, 75%). NMR $^1$H (DMSO- $d_6$, δ ppm): 2.14 (m, 2H, CH$_2$-6), 3.08 (t, 2H, J 7.6 Hz, CH$_2$-7), 3.69 (t, 2H, J 7.6 Hz, CH$_2$-5), 7.51–7.57 (m, 2H, C$_6$H$_4$Br), 7.66–7.71 (m, 2H, C$_6$H$_4$Br), 7.86 (dd, 1H, J 8.8 Hz, J 1.6 Hz, H-7(qui)), 8.02 (d, 1H, J 8.8 Hz, H-8(qui)), (d, 1H, J 1.6 Hz, H-5'(qui)), 8.40 and 8.56 (both d, 1H, J 8.8 Hz, H-3 and H-4 (qui)), 8.54 (s, 1H, H-3). ESI–MS, m/z: 478.96 (M+H)$^+$. Found, %: C 57.41, H 3.22, N 8.67. C$_{23}$H$_{16}$Br$_2$N$_2$. Calculated, %: C 57.53, H 3.36, N 8.53.
1-(4-Bromophenyl)-4-(thiophen-2-yl)-6,7-dihydro-5H-cyclopenta[c]pyridine (8). Yield 228 mg (0.64 mmol, 80%). NMR $^1$H (DMSO-$d_6$, δ, ppm): 2.14 (m, 2H, CH$_2$-6), 3.15 (t, 2H, $^3$J 7.6 Hz, CH$_2$-7), 3.20 (t, 2H, $^3$J 7.6 Hz, CH$_2$-5), 7.16 (dd, 1H, $^3$J 5.2 Hz, 3.8 Hz, H-4(thio)), 7.33 (dd, 1H, $^3$J 3.8 Hz, 4$^4$J 0.8 Hz, H-3(thio)), 7.41 (dd, 1H, $^3$J 5.2 Hz, $^4$J 0.8 Hz, H-5(thio)), 7.57–7.62 (m, 2H, C$_6$H$_4$Br), 7.65–7.70 (m, 2H, C$_6$H$_4$Br), 8.73 (s, 1H, H-3). ESI–MS, m/z: 356.01 (M+H$^+$). Found, %: C 60.53, H 3.81, N 4.07. C$_{18}$H$_{14}$BrNS. Calculated, %: C 60.68, H 3.96, N 3.93.

1-(4-Bromophenyl)-4-(5-bromothiophen-2-yl)-6,7-dihydro-5H-cyclopenta[c]pyridine (9). Pyridine 8 (307 mg, 0.86 mmol) was dissolved in DMF (30 mL). N-Bromosuccinimide (184 mg, 1.0 mmol) was added and the resulting mixture was stirred for 8 h at 50 °C. Then water (100 mL) was added to the mixture and precipitate formed was filtered off. The analytical sample was obtained by recrystallization (ethanol). Yield 329 mg (0.76 mmol, 88%). NMR $^1$H (CDCl$_3$, δ, ppm): 2.19 (m, 2H, CH$_2$-6), 3.17 (t, 2H, $^3$J 7.6 Hz, CH$_2$-7), 3.20 (t, 2H, $^3$J 7.6 Hz, CH$_2$-5), 7.10 and 7.13 (d, 1H, $^3$J 3.8 Hz, H-3 and H-4 (thio)), 7.61–7.65 (m, 2H, C$_6$H$_4$Br), 7.67–7.71 (m, 2H, C$_6$H$_4$Br), 8.69 (s, 1H, H-3). ESI–MS, m/z: 433.92 (M+H$^+$). Found, %: C 49.53, H 3.14, N 3.39. C$_{18}$H$_{13}$Br$_2$NS. Calculated, %: C 49.68, H 3.01, N 3.22.

Results and discussion

The “1,2,4-triazine” methodology has been used for the preparation of the target compounds [7–9]. In particular, we used the modified synthetic route previously used for preparation of the luminophores of 2,2’-bipyridine [10] and 2-(2-pyridyl)quinoline series [11]. Namely, heterocyclization [6] of the corresponding commercially available aldehydes 1a,b and hydrazone of 4’-bromoisonitrosoacetophenone 2 [11] allowed to obtain the 1,2,4-triazine precursors 3, which are also of interest as monomers (Scheme 1). The further solvent-free inverse demand Diels-Alder reaction with 1-morpholinocyclopentene [12] allowed to synthesize compounds 4 of 2,2’-bipyridine and 2-(2-pyridyl)quinoline series.

We have also suggested an approach for obtaining the monomer of monopyridine series. In this case we also used the “1,2,4-triazine” methodology. Namely,
the condensation of 2-bromoacetyltio-
phene 5 with two equivalents of hydrazide
of 4-bromobenzoic acid 6 allowed to ob-
tain the triazine precursor 7 (Scheme 2).
This heterocyclization has been known
for a long time [13]. In this case reaction
was realized during heating in DMF with
no sodium acetate [14, 15]. The further
solvent-free inverse demand Diels-Alder
reaction [12] with 1-morpholinocyclo-
pentene allowed to obtain the condendes
pyridine 8. For preparation of monomer
9 we used the bromination of thiophene
ring of compound 8 at position C5 by N-
bromosuccinimide in DMF. This reaction
is a well-known effective method [16, 17].
For the full conversion of compound 8 to 9
it is necessary the heating reaction mass
at 50 °C.
The structure of compounds 4 and 9 was
confirmed by data of NMR $^1$H, mass-spe-
trometry and elemental analysis. The char-
acteristics of compounds 4 correlate with
ones for the previously published similar
compounds [10, 11]. For compound 9 there
are the signals of protons of thiophene
ring as two doublets, protons of cyclopentene
fragment, protons of 4-bromophenyl moi-
ety, as well as proton of 6,7-dihydro-5H-
cyclopenta[c]pyridine as singlet.

**Conclusions**

In conclusion, we have reported herein
effective synthetic protocols for the prep-
aration of functionalized (bi)pyridines
as potential monomers for the further
synthesis of (bi)pyridines-based polymers
for different applications.

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