



New 2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione-2,2'-bipyridine-based co-polymer, synthesis, photophysical properties and response to metal cations

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Abstract

A new co-polymer based on fragments of 2-(2-pyridyl)monoazatriphenylene and 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione was prepared by using the Sonogashira reaction. The photophysical properties of the polymer were studied. The presence of a strong bathochromic shift of the absorption and emission maxima in comparison with the previously described monomer units is shown. The polymer exhibits an intense “turn-off” response toward Cu²⁺ cations.

Keywords

Sonogashira coupling
polymer
monoazatriphenylene
3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione
fluorescence
Cu²⁺ “turn-off” response

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1. Introduction

Acetylene-based polymers find a variety of applications as functional materials for sensorics and molecular electronics [1]. In particular, conjugated polymers containing 2,2'-bipyridine moieties [2] as monomer units are of interest in terms of optical response to metal cations [3]. Thus, the selective determination of Cu²⁺ [4] and Hg²⁺ [5] cations has been described with the help of such polymers. On the other hand, bis-pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-diones (DPPs) were widely used as components of donor-acceptor alternating co-polymers, which were reported as promising hole-transport materials [6,7], as materials for molecular electronics and photovoltaics [8,9], components of laser dyes [10], dyes for two-photon fluorescence microscopy [11], chemosensors for Cu²⁺ [12] and Hg²⁺ [13] cations, and many other applications [14]. One of the most important application of DPP-based materials was in their use as rea-

gents for photothermal therapy of cancer [15], including photoacoustic imaging-guided photothermal therapy [16].

In this work, we wish to report the synthesis of a polymer containing fragments of 2-(2-pyridyl)monoazatriphenylene and 2,5-bis(2-ethylhexyl)-3,6-bis(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione.

2. Experimental

¹H NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 MHz), the internal standard was SiMe₄. Elemental analysis was performed on a Perkin Elmer PE 2400 II CHN analyzer. UV-visible absorption spectra were recorded on a Perkin Elmer Lambda 45. Luminescence spectra were obtained using a HORIBA Scientific FluoroMax-4 spectrofluorometer. GPC measurements were performed using a chromatograph Agilent 1200 with an aerosol light scattering detector (ELSD) (Agilent technologies,

USA). The starting monomers **1** [17] and **2** [18] were obtained as described in the literature.

The chemical polymerization process was carried out in accordance with the modified method [19]. The compounds **1** (33 mg, 0.048 mmol) and **2** (19.1 mg, 0.048 mmol) were dissolved in the mixture of diisopropylamine/toluene (2:3, 4.0 ml). Then CuI (5.8 mg, 0.030 mmol), Pd(tpp)₂Cl₂ (3.4 mg, 0.0048 mmol) and PPh₃ (2.5 mg, 0.01 mmol) were added. The reaction mixture was stirred in an autoclave under argon atmosphere at 65 °C for 3 days. Then the solvents were evaporated under reduced pressure. Water (10 ml) was added to the residue and the product was extracted with methylene chloride (3×10 ml). The organic phase was washed with an aqueous solution of NH₄Cl and then dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure. The polymer was obtained as a purple powder. Yield 32 mg (70%). NMR ¹H (CDCl₃, δ, ppm): 0.77–0.96 (*m*, 14H, 2-ethylhexyl), 1.14–1.40 (*m*, 28H, 2-ethylhexyl), 1.49–1.63 (*m*, 9H, 2-ethylhexyl), 7.44–7.49 (*ddd*, 2H, ³*J* 7.6 Hz, 7.6 Hz, ⁴*J* 2.6 Hz, CH_{arom}), 7.52–7.58 (*m*, 1H, CH_{arom}), 7.64–7.67 (*m*, 1H, CH_{arom}), 7.67–7.70 (*m*, 1H, CH_{arom}). IR (ν, cm⁻¹): 1660 (C=O).

3. Results and discussion

The synthesis of monomers **1** [17] and **2** [18] was carried out according to the described methods. Thus, compound **1** was obtained on the basis of commercially available precursor **3** as a result of successive *N*-alkylation and bromination of thiophene rings (Scheme 1). In the case of pyridylmonoazatriphenylene **2**, the starting compound is the previously described 3,11-dibromo-6-(pyridin-2-yl)-8,9-dihydro-7*H*-dibenzo[*f,h*]cyclopenta[*c*]quinoline **4** [20]. The monomer was obtained as a result of the Sonogashira reaction at two bromine atoms, followed by removal of the trimethylsilyl protection. The polymerization process was carried out in accordance with a modified technique under the conditions of the Sonogashira reaction [19]. The data of the ¹H NMR spectrum of the obtained polymer do not contradict its proposed structure. In the IR spectra, the presence of a vibration band corresponding to carbonyl groups in the region of 1660 cm⁻¹ can be noted.

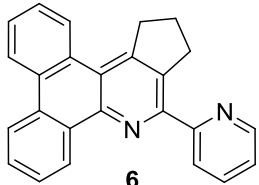
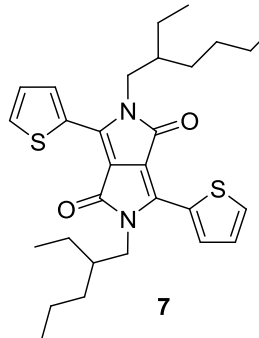
Next, we studied the photophysical characteristics of the obtained polymer **5**. In the solution of acetonitrile this polymer demonstrates absorption maxima around 550 nm (Table 1). Analysis of the literature data showed that, in the case of polymer **5**, there is a bathochromic shift of the absorption maximum relative to the monomer units. Thus, for unsubstituted pyridylmonoazatriphenylene **6** [20], the longest wavelength absorption maximum corresponds to 357 nm, and in the case of 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4-(2*H*,5*H*)-dione **7** [21] this parameter was 541 nm. A similar bathochromic shift is observed for the emission maxima of polymer **5** relative to compounds **6** and **7**. For example, there is a

shift from 541 nm to 55 nm. The absorption and emission spectra of the polymer are shown in Fig. 1.

Next, we studied the fluorescent response of the new polymer **5** with respect to cations of a number of metals. Thus, it was found that the addition of Cu²⁺ cation to the solution of polymer **5** in acetonitrile results in almost complete quenching of its fluorescence, which is due to the influence of both monomer units on the supramolecular properties of the whole polymer.

Fig. 2 depicts GPC chromatography for the resulting polymer **5**. According to the obtained data, the resulting product **5** is a mixture of oligomers/short polymers, among which there are structures with molecular weights of up to 3–4 kDa. Thus, the method reported herein for the preparation of the polymer **5** requires further development in order to increase its average molecular weight.

Table 1 The photophysical characteristics for polymer **5** and compounds **6** and **7** in MeCN at room temperature

Compound	Absorption maxima, nm	Emission maxima, nm
 6 [20]	263, 313, 339, 357	364, 381, 403 (sh)
 7 [21]	341, 353, 508, 541	560, 600
Polymer 5	550	571, 616

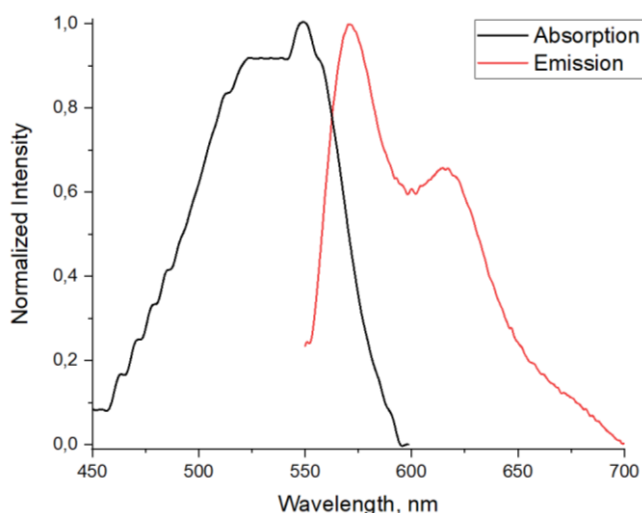
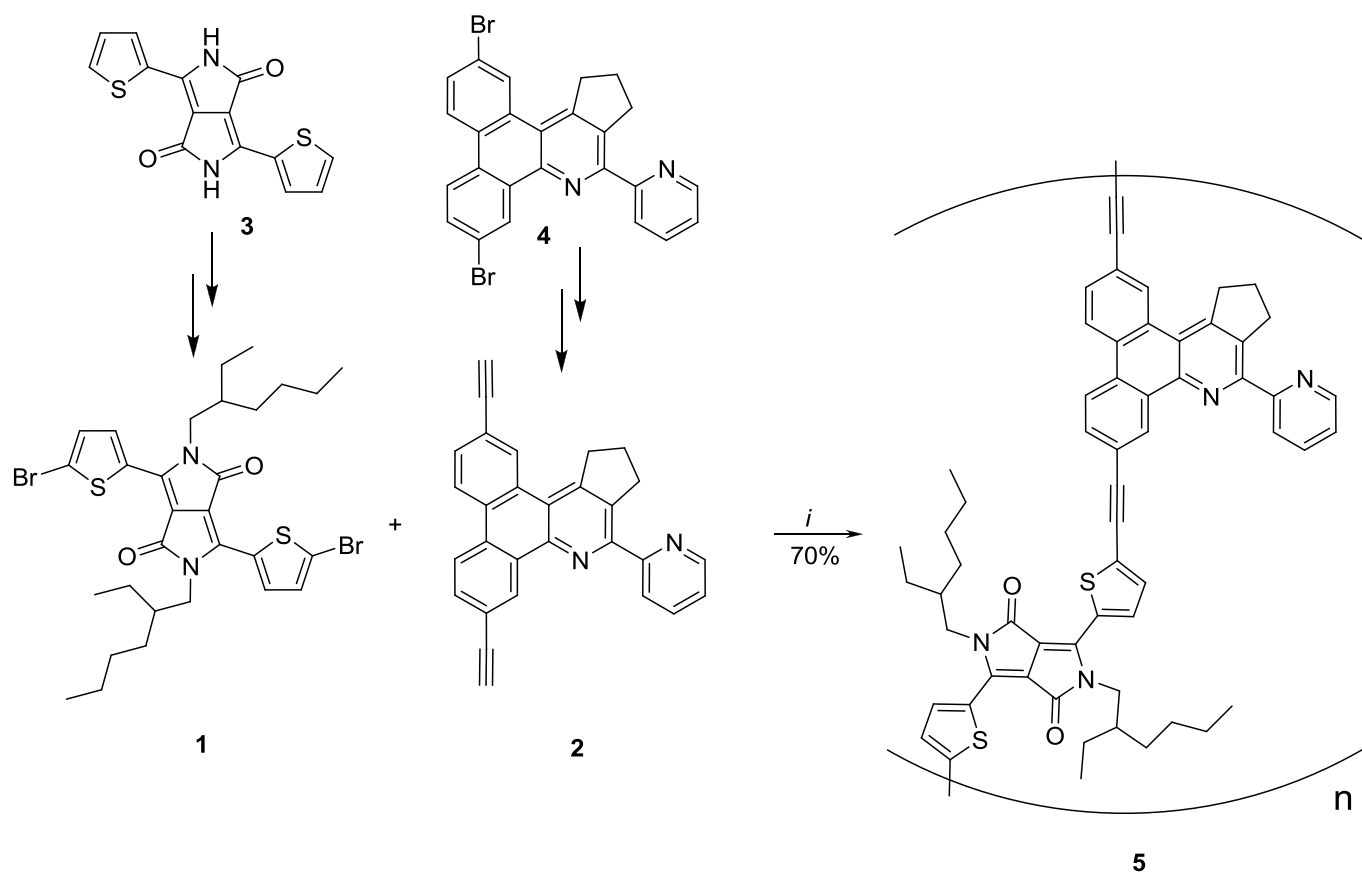


Fig. 1 Absorption and emission spectra of polymer **5** in acetonitrile at room temperature



Scheme 1 Synthesis of polymer 5. Reagents and conditions: i) CuI, PPh₃, Pd(tpp)₂Cl₂/diisopropylamine, 65 °C, 3 days

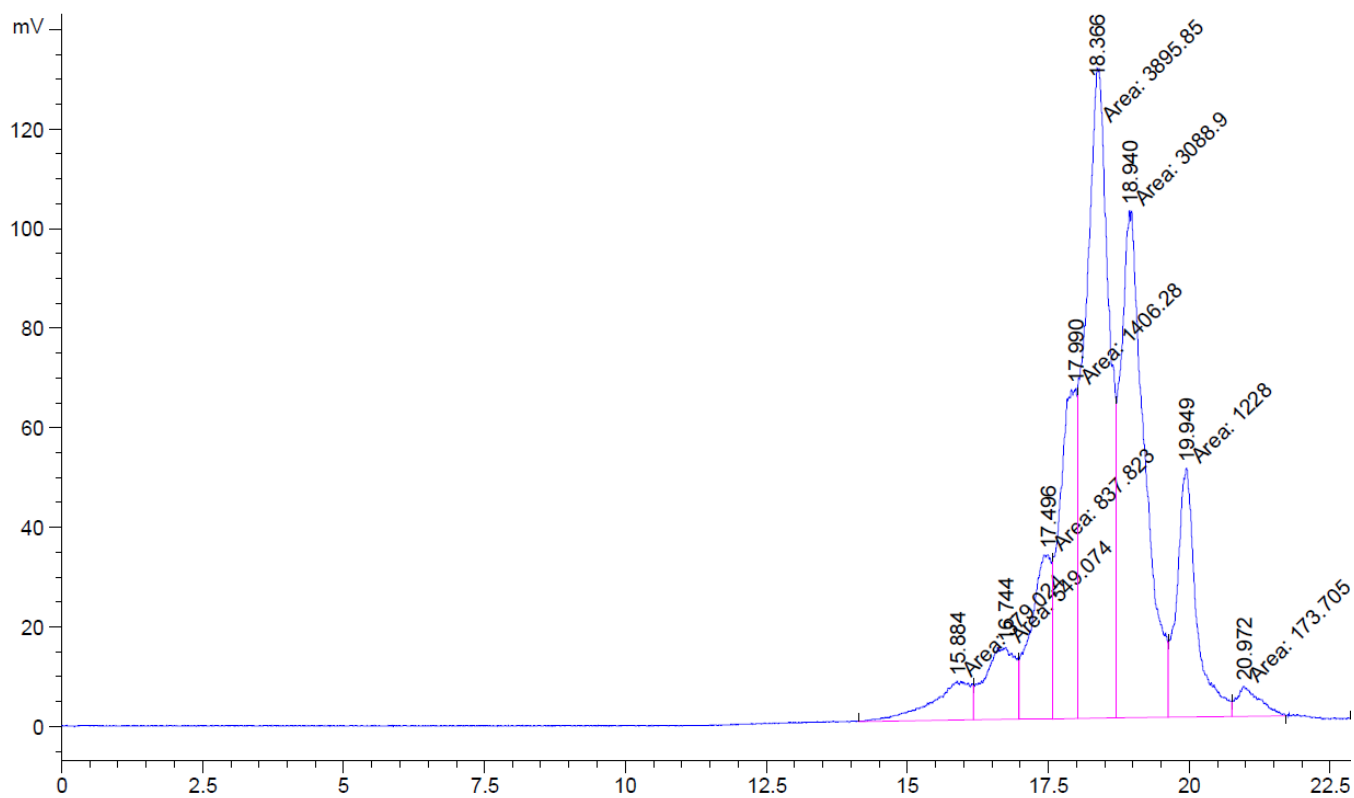


Fig. 2 GPC chromatogram for polymer 5

4. Conclusions

In conclusion, a co-polymer containing 2-(2-pyridyl)monoazatriphenylene and 2,5-bis(2-ethylhexyl)-3,6-bis(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione fragments as monomer units was prepared. Its photophysical properties were studied, and the bathochromic shift of the absorption and emission maxima in compare to those for monomer units was shown. Quenching of the fluorescence of the polymer in the presence of copper cations in solution was observed.

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