New 2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-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(2H,5H)-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 monoaazatriphenylene 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione fluorescence Cu²⁺ “turn-off” response

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1. Introduction

Acetylene-based polymers find a variety of applications as functional materials for sensors and molecular electronics [1]. In particular, conjugated polymers containing 2,2′-bipyridine moiety [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(2H,5H)-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 reagents 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)monoaazatriphenylene and 2,5-bis(2-ethylhexyl)-3,6-bis(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-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,
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 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(dppe)Cl2 (3.4 mg, 0.0048 mmol) and Ph3P (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), 2.44–2.49 (ddd, 2H, J7.6 Hz, 7.6 Hz, J2.6 Hz, CH2rom), 2.65–2.75 (m, 1H, CH2rom), 7.64–7.67 (m, 1H, CH2rom), 7.67–7.70 (m, 1H, CH2rom). IR (ν, cm⁻¹): 1660 (C=O).

The photophysical characteristics for polymer 5 in acetonitrile at room temperature 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        | 263, 313, 339, 357    | 364, 381, 403 (sh)  |
| 7        | 341, 353, 508, 541    | 560, 600            |

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),Cl/diisopropylamine, 65 °C, 3 days.

Fig. 2 GPC chromatogram for polymer 5.
4. Conclusions

In conclusion, a co-polymer containing 2-(2-pyriddy1)monoazatriphenylene and 2,5-bis(2-ethylhexyl)-3,6-bis(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione fragments as monomer units was prepared. Its photophysical properties were studied, and the bathochromic shift of the absorption and emission maxima in comparison 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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