








Mechanosynthesis of pentiptycene-based polyesters and polycarbonates

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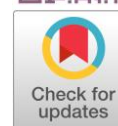
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Abstract

Iptycenes are common building blocks for the small-molecules or polymer-based chemosensors and fluorophores. In addition, iptycene derivatives are widely presented in polymers of intrinsic microporosity (PIMs) as materials for the separation and purification technologies. In this manuscript we wish to report a mechanochemical approach to pentiptycene-based polyesters and polycarbonates as, possibly, new representatives of PIMs. Our approach involves the polycondensation reaction between 5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene-6,13-diol (pentiptycene-6,13-diol) and triphosgene or oxalyl chloride under ball-milling conditions. The obtained polymers were characterized by means of ¹H NMR- and IR-spectroscopy. As the last step, the fluorescence “turn-off” response of pentiptycene-6,13-diol and two pentiptycene-based polymers towards nitroanalytes (2,4-dinitrotoluene (DNT) and 2,4,6-trinitrophenole (picric acid, PA)) was investigated, and Stern-Volmer constants as high as 10⁴ M⁻¹ were observed.

Keywords

pentiptycene
mechanosynthesis
polyester
polycarbonate
porous polymers
detection of nitroanalytes

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1. Introduction

Polymers of intrinsic microporosity (PIMs) comprise a well-recognized class of macromolecules for application for the separation and purification purposes [1–4]. The main constriction element of PIMs are high-free-volume (free volume is the unoccupied space between molecules) molecules, such as spirobisindanes [5–7], ethanoanthracenes [8], spirobifluorenes [9, 10] and Tröger's bases [11, 12]. Triptycenes are especially important, and these molecules are very frequently used in PIMs [13, 14]. The main reason for that is an unique 3D structure of triptycene core provided by aromatic rings attached to the [2,2,2]bicyclooctatriene bridgehead system (Figure 1). These three aromatic rings are bound by a single hinge, and this provides a high energy barrier to molecular twisting or deformation. As a result, the triptycene-based polymers usually demonstrate a poor polymer chain packing with a high so called “internal

molecular free volume” (IMFV) [15]. Compared with triptycene, pentiptycene possesses even bulkier structure that can effectively hinder polymer chains packing leading to much higher fractional free volume (Figure 1). According to both theoretical calculations [16] and experimental [17] data, the size of pentiptycene (ca. 8 Å width and ca. 10 Å high), is much higher than that of the triptycene (ca. 8 Å width and ca. 7 Å high). And this provides higher free volume values for the pentiptycene-based materials.

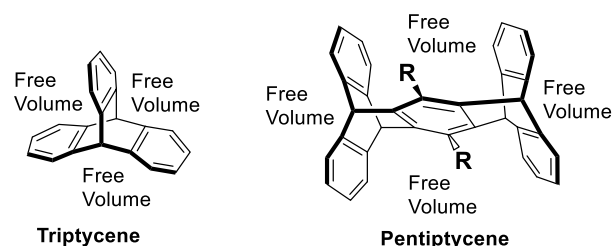


Figure 1 Free volume of triptycene vs pentiptycene.

Pentptycene-based PIMs are widely reported as materials for the carbon dioxide separation or removal [18, 19].

The most common method for the construction of various types of PIMs is two- or multicomponent reactions between the high-free-volume component(s) and connection unit(s) in solution. The main drawbacks of solution-based methods are: long reaction time, a critical dependence on an initial intensive mixing, a possible shrinkage of the obtained polymer upon the drying step after the removal of the absorbed organic vapors/liquids, and finally, the low solubility of high-molecular weight PIMs, which makes the solution-based procedures suffer from the precipitation of reagents/products, resulting in a low degree of polymerization for the target polymers [20].

Mechanosynthesis (under ball-milling conditions) of polymers has such advantages as: an easy synthetic set-up (ball-milling jar), low-cost, a simple pre- and post-treatment, and others. Therefore, ball-milling-assisted polymerization/polycondensation may be considered as a versatile tool for the synthesis of PIMs as well as other functional polymers. Previously, we have reported several successful approaches for the preparation of polymers by means of polycondensation reaction upon ball-milling [21–22].

In this manuscript we wish to report a mechanochemical (under solvent-free conditions in ball-milling) synthesis of pentiptycene-based polyesters and polycarbonates as possible representatives of PIMs.

2. Experimental part

All reagents were purchased from commercial sources and used without further purification. Silica gel 60 (Kieselgel 60, 230–400 mesh) was used for the column chromatography. NMR spectra were recorded on a Bruker Avance-400 spectrometer at 298 K with a digital resolution ± 0.01 ppm using TMS as internal standard. Ball-milling experiments were carried out on a Retsch PM 100 CM ball mill in 25 mL stainless still milling jar loaded with 4 stainless still milling balls of 10 mm diameter. Elemental analyses were performed on a PE 2400 II CHN-analyzer (Perkin Elmer).

2.1. 5,7,12,14-Tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene-6,13-diol (pentiptycene-diol) 1

Pentiptycene quinone [23] (1.5 g, 3.25 mmol), NaHCO_3 (2.73 g, 32.5 mmol) and $\text{Na}_2\text{S}_2\text{O}_4$ (2.77 g, 15.9 mmol) were suspended in 150 mL of DMF in a three-neck flask. The mixture was stirred at ambient temperature for 15 min. The reaction temperature was then gradually increased to 100 °C. The reaction temperature was maintained at 100 °C for 16 h under a nitrogen atmosphere by adding 2.77 g of $\text{Na}_2\text{S}_2\text{O}_4$ to the reaction mixture three times (at $t = 4, 8$ and 12 h). After cooling the reaction mixture to room temperature it was poured into the flask with water (2.0 L). The resulting precipitate was filtered off, washed with water (2.0 L) and

dried in a vacuum desiccator, and the resulting precipitate was recrystallized from DMF. Light orange precipitate, 7.35 g (98% yield). ^1H NMR (400 MHz, DMSO-d_6 , δ , ppm): δ : 8.70 (s, 1H, OH), 7.35–7.30 (m, 4H), 6.93–6.89 (m, 4H), 5.83 (s, 2H). ^{13}C (100 MHz, DMSO-d_6 , δ , ppm): 146.4, 131.4, 125.7, 125.0, 124.7, 123.9. Found (%): C, 88.01; H, 5.03. $\text{C}_{34}\text{H}_{22}\text{O}_2$. Calculated (%): C, 88.29; H, 4.79. ESI-MS, m/z : 462. IR (KBr), ν , cm^{-1} : 3473 (OH), 3066 (CH(arom)), 2992 ($\text{C}(sp^3)\text{H}$).

2.2. Mechano-synthesis of pentiptycene-based polymers 2,3

General procedure. Pentiptycene-diol **1** (300 mg, 0.64 mmol), oxalyl chloride (82 mg, 0.64 mmol) or triphosgene (192.5 mg, 0.64 mmol) in the presence of pyridine (3–5 drops (ca. 50 μL)) and 1,4-dioxane (10 μL) were ball-milled at 500 rpm for 4 h. The resulting precipitate was suspended in a mixture $\text{MeOH}:\text{DMF} = 10:1$ (20 mL), filtered and washed with MeOH (3x5 mL). After that, it was redissolved in DMF (2 mL) and poured into MeOH (20 mL). The precipitate formed was filtered, washed with MeOH (3x5 mL) and air-died for 24 h.

Polymer 2. Colorless crystals. Mp. > 250 °C. ^1H NMR (400 MHz, DMF-d_7 , δ , ppm): 7.75–7.35 (*m*, 4H), 7.25–6.95 (*m*, 4H), 5.97 (b.s., 2H). IR (KBr), ν , cm^{-1} : 3066 (CH(arom)), 2992 ($\text{C}(sp^3)\text{H}$), 1747 (C=O).

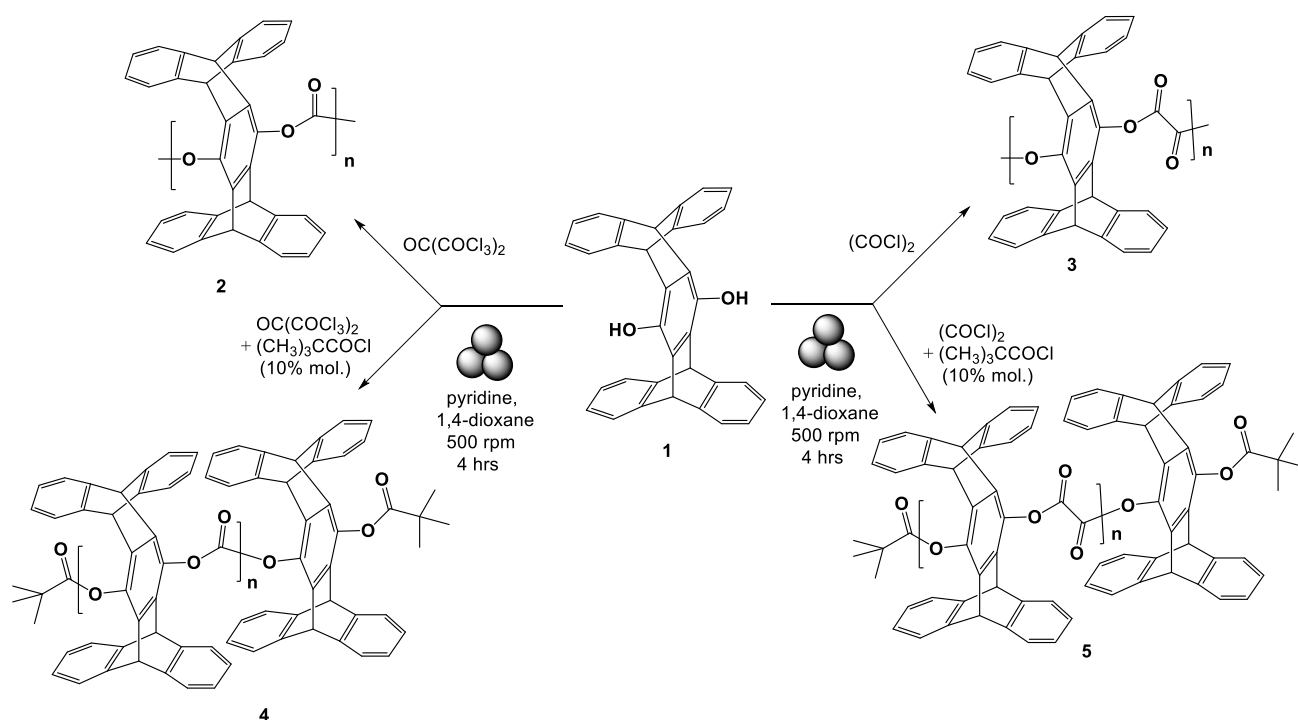
Polymer 3. Colorless crystals. Mp. > 250 °C. ^1H NMR (400 MHz, DMF-d_7 , δ , ppm): 7.73–7.40 (*m*, 4H), 7.20–6.93 (*m*, 4H), 6.07 (b.s., 2H). IR (KBr), ν , cm^{-1} : 3067 (CH(arom)), 2994 ($\text{C}(sp^3)\text{H}$), 1751 (C=O).

2.3. Mechano-synthesis of pentiptycene-based polymers 4, 5

General procedure. Pentiptycene-diol **1** (300 mg, 0.64 mmol), oxalyl chloride (82 mg, 0.64 mmol) or triphosgene (192.5 mg, 0.64 mmol) and pivaloyl chloride (7.7 mg, 7.8 μL , 0.064 mmol) in the presence of pyridine (3–5 drops (ca. 50 μL)) and 1,4-dioxane (10 μL) were ball-milled at 500 rpm for 4 h. The resulting precipitate was suspended in MeOH (20 mL), filtered, and washed with MeOH (3x5 mL). After that the obtained residue was redissolved in DMF (2 mL) and poured into MeOH (20 mL). The precipitate formed was filtered, washed with MeOH (3x5 mL) and air-died for 24 h.

Polymer 4. Colorless crystals. Yield 73%. Mp. > 250 °C. ^1H NMR (400 MHz, DMSO-d_6 , δ , ppm): 7.43–7.26 (*m*, 4H), 7.03–6.90 (*m*, 4H), 5.95 (b.s., 2H), 1.16 (b.s., 9H). IR (KBr), ν , cm^{-1} : 3066 (CH(arom)), 2976 ($\text{C}(sp^3)\text{H}$), 1783 (C=O), 1727 (C=O). $M_n = 26$ kDa.

Polymer 5. Colorless crystals. Yield 69%. Mp. > 250 °C. ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 7.49–7.01 (*m*, 4H), 6.99–6.59 (*m*, 4H), 5.99 (b.s., 2H), 1.28 (b.s., 9H). IR (KBr), ν , cm^{-1} : 3066 (CH(arom)), 2951 ($\text{C}(sp^3)\text{H}$), 1783 (C=O), 1754 (C=O). $M_n = 27$ kDa.



Scheme 1 Mechano-synthesis of pentiptycene-based polycarbonates **2,4** and polyesters **3,5**.

3. Results and Discussions

As a first step, 5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene-6,13-diol (pentiptycene-diol) **1** was synthesized from pentiptycene quinone [23] by means of reduction reaction [24]. According to a literature pentiptycene-diol is one of the common components for the construction of PIMs via polycondensation reactions (hydroxy-groups are involved) [25] or polymerization processes (benzene rings of pentiptycene core are involved) [26]. In the latter case the solubility of the obtained polymer was very low, and few methods can be used for the analysis of such polymers. Keeping in mind our successful approaches for the preparation of polymers under ball-milling conditions [27] similar approach was selected for the construction of polyiptycenes in the framework of this study. Two approaches can be suggested, namely, the reaction between iptycene diol **1** and phosgene or its derivatives, such as triphosgene, to afford polycarbonate **2**, or the reaction between **1** and chloroanhydrides of bis-carboxylic acids, such as oxalyl chloride, to afford polyester **3**. As a first step the reactions between pentiptycene diol **1** and triphosgene or oxalyl chloride in the presence of pyridine as a base and 1,4-dioxane as a co-solvent was carried out under ball-milling conditions. According to the optimization studies (Table S1) the optimal reaction conditions were 500 rpm for 4 h (Scheme 1). As a result, polycarbonate **2** and polyester **3** were isolated by means of precipitation from the solution of MeOH:DMF = 10:1 as colorless precipitates. The structures of polymers **2-3** were confirmed by ^1H NMR (Figures S4, S6) and IR-spectroscopy (Figures S5, S7). Thus, in ^1H NMR the signals of protons of aromatic fragments of pentiptycene moieties as multiplets in the area of 6.95–7.75 ppm,

as well as the signals of protons of sp^3 -hybridized carbon atoms in the form of a broadened singlets in the region of 5.97–6.07 ppm were observed. In IR-spectra (KBr) the absorption bands of C=O groups were observed near 1747 (polycarbonate **2**) and 1751 cm^{-1} (polyester **3**) along with signals of stretching of C–H groups (2900–3100 cm^{-1}) of pentiptycene moieties. In addition, intense absorption peaks near 3400 cm^{-1} were observed in IR spectrum (Figures S5, S7), which may be attributed to the presence of residual MeOH, which is absorbed into the free volume of polymers during the precipitation upon the purification procedure. Since our attempts to remove the residual methanol were unsuccessful, for the both polymer **2** and polymer **3** some extra peaks were observed in ^1H NMR spectra (Figure S4, S6), which may be attributed to the presence of residual MeOH. Unfortunately, both polymers were insoluble in THF, and their characterization in solution by using gel penetration chromatography (GPC) seemed impossible. On the other hand, the end-groups can be introduced to polymers both for reducing of polymer lengths/polycondensation degree/increasing solubility of polymers and for the determination of number average molecular weight (M_n) of polymers by means of end-group analysis. Therefore, as the second step the end groups, such as pivaloyl ones, were introduced to polypentiptycenes by means of reaction between pentiptycene diol **1**, triphosgene and pivaloyl chloride in the presence of pyridine as a base and 1,4-dioxane as co-solvent. As a result, C(O)C(CH₃)₃-caped pentiptycene-based polycarbonate **4** was obtained (Scheme 1). The structure of the polymer was confirmed by means of ^1H NMR (Figure S8). Thus, in the ^1H NMR spectra of **4** the signals of protons of aromatic fragments of pentiptycene as multi-

plets in the area of 6.50–7.50 ppm, and the signals of protons of sp^3 -hybridized carbon atoms as a broadened singlet near 5.50 ppm were observed, as well as the signals of protons of the *tert*-butyl-based end-groups, seen as broadened singlets near 1.00 ppm. In the IR spectrum the signals of carbonyl groups near 1727 and 1783 cm^{-1} were observed (Figure S9). The number average molecular weight for polymer **4** were determined by means of ^1H NMR analysis as a ratio of integral intensities of the signals of protons of $(\text{CH}_3)_3\text{C}$ end-groups to the integral intensity of the signals of protons of sp^3 -hybridized carbon atoms of the main polymer chain. According to the data of end-group analysis the M_n of polymer **4** was equal to 26 kDa. In a similar manner $\text{C}(\text{O})\text{C}(\text{CH}_3)_3$ -ended polyester **5** was obtained when oxalyl chloride was used instead of triphosgene. In the ^1H NMR spectra of **5** there are signals of protons of aromatic fragments of pentiptycene as multiplets at 6.50–7.50 ppm; in addition, the signals of protons of sp^3 -hybridized carbon atoms as a broadened singlet near 5.50 ppm were observed, as well as the signals of protons of the *tert*-butyl-based end groups as broadened singlets near 1.00 ppm (Figure S10). In the IR spectrum of **5** the signals of carbonyl groups as absorption bands at 1783 and 1754 cm^{-1} were detected (Figure S11). The number average molecular weight for the polyester **5** was determined by the same way as for polymer **4**, and the obtained value $M_n = 27\text{kDa}$ was very close to the that of polymer **4**. It is worth to mention that, compared to the IR spectrum pentiptycene-diol **1**, in the IR spectra of end-capped polymers **4–5** the signals of OH groups (an intensive band near 3400–3450 cm^{-1}) were not observed, and this fact may confirm the substitution of both OH groups of a parent pentiptycene **1**. Keeping in mind that the introduction of end-groups usually results in the termination of the polymer chain, one may suggest the much higher molecular weights for the polymers **2–3**. In addition to ^1H NMR studies, experiments on gel permeation chromatography (GPC) were attempted as another way for the determination of molecular weights for the polymers **2–3** and **4–5**. However, these experiments failed due to the partial precipitation of polymers from the THF solutions.

Pentiptycene-based small molecules and pentiptycene-based polymers have already found application as fluorescence-based chemosensors for various analytes, including those for the detection of nitroaromatic compounds [15]. Therefore, as a next step, the fluorescence response of pentiptycene diol **1** and pentiptycene-based polymers **2,5** to DNT and PA was evaluated.

Thus, in DMF solutions both pentiptycene **1** and pentiptycene-based polymers **2,5** exhibited emission bands near 350 nm, as well as strong fluorescence “*turn-off*” response upon the titration with solutions of DNT (10^{-3} M) or PA (10^{-3} M) (Figures S12–S17). According to the obtained results (Table 1), both pentiptycene-6,13-diol **1** and pentiptycene-based polymers **2,5** exhibited similar “*turn-off*” response to DNT and PA with the Stern-Volmer constant of

10^4 M^{-1} . This fact might be explained by the lack of the conjugation between the iptycene units within the polymer, which does not result in the signal amplification [28]. The best detection limit for DNT of 2819 ppm was calculated for the polyester **5**, while polycarbonate **2** exhibited the best one for the PA (2100 ppm).

Table 1 Stern-Volmer constant values and LOD for the pentiptycene-based chemosensors **1,2,5** in DMF solutions in the presence of DNT (10^{-3} M) and PA (10^{-3} M).

Chemosensor ^a	$K_{\text{DNT}}^{\text{sv}}, \text{M}^{-1}$	$K_{\text{PA}}^{\text{sv}}, \text{M}^{-1}$	LOD DNT/PA, ppm
1	$1.62 \cdot 10^4$	$1.20 \cdot 10^4$	4049/2709
2	$1.23 \cdot 10^4$	$1.12 \cdot 10^4$	3674/2100
5	$0.72 \cdot 10^4$	$1.09 \cdot 10^4$	2819/3958

^a Excitation at 305 nm.

4. Limitations

For the determination of molecular weight of polymers **2–5** gel permeation chromatography (GPC) experiments were attempted. However, these experiments failed due to the partial precipitation of polymers **2–5** from the THF solutions. Therefore, number average molecular weight (M_n) was estimated for the more soluble $\text{C}(\text{O})\text{C}(\text{CH}_3)_3$ -capped polymers **4–5** by means of ^1H NMR assisted end-group analysis.

In the experiments on studying sensory response of the obtained polymers **2,5** towards nitroanalytes a very weak fluorescence “*turn-off*” response was observed in DMSO solutions. Therefore, the experiments were carried out in a freshly distilled DMF, and a well-pronounced “*turn-off*” response was observed.

5. Conclusions

In summary, pentiptycene-based polyesters and polycarbonates as possible representatives of PIMs were synthesized by means of polycondensation reaction between pentiptycene-6,13-diol and triphosgene or oxalyl chloride under ball-milling conditions. The obtained polymers were characterized by means ^1H NMR- and IR-spectroscopy. In addition, number average molecular weight (M_n) of end-capped polyiptycenes was calculated by means of ^1H NMR assisted end-group analysis. Both pentiptycene-6,13-diol **1** and pentiptycene-based polymers **2,5** exhibited a well-pronounced fluorescence “*turn-off*” response to the presence of such common nitroanalytes as DNT and PA in the solution of DMF; 10^4 M^{-1} Stern-Volmer constants were observed. Based on all mentioned above, the polyiptycenes obtained herein can be considered as promising materials for the visual detection of nitroanalytes in solutions.

• Supplementary materials

This manuscript contains supplementary materials, which are available on the corresponding online page.

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МИНИСТЕРСТВО НАУКИ
И ВЫСШЕГО ОБРАЗОВАНИЯ
РОССИЙСКОЙ ФЕДЕРАЦИИ

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● Conflict of interest

The authors declare no conflict of interest.

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