

The first soluble conjugated poly(2,6-anthrylene): synthesis and properties†

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Received (in Cambridge, UK) 3rd September 2007, Accepted 4th December 2007

First published as an Advance Article on the web 18th December 2007

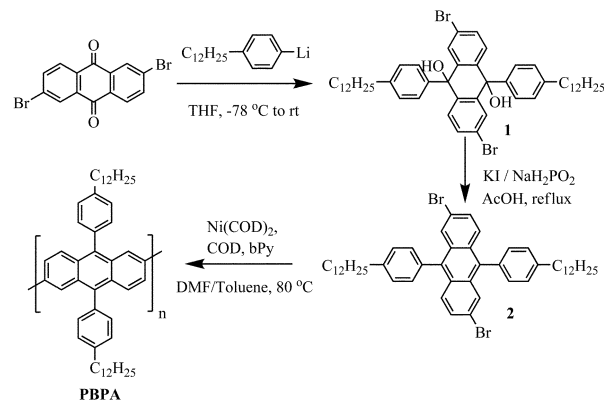
DOI: 10.1039/b713463k

The first soluble conjugated poly(2,6-anthrylene) with 9,10-diphenyl-anthracene as the repeating unit is reported; photophysical studies reveal that this polymer represents a novel well-conjugated system.

Conjugated polymers are of current interest due to their intriguing optoelectronic properties and advantageous low-cost solution processing, and as a result they have been intensively studied in a variety of optoelectronic applications.¹ These applications in turn encourage the incessant exploration of conjugated polymers with new structures. Anthracene is a very important aromatic unit during the development of organic optoelectronics. For instance, organic electroluminescence was first demonstrated from its single crystals.² Due to its promising light-emitting properties and charge carrier transport properties, anthracene has been widely used as a building block for conjugated small molecules, oligomers and polymers with promising optoelectronic properties.^{3–8} Several groups have reported oligomers and polymers composed of 9,10-linked anthracene derivatives.^{9–11} Ladder-type conjugated polymers containing 9,10-diaryl-anthracene and naphthylene have also been reported by Zheng and Scherf, respectively.¹² Müllen *et al.* reported the synthesis and properties of oligo(9,10-anthrylene)s and poly(*p*-phenylene-*alt*-9,10-anthrylene)s.^{9,10} In this case, the main chain of the oligomers and polymers is strongly twisted because of the high steric hindrance. For example, the dihedral angle between neighboring repeating units in 9,9'-bianthryl is up to 81.5°.¹³ Thereby the conjugation of these molecules is severely limited. Extending the molecular length along the 2 and 6 positions of anthracene should enable elimination of the detrimental effect of steric hindrance on molecular conjugation. However, to date only a few poly(2,6-anthrylene)s and oligo(2,6-anthrylene)s, which are insoluble in common organic solvents, have been reported.^{14,15} Hodge *et al.* synthesized the first poly(2,6-anthrylene) *via* a precursor approach.¹⁴ Oligo(2,6-anthrylene)s up to trimers were demonstrated by Ito *et al.*, and were used in fabrication of organic thin-film transistors (OTFTs) by vacuum deposition technique.¹⁵ We recently also reported the synthesis and properties of the first solution processable con-

jugated oligo(2,6-anthrylene)s through introducing alkynyl substituents at 9 and 10 positions of anthracene units.¹⁶ However, their solubility decreases dramatically with increasing repeating unit up to 5. Consequently, synthesis of soluble poly(2,6-anthrylene) was not successful. In the current paper, we report the synthesis and properties of the first solution processable poly(2,6-anthrylene), *i.e.* poly[9,10-bis(*p*-dodecylphenyl)anthracen-2,6-diyl] (**PBPA**), through introduction of one pair of *p*-dodecylphenyl groups at the 9 and 10 positions of the anthracene units. Photophysical studies of this polymer and its oligomeric model compounds reveal that extending the molecular length along the 2 and 6 positions of anthracene does endow the molecules with better conjugation.

The chemical structure and the synthesis of the polymer **PBPA** are depicted in Scheme 1. The repeating unit, diphenylanthracene, is a well-known blue light-emitting unit with high photoluminescence (PL) quantum yield and high mobility for both electrons and holes.¹⁷ To synthesize the polymer, *p*-bromododecylbenzene was first treated with *n*-BuLi. Then 2,6-dibromoanthraquinone was reacted with the resulting *p*-dodecylphenyllithium followed by reduction with KI–NaH₂PO₂ to afford 2,6-dibromo-9,10-bis(*p*-dodecylphenyl)anthracene (**2**) in a yield of 40% over two steps. The polymer **PBPA** was finally synthesized by means of a typical Yamamoto coupling reaction in a yield of 60% as a light-yellow fiber after purification by Soxhlet extraction and repetitive precipitation. The polymer is soluble in chloroform and chlorobenzene with the solubility > 10 mg mL⁻¹. The number-average molecular weight (*M_n*) and polydispersity (PDI) are 3.85 × 10⁴ g mol⁻¹ and 2.54, respectively, measured by means of gel-permeation chromatography (GPC) corresponding to a polystyrene standard. This *M_n* value might be overestimated as



Scheme 1 Synthesis of the polymer **PBPA**.

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† Electronic supplementary information (ESI) available: Complete synthetic and experimental data. See DOI: 10.1039/b713463k

observed in other conjugated polymers.¹⁸ Thermogravimetric analysis (TGA) measurements reveal that **PBPA** is highly stable with a decomposition temperature of 353 °C (5 wt% weight loss) in a N₂ atmosphere. Neither a glass transition nor crystal melting or a liquid crystalline–isotropic transition was observed in the temperature range of 25–300 °C by means of both differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

The polymer **PBPA** exhibits similar optical properties to ladder-type **P3** in ref. 12*a*. Displayed in Fig. 1 are UV-Vis absorption and PL spectra of **PBPA** in chloroform solution (10⁻⁵ M of repeating unit) and in the film state. In dilute solution, **PBPA** exhibits an absorption maximum of 462 nm, corresponding to the π - π^* transition of the conjugated backbone. This polymer emits bluish green PL with a maximum of 482 nm and a quantum yield of 0.53 (Measured in chloroform with quinine as a standard¹⁹). Only a 20 nm Stokes shift and the well-resolved absorption spectrum indicate that the polymer backbone is fairly rigid. From the dilute solution to the film, both absorption and PL spectra display a small red-shift of 5 nm. This indicates that there is almost no conformation change of the polymer backbone from solution to film state. Meanwhile, no any new peak corresponding to aggregation was observed, probably ascribed to that the twist phenyl groups in diphenylanthracene unit can suppress the close packing of the polymer chain. As known from the reference, there is an internal rotation of the phenyl ring by $\sim 70^\circ$ from the plane of anthracene.²⁰

To fully understand the structure–property correlation of the current conjugated system, oligo[9,10-di(*p*-tolyl)anthracen-2,6-diyls (**OA-*n***, Fig. 2) with number of repeating units $n = 1$ –3 have been synthesized (ESI†). As shown in Fig. 3, with increasing number of repeating units, the absorption maximum is red-shifted from 397 nm for **OA-1** to 419 nm for **OA-2** and then to 439 nm for **OA-3**. Introduction of one more unit results in a red shift of 22 and 20 nm for **OA-1** to **OA-2** and **OA-2** to **OA-3**, respectively. Moreover, there is still a 23 nm red-shift from **OA-3** to the polymer **PBPA**. In contrast, the absorption of oligo(9,10-anthrylene)s from the dimer to the trimer is only red-shifted around 10 nm.^{9*b*} This indicates that extending the molecular length along the 2 and 6 positions does endow the molecules with better conjugation.

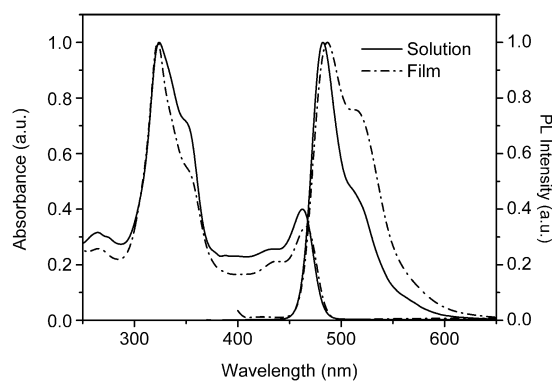


Fig. 1 Solution (10⁻⁵ M of the repeating unit in chloroform) and film UV-Vis absorption (left hand peaks) and PL (right hand peaks) spectra of **PBPA**.

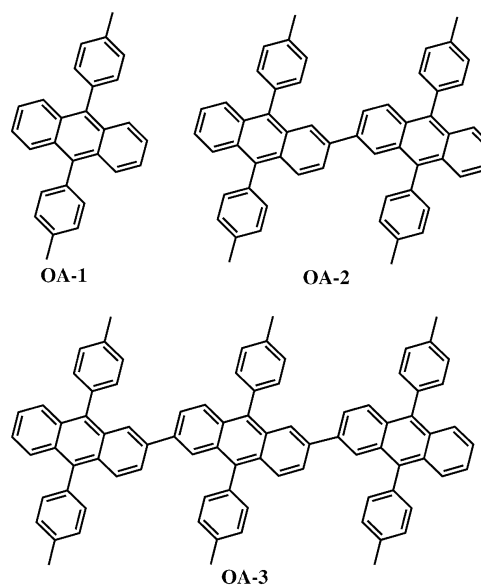


Fig. 2 Structures of the oligomers **OA-*n***.

In a similar trend, the PL maximum of **OA-*n*** is red-shifted from 418 nm for **OA-1** to 458 nm for **OA-2** and 467 nm for **OA-3**.

The electrochemical properties of **OA-1**, **OA-2** and **OA-3** were characterized in methylene chloride in a three-electrode electrochemical cell with Bu₄NPF₆ (0.1 M) and Ag/AgCl as the electrolyte and reference electrode, respectively. All oligomers exhibit one or several reversible redox processes at positive potential, and the number of redox waves is related to the number of repeating units. As depicted in Fig. 4, the oligomers **OA-1**, **OA-2** and **OA-3** exhibit one redox couple at (1.23 V, 1.11 V), two redox couples at (1.15 V, 1.03 V) and (1.40 V, 1.28 V), and three redox couples at (1.09 V, 0.99 V), (1.26 V, 1.16 V) and (1.47 V, 1.37 V), respectively. With increasing molecular length, the first oxidation potential decreases gradually, indicating an easier oxidation process. Meanwhile, the potential difference between the first and second oxidation processes also decreases in the order of **OA-2** (250 mV) and **OA-3** (170 mV). All these features are typical behaviors of conjugated π -systems, such as oligophenylenes,²¹ oligo(phenylenevinylene)s,²² oligo-thiophenes,²³ and oligo(fluorene-*co*-bithiophene)s.²⁴ In contrast, the first

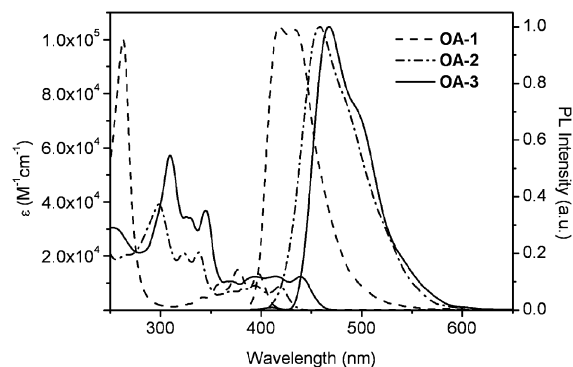


Fig. 3 UV-Vis absorption and PL spectra of **OA-*n*** in chloroform with the concentration of 10⁻⁵ M.

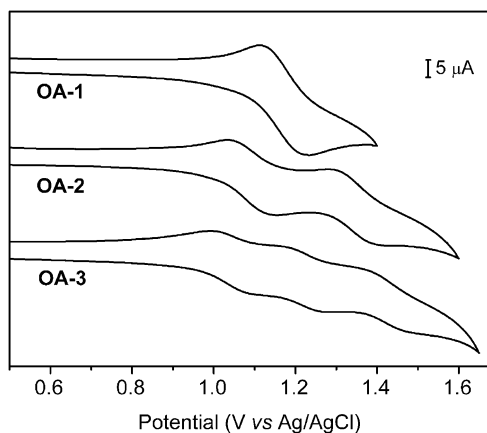


Fig. 4 Cyclic voltammograms of the **OA-1**, **OA-2** and **OA-3** at a scan rate of 50 mV s^{-1} .

oxidation potential of oligo(9,10-anthrylene)s is almost the same from 9,9'-bianthryl to 2',3'-dihexyl-9,10-trisanthrylene.^{9a} From the onset oxidation potentials, the highest occupied molecular orbital (HOMO) energy levels of oligomers **OA-1**, **OA-2** and **OA-3** were estimated to be -5.49 , -5.41 and -5.37 eV, respectively. A satisfactory cyclic voltammogram of polymer **PBPA** could not be obtained in methylene chloride due to its low solubility. However, its HOMO energy level should be higher than -5.37 eV.

In summary, we have successfully synthesized the first soluble conjugated poly(2,6-anthrylene) and its oligomeric model compounds with 9,10-diphenylanthracene as the repeating unit. Photophysical studies confirm that they represent a novel well-conjugated system. Further investigation of their optoelectronic properties is under the way.

This work is supported by NSFC (Nos. 20423003, 20674083 and 20521415), and Science Fund for Creative Research Groups of NSFC (20621401).

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