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Synthesis and magnetic characterization of monodisperse oligo(9,10-anthryleneethynylene)-based polyradicals with two pendant stable phenoxyls in one anthracene skeleton

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Abstract

We synthesized monodisperse oligo(9,10-anthryleneethynylene)s with pendant phenol residues at the 2- and 7-positions. The absorption maxima of oligomers shifted to longer wavelength with the degree of polymerization, suggesting a developed π-conjugation correlated with the chain length. The static magnetic susceptibility of the dimeric radical was measured using a SQUID magnetometer, and the $2J$ (J: spin coupling constant through the dianthrylacetylene unit) value of the dimeric radical was 34 cm^{-1}, which agreed with the $2J$ value of the corresponding 2-substituted dimeric radical (31 cm^{-1}). These large $2J$ values of the dimeric radicals can be explained from less steric hindrance between the side chain radicals and the backbone.

Keywords: Conjugated polymer; Polyradical; Phenoxyl; Poly(aryleneethynylene); Anthracene; High-spin polymer

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1. Introduction

π-Conjugated polymers bearing a number of free radical groups, so-called π-conjugated pendant polyradicals, have been regarded as one of the possible candidates for pure organic magnetic materials for the following reasons [1]: (1) magnetic through-bond interaction between the pendant spins is theoretically predicted by the regioregularity or substitution positions of the radical centers at the π-conjugated polymers; (2) a great number of spin sites are accumulated along one backbone or within one molecule via one-pot polymerization, and spin exchange coupling between electron spins through the π-conjugation system can be relatively strong; (3) various polyradicals are designed by the combination of π-conjugated polymers as the backbone and chemically stable radical species as the pendant group; (4) the regioregular head-to-tail π-conjugated polymers possessing pendant radicals essentially have insensitivity to spin defects due to their connectivity in that the multiple spins are connected by one ferromagnetic coupler. We have already succeeded in synthesizing a poly(9,10-anthryleneethynylene) (**Anc**) with pendant phenoxyl radicals at the 2- and 7-positions which has high durability to spin defects and a large average S value ($S = 5/2$) corresponding to the ferromagnetic spin coupling network spreading throughout the π-conjugated chain [2,3]. In this study, we synthesized the corresponding monodisperse oligomeric radicals to clarify the magnetic interaction and electronic properties of the polyradical (see Chart 1).

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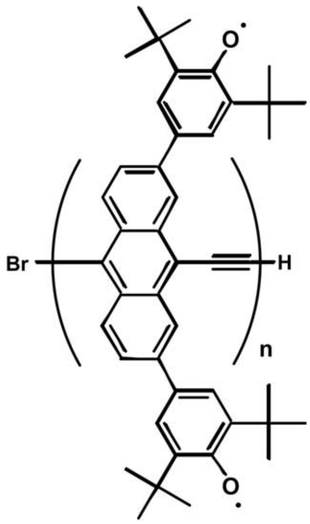

Anc

Chart 1.

2. Experimental

2.1. Materials

The monomers, 2,7-bis(4-acetoxy-3,5-di-*tert*-butylphenyl)-10-bromo-9-(3-hydroxy-3-methyl-1-butynyl)anthracene (**A1a**) and 2,7-bis(4-acetoxy-3,5-di-*tert*-butylphenyl)-9-bromo-10-(3-hydroxy-3-methyl-1-butynyl) anthracene (**B1a**), were synthesized as previously described [2]. Other conventional reagents were used as received or purified by conventional method.

2.2. Polymerization and fractionation

Polymerization was carried out by modifying the conditions described in [2,4]. The monomer **A1a** (166 mg, 0.2 mmol), tetrakis(triphenylphosphine)palladium(0) (2.3 mg, 0.002 mmol), and copper iodide (0.38 mg, 0.002 mmol) were placed in an Schlenk tube under a nitrogen atmosphere. Freshly distilled toluene (2 ml) was transferred to the tube, and the monomers were dissolved with stirring. 5 M KOH methanol solution (0.02 ml) was added to the monomer solution, and the mixture was heated at 110 °C for 3 h. After cooling, the reaction mixture was poured into methanol to yield polymer precipitate. The methanol soluble fraction was purified by silica gel column separation with chloroform and hexane/ethyl acetate (16/3 v/v) as an eluent to give the dimer **A2a** and the trimer **A3a**. The precipitate was purified by preparative GPC with chloroform as an eluent to give the monodisperse oligomers **A2a**–**A5a**. The dimer **B2a** was synthesized as described above.

A2a: Yield 8.7%. TLC (hexane/ethyl acetate = 4/1 v/v): $R_f = 0.28$. IR (KBr, cm^{-1}) 3460 ($\nu_{O–H}$), 2968–2860 ($\nu_{C–H}$, *tert*-butyl), 1768 ($\nu_{C=O}$). ^{1}H NMR (CDCl$_3$, 500 MHz; ppm) δ 1.27 (s, 36H, *tert*-butyl), 1.45 (s, 36H, *tert*-butyl), 1.87 (s, 6H, CH$_3$), 2.22 (s, 1H, OH), 2.32 (s, 6H, COCH$_3$), 2.41 (s, 6H, COCH$_3$), 7.77 (s, 4H, PhH), 7.79 (s, 4H, PhH), 7.87 (dd, 2H, $J = 8.9$, 1.7 Hz, ArH), 7.99 (dd, 2H, $J = 9.2$, 1.7 Hz, ArH), 8.71 (d, 2H, $J = 9.2$ Hz, ArH), 8.81 (d, 2H, $J = 1.7$ Hz, ArH), 8.92 (d, 2H, $J = 8.8$ Hz, ArH), 9.12 (d, 2H, $J = 1.7$ Hz, ArH). ^{13}C NMR (CDCl$_3$; ppm): δ 22.61, 22.73, 31.35, 31.39, 31.51, 31.60, 31.79, 35.57, 35.69, 66.23, 79.19, 98.35, 98.88, 107.60, 118.00, 118.25, 118.36, 124.43, 124.53, 124.71, 125.56, 125.61, 127.45, 127.52, 127.64, 127.71, 129.09, 129.57, 131.36, 132.76, 133.85, 136.82, 137.56, 139.46, 139.71, 143.05, 147.99, 148.07, 170.97, 171.15.

A3a: Yield 5.0%. TLC (hexane/ethyl acetate = 4/1 v/v): $R_f = 0.17$. ^{1}H NMR (CDCl$_3$, 500 MHz; ppm) δ 1.27 (s, 36H, *tert*-butyl), 1.30 (s, 36H, *tert*-butyl), 1.46 (s, 36H, *tert*-butyl), 1.87 (s, 6H, CH$_3$), 2.04 (s, 1H, OH), 2.31 (s, 6H, COCH$_3$), 2.32 (s, 6H, COCH$_3$), 2.41 (s, 6H, COCH$_3$), 7.76 (s, 4H, PhH), 7.80 (s, 4H, PhH), 7.81 (s, 4H, PhH), 7.91 (dd, 2H, $J = 9.0$, 1.7 Hz, ArH), 7.94 (dd, 2H, $J = 9.0$, 2.0 Hz, ArH), 8.01 (dd, 2H, $J = 9.3$, 1.7 Hz, ArH), 8.74 (d, 2H, $J = 9.3$ Hz, ArH), 8.83 (d, 2H, $J = 1.7$ Hz, ArH), 8.99 (d, 2H, $J = 9.0$ Hz, ArH), 9.01 (d, 2H, $J = 9.0$ Hz, ArH), 9.17 (br, 4H, ArH).

A4a: Yield 1.8% (estimated from chromatogram of GPC). TLC (hexane/ethyl acetate = 4/1 v/v): $R_f = 0.08$. ^{1}H NMR (CDCl$_3$, 500 MHz; ppm) δ 1.27 (s, 36H, *tert*-butyl), 1.29 (s, 36H, *tert*-butyl), 1.31 (s, 36H, *tert*-butyl), 1.47 (s, 36H, *tert*-butyl), 1.88 (s, 6H, CH$_3$), 2.31 (s, 6H, COCH$_3$), 2.316 (s, 6H, COCH$_3$), 2.32 (s, 6H, COCH$_3$), 2.41 (s, 6H, COCH$_3$), 7.78 (s, 4H, PhH), 7.79 (s, 4H, PhH), 7.81 (s, 8H, PhH), 7.92 (dd, 2H, $J = 9.0$, 1.7 Hz, ArH), 7.96 (dd, 2H, $J = 9.0$, 2.0 Hz, ArH), 7.98 (dd, 2H, $J = 9.0$, 2.0 Hz, ArH), 8.01 (dd, 2H, $J = 9.3$, 1.7 Hz, ArH), 8.74 (d, 2H, $J = 9.3$ Hz, ArH), 8.83 (d, 2H, $J = 1.7$ Hz, ArH), 9.01 (d, 2H, $J = 9.0$ Hz, ArH), 9.03 (d, 2H, $J = 9.0$ Hz, ArH), 9.08 (d, 2H, $J = 9.0$ Hz, ArH), 9.18 (br, 4H, ArH), 9.22 (d, 2H, $J = 1.7$ Hz, ArH).

A5a: Yield 1.0% (estimated from chromatogram of GPC). TLC (hexane/ethyl acetate = 4/1 v/v): $R_f = 0.06$. ^{1}H NMR (CDCl$_3$, 500 MHz; ppm) δ 1.28 (s, 36H, *tert*-butyl), 1.302 (s, 36H, *tert*-butyl), 1.305 (s, 36H, *tert*-butyl), 1.31 (s, 36H, *tert*-butyl), 1.47 (s, 36H, *tert*-butyl), 1.88 (s, 6H, CH$_3$), 2.315 (s, 6H, COCH$_3$), 2.318 (s, 6H, COCH$_3$), 2.32 (s, 6H, COCH$_3$), 2.33 (s, 6H, COCH$_3$), 2.41 (s, 6H, COCH$_3$), 7.79 (s, 4H, PhH), 7.80 (s, 4H, PhH), 7.81 (m, 12H, PhH), 7.91–8.03 (m, 10H, $J = 9.3$, 1.7 Hz, ArH), 8.74 (d, 2H, $J = 9.3$ Hz, ArH), 8.83 (d, 2H, $J = 1.7$ Hz, ArH), 9.01 (d, 2H, $J = 9.0$ Hz, ArH), 9.04 (d, 2H, $J = 9.0$ Hz, ArH), 9.10 (d, 2H, $J = 9.0$ Hz, ArH), 9.11 (d, 2H, $J = 9.0$ Hz, ArH), 9.19 (br, 4H, ArH), 9.23 (br, 4H, ArH).

B2a: Yield 5.0%. TLC (hexane/ethyl acetate = 4/1 v/v): $R_f = 0.26$. IR (KBr, cm^{-1}) 3460 ($\nu_{O–H}$), 2972–2860 ($\nu_{C–H}$, *tert*-butyl), 1762 ($\nu_{C=O}$). ^{1}H NMR (CDCl$_3$,