

Photoresponsive palladium(II) complexes with azobenzene incorporated into benzyl aryl ether dendrimers

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Abstract

Palladium(II) complexes, $[\text{Pd}(\text{GX-azb})_2\text{Cl}_2]$ (where *azb* = azobenzene, *GX* = benzyl-aryl ether dendron of generation $X = 1, 2, 3$), were prepared and their photophysical properties were examined. The synthesized complexes were characterized by chemical analysis, ^1H NMR and UV spectroscopy. The photochromic dendritic azobenzene ligands within the complexes $[\text{Pd}(\text{GX-azb})_2\text{Cl}_2]$ undergo a reversible *trans/cis* isomerization upon exposure to ultraviolet light.

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1. Introduction

Conformational changes and isomerization of the molecules under the influence of appropriate external stimulus (light irradiation, electric and magnetic field, temperature, pressure, etc.) play a central role in diverse natural and artificial molecular machinery [1]. For instance, photoisomerization reactions are at the basis of the natural visual processes [2], and often used in artificial nanomachines to promote mechanical movements [3]. Molecular-scale logic gates allow the usage of light signals for information processing at the nano-level [4]. Energy migration is exploited for light harvesting in natural and artificial antenna devices [5]. Photoinduced electron transfer is the basic process for the conversion of light into chemical energy in natural photosynthesis [6], as well as in attempts to perform artificial photosynthesis [7]. Photoisomerization and photocatalytic reactions of azobenzenes have attracted much attention for over half a century because of both theoretical and

industrial interests [8]. Recently, photoresponsive dendrimers were prepared on this basis [9]. Dendrimers, a new class of macromolecules with well-defined three-dimensional shapes, allow incorporation of great number of chromophore units and precise placement of a photoactive moiety within the center of hyperbranched molecule. Thus, light-induced small configurational changes in that center will effect in a large configurational change of the whole dendritic macromolecule. At the same time, azobenzene derivatives can serve as ligands in the syntheses of coordination complexes. Many interesting examples of *ortho*-palladated complexes using the azobenzene unit as a building block for metallomesogenic and metallopolymer structures have been synthesized [10]. Increasing interest to multiple cyclopalladated derivatives was connected with their exceptional electronic and structural properties. A number of studies concerned with the photoisomerization of azo-conjugated metal complexes have been reported [11]. This recent activity is due to the great potential of azo-conjugated transition metal complexes for providing new advanced molecular functions based on combinations of photoisomerization of the azo-group and subsequent changes in the intrinsic properties of transition metal ions,

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i.e. in the optical, redox, and magnetic properties from the d-electrons. However, up to this time there is no reported examples of reversible *trans/cis* isomerization in the metal-complexes where azobenzene molecule is solely bonded by an N: \rightarrow M σ -bond [12]. Recently, we have synthesized the mesogenic palladium complexes without *ortho*-cyclopalladation by a ligand exchange reaction of $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ with the corresponding imine ligands [13]. Here, we report the synthesis of similar N: \rightarrow M σ -bonded palladium(II) complexes with benzyl-aryl ether dendron-containing azobenzene ligands, which undergo reversible configurational changes in response to light exposure.

2. Experimental

2.1. General remarks

Dendritic azobenzene ligands **1a–c** were prepared according to the literature method [9a], and $[(\text{PhCN})_2\text{PdCl}_2]$ complex was synthesized according to the described procedure [14]. All solvents were distilled and dried before using. TLC plates from Merck (Silica Gel 60, F-254, 0.25 mm) were used for monitoring of the reactions. Neutral alumina (activated, Brockman I, standard grade, 150 mesh) from Aldrich was used for the column flash-chromatography. Elemental analyses were performed in Seoul National University using EA1110 (CHNS) element analyzer. ^1H NMR spectra were obtained on Bruker AM-250 spectrometer. UV–Vis absorption spectra were recorded on Hewlett–Packard HP-8453 spectrometer in a 1 cm quartz cell. MALDI-TOF experiments with compound **2a** (CH_2Cl_2 solution) were carried out on 4700-Proteomics analyzer (Voyager STR Bioworkstation, Applied Biosystems) using an α -cyano-4-hydroxycinnamic acid matrix. Photoisomerization experiments were performed by irradiation of CH_2Cl_2 solutions (1×10^{-4} M) of complexes **2a–c** in a quartz cell of 1 cm path thickness by a 300W xenon arc lamp through a band pass filter 350 ± 20 nm. ^1H NMR studies of the *trans/cis* isomerization were performed by irradiation of solutions of **2a–c** in an NMR tube. Molecular modeling of compound **2c** for illustrative purpose without full energy minimization was performed using a computer program HYPERCHEM-7 (Hypercube, Inc.).

2.2. Synthesis of **2a**

Compound **1a** (0.100 g, 0.12 mmol) was dissolved in 5 ml of benzene, and then $(\text{PhCN})_2\text{PdCl}_2$ (0.023 g, 0.06 mmol) was added to the mixture as a solid. The reaction mixture was stirred for 1 h, and the solvent was removed by evaporation under reduced pressure, and the crude product was purified by column (neutral alumina using methylene chloride and ethyl acetate as the eluent) to yield 0.087 g (80%) of yellow solid. ^1H NMR (250 MHz, CDCl_3): δ 4.96 (s, 8H, $\text{CH}_2\text{--C}_6\text{H}_5$), 4.97 (s, 8H, $\text{CH}_2\text{--C}_6\text{H}_5$), 4.99 (s, 4H, $\text{CH}_2\text{--C}_6\text{H}_3\text{O}_2$), 5.21 (s, 4H,

$\text{CH}_2\text{--C}_6\text{H}_3\text{O}_2$), 6.55 (t, 2H, $\text{C}_6\text{H}_3\text{O}_2$), 6.59 (d, 4H, $\text{C}_6\text{H}_3\text{O}_2$), 6.71 (t, 2H, $\text{C}_6\text{H}_3\text{O}_2$), 6.75 (d, 4H, $\text{C}_6\text{H}_3\text{O}_2$), 6.94 (d, 4H, $\text{C}_6\text{H}_4\text{--N}$), 7.27–7.41 (m, 44H, C_6H_5 overlapped with $\text{C}_6\text{H}_4\text{--N}$), 8.32 (d, 4H, $\text{C}_6\text{H}_4\text{--N}$), 8.55 (d, 4H, $\text{C}_6\text{H}_4\text{--N}$). MS (MALDI-TOF) m/z calc. 1815; found 1816 ($\text{M}+\text{H}$) $^+$. Anal. Calc. for $\text{C}_{108}\text{H}_{92}\text{Cl}_2\text{N}_4\text{O}_{12}\text{Pd}$: C, 71.46; H, 5.11; N, 3.09. Found: C, 71.15; H, 5.37; N, 3.01%.

2.3. Synthesis of **2b**

Pd(II) complex **2b** was prepared as described above by the reaction of compound **1b** (0.200 g, 0.12 mmol) with $(\text{PhCN})_2\text{PdCl}_2$ (0.023 g, 0.06 mmol). Yield 0.164 g (78%). ^1H NMR (250 MHz, CDCl_3): δ 4.84–5.19 (m, 56H, CH_2), 6.52–6.83 (m, 36H, $\text{C}_6\text{H}_3\text{O}_2$), 6.93 (d, 4H, $\text{C}_6\text{H}_4\text{--N}$), 7.27–7.39 (m, 84H, C_6H_5 overlapped with $\text{C}_6\text{H}_4\text{--N}$), 8.28 (d, 4H, $\text{C}_6\text{H}_4\text{--N}$), 8.49 (d, 4H, $\text{C}_6\text{H}_4\text{--N}$). Anal. Calc. for $\text{C}_{220}\text{H}_{188}\text{Cl}_2\text{N}_4\text{O}_{28}\text{Pd}$: C, 75.21; H, 5.39; N, 1.59. Found: C, 75.25; H, 5.44; N, 1.45%.

2.4. Synthesis of **2c**

Pd(II) complex **2c** was prepared as described above by the reaction of compound **1c** (0.200 g, 0.06 mmol) with $(\text{PhCN})_2\text{PdCl}_2$ (0.012 g, 0.03 mmol). Yield 0.155 g (75%). ^1H NMR (250 MHz, CDCl_3): δ 4.89–5.05 (m, 120H, CH_2), 6.55–6.69 (m, 84H, $\text{C}_6\text{H}_3\text{O}_2$), 6.91 (d, 4H, $\text{C}_6\text{H}_4\text{--N}$), 7.26–7.40 (m, 164H, C_6H_5 overlapped with $\text{C}_6\text{H}_4\text{--N}$), 8.34 (d, 4H, $\text{C}_6\text{H}_4\text{--N}$), 8.61 (d, 4H, $\text{C}_6\text{H}_4\text{--N}$). Anal. Calc. for $\text{C}_{444}\text{H}_{380}\text{Cl}_2\text{N}_4\text{O}_{60}\text{Pd}$: C, 77.18; H, 5.54; N, 0.81. Found: C, 77.22; H, 5.67; N, 0.72%.

3. Results and discussion

3.1. Synthesis and characterization

The palladium(II) complexes **2a–c** with η^1 -azobenzene were prepared by ligand exchange reaction of $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ [14] with the corresponding dendrimer-containing azobenzene ligands **1a–c** [9a] (Scheme 1). The crude products were purified by column chromatography (neutral alumina using methylene chloride and ethyl acetate as the eluent) to afford yellow solids.

Bulky dendritic substituents surrounding the azobenzene coordination site cause steric hindrances for the coordination of two ligands into a planar Pd(II) chelates. Single-bonded coordination to a Pd(II) central ion in N: \rightarrow Pd σ -bond complexes makes the cross-like orientation of dendritic azobenzene ligands in relation to each other possible. The azobenzene coordination sites of two dumb-bell shaped ligands in the latter case can easily approach each other and bound to the Pd(II) central ion, as is illustrated by computer simulation of the molecule of **2c** (see Fig. 1). Thus, the possibility of free-rotation around N: \rightarrow M σ -bond makes it feasible for Pd atom to bind two ligands into one dendromeric macromolecule

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