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Preparation and properties of DNA–lipid complexes carrying pyrene and anthracene moieties

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ABSTRACT

Novel DNA–lipid complexes carrying pyrene and anthracene were prepared by substituting sodium counter cations with cationic amphiphilic lipids, namely lipid(PY) and lipid(Anth), in which the actual mole ratios of phosphate to lipid were 1:1.11 and 1:1.03, respectively. DNA–lipid(PY) and DNA–lipid(Anth) complexes were soluble in common organic solvents including $CHCl_3$, CH_2Cl_2, methanol and ethanol, while insoluble in THF, toluene, and aqueous solutions. CD spectroscopy revealed that DNA–lipid(PY) and DNA–lipid(Anth) complexes took a predominantly double helical structure in methanol and that the helical structure was fairly stable against heating. The solution of DNA–lipid(PY) complex emitted fluorescence in 27.8% quantum yield, which were higher than that of the corresponding lipid(PY) (16.8%), while the fluorescence quantum yields of the solution of DNA–lipid(Anth) (45.4%) was lower than that of the lipid(Anth) (53.0%). The onset temperatures of weight loss of DNA–lipid(PY) and DNA–lipid(Anth) were both 220 °C according to TGA in air.

1. Introduction

DNA is an anionic polyelectrolyte, which can be quantitatively precipitated with cationic surfactants in water to form DNA/cationic–lipid complexes. DNA complexes have been studied intensively over recent years due to their potential in gene delivery and transfection methodologies. DNA complexes also remind us of the coil-to-globule transition in synthetic polymers, exhibiting intriguing liquid crystalline and polyelectrolyte behavior [1–3]. Much work has been dedicated to revealing supramolecular structures and morphologies in DNA/cationic–lipid complexes, which is primarily stimulated by nonviral gene delivery [4–9]. Specifically, cryo-TEM [10], freeze-fracture electron microscopy [11], synchrotron X-ray scattering [12], optical and fluorescence microscopies [13], and small-angle X-ray scattering (SAXS) [14] have given a fairly good picture of the structure of these complexes as a function of the lipid content and charge ratio between the cationic lipid and DNA. However, few efforts have been made about the development of DNA–cationic lipid complexes carrying functional groups in the lipid moieties as organic advanced materials for electronic optical applications and DNA molecule probes used in various biological studies.

On the other hand, pyrene and its derivatives have attracted special attention because of their interesting photophysical properties such as high fluorescence quantum yield, well characterized long-lived excited state, the sensitivity of its excitation spectra to microenvironment changes, high ability for excimer formation, and the sensitivity of its fluorescence to quenching. These characteristics of pyrene and its derivatives are suitable for the application as a sensor to microscopically probe an environment around the molecules under study [15,16]. Polymers containing pyrene moieties in the main chain or side chain have been widely studied because of their unique properties, which allow them to be applied to various photoelectronic materials including photoconductive,

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electroluminescent, and photorefractive materials [17,18]. Meanwhile, anthracene-based polymers consisting of layered π-electron and oriented π-electron systems have potential applications in optoelectronic devices and single-molecular devices such as single molecular wires [19,20]. Thus far, most of the studies on pyrene- and anthracene-containing polymer materials have been carried out using synthetic polymers. However, there is a growing interest in natural polymers and biomacromolecules for practical applications as functional materials especially from the viewpoints of bio- and nanotechnologies and sustainable materials science. Among various biomacromolecules, DNA is one of the most abundant substances in the biosphere and quite interesting as a candidate of source material for these applications.

Previously, we synthesized DNA–cationic lipid complexes carrying 2,2,6,6-tetramethyl-1-piperidine-1-oxy (TEMPO), applied them as positive electrode materials of organic radical battery (ORB), and found that the complexes displayed two-stage discharge process [21]. The total capacity of one TEMPO-containing DNA–cationic lipid complex reached 192% of the theoretical value for one electron redox reaction, suggesting two-electron redox reactions between the cation and the anion. We have also studied the DNA–lipid complexes carrying carbazole, triphenylamine [22,23], and azobenzene [24] moieties and found that their solution displayed electrochemical properties. Although no research has been performed about DNA complexes carrying pyrene and anthracene, incorporation of pyrene and anthracene moieties into DNA will possibly lead to the development of novel functional materials based on synergistic actions of pyrene and anthracene and DNA main chain. Such polymeric materials may form helical pyrene and anthracene strands based on the helical DNA main chain, which may endow efficient photoelectronic properties for potential applications such as nonlinear optics, field-effect transistors, photovoltaics, and so on. Especially, DNA–lipid complexes carrying pyrene and anthracene should be useful as photoluminescence probes in various biological gene therapies [25]. In the present paper, we would like to report for the first time the preparation and properties of pyrene- and anthracene-carrying DNA–lipids, namely Dna–lipid(PY) and DNA–lipid(Anth) (Scheme 1), aiming at the future development of advanced polymeric functional materials.

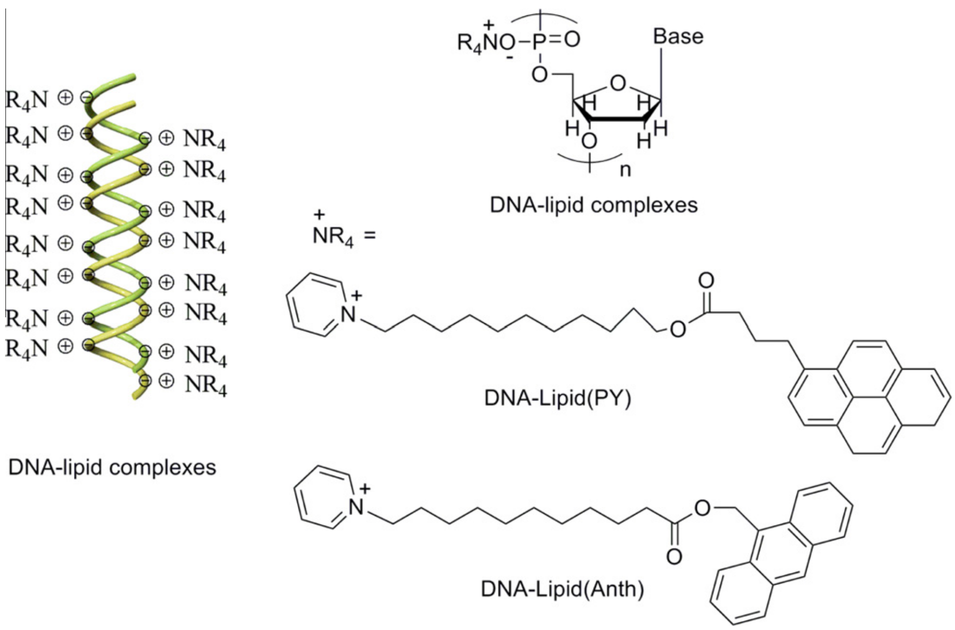
2. Experimental part

2.1. Materials

Sodium salts of DNA from salmon testes (>95%) were donated from Japan Chemical Feeding Company, and used without farther purification. According to the data of Japan Chemical Feeding Company, the weight-average molecular weight of the DNA sample is 6.6×10^6 (ca. 30 000 bp) (tested by electrophoresis). *N,N′*-Dicyclohexylcarbodiimide (DCC, Aldrich), 4-dimethylaminopyridine (DMAP; Wako), 11-bromoundecanoic acid (Aldrich), 4-(pyren-2-yl)butanoic acid (Aldrich), 11-bromoundecan-1-ol (Aldrich); (anthracen-10-yl)methanol (Aldrich) were purchased and used without further purification.

2.2. Measurements

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL EX-400 spectrometer using tetramethylsilane as an internal standard. IR, UV–vis, and fluorescence spectra were measured on JASCO FT/IR-4100, V-550, and FP750 spectrophotometers, respectively. Circular dichroism (CD) spectra were recorded on a JASCO



Scheme 1. The structure of DNA–lipid complexes.