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DNA–lipid complexes carrying carbazole and triphenylamine moieties: Synthesis, and chiroptical and photoelectronic properties

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ABSTRACT

Novel DNA–lipid complexes carrying carbazole and triphenylamine moieties were prepared by substituting the sodium counter cation with cationic amphiphilic lipids, namely lipid(Cz) and lipid(TPA), in which the actual mole ratios of phosphate to lipid were 1:1.10 and 1:0.83, respectively. The DNA–lipid(Cz) and DNA–lipid(TPA) 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 the DNA–lipid complexes took a predominantly double helical structure in $CHCl_3$ and methanol and that the helical structure was fairly stable against heating. Solutions of DNA–lipid(Cz) and DNA–lipid(TPA) complexes emitted fluorescence in 5.7 and 76.4% quantum yields, which were higher than those of the corresponding lipid(Cz) and lipid(TPA) (4.4 and 55.3%). The cyclic voltammograms of the complexes indicated that the oxidation potentials of DNA–lipid(Cz) and DNA–lipid(TPA) were 0.95 and 0.85 V, respectively. The onset temperatures of weight loss of the DNA–lipid complexes were both 220 °C according to TGA in air.

1. Introduction

Recently much attention has been paid to carbazole (Cz), triphenylamine (TPA) and their derivatives because they are promising candidates for photoluminescence and electroluminescence materials [1,2]. Polymers containing carbazole or triphenylamine 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, electroluminescent, and photorefractive materials [3,4]. Thus far, most of the studies have been carried out with 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 nanotechnology 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.

Since DNA is an important source of biological information depending on the base sequence [5], it has been gathering much attention as a powerful protocol for gene therapy, vaccination in biotechnology, and medical applications. Okahata et al. developed a facile method of synthesizing DNA–cationic lipid complexes and succeeded in the fabrication of membranes therefrom by casting their organic solutions [6]. DNA–cationic lipid complexes appear as promising gene delivery vehicles, and the structural and morphological studies have been reported. Specifically, cryo-TEM [7], freeze-fracture electron microscopy [8], synchrotron X-ray scattering [9], optical and fluorescence microscopies [10], and small-angle X-ray scattering (SAXS) [11] 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. Properties and electronic functions of DNA and its organosoluble derivatives were studied considerably either in the pure form or in the complexed form with the double helix [12–14].

To the best of our knowledge, however, no 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 and optical applications. For instance, although no research has been performed about DNA complexes carrying carbazoles and triphenylamines, incorporation of carbazole and triphenylamine moieties into DNA will possibly lead to the development of novel functional materials based on synergistic actions of carbazole and triphenylamine with DNA main chain.

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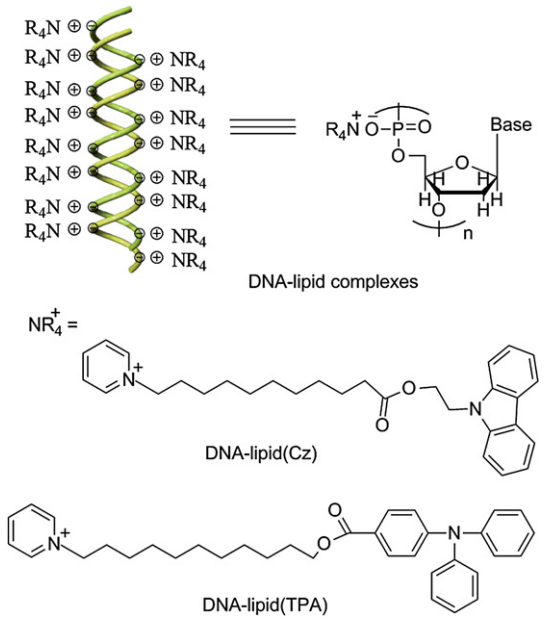


Scheme 1. The structure of DNA–lipid complexes.

Such polymers may form helical carbazole and TPA strands as well as a helical DNA main chain, which may endow efficient photoelectronic properties for potential applications such as one-dimensional semiconductors, nonlinear optics, field-effect transistors, photovoltaics, and so on. In the present paper, we would like to report for the first time the preparation and properties of DNA–lipids carrying carbazole and triphenylamine moieties, namely DNA–lipid(Cz) and DNA–lipid(TPA) (Scheme 1), aiming at the future development of advanced polymeric materials based on these materials.

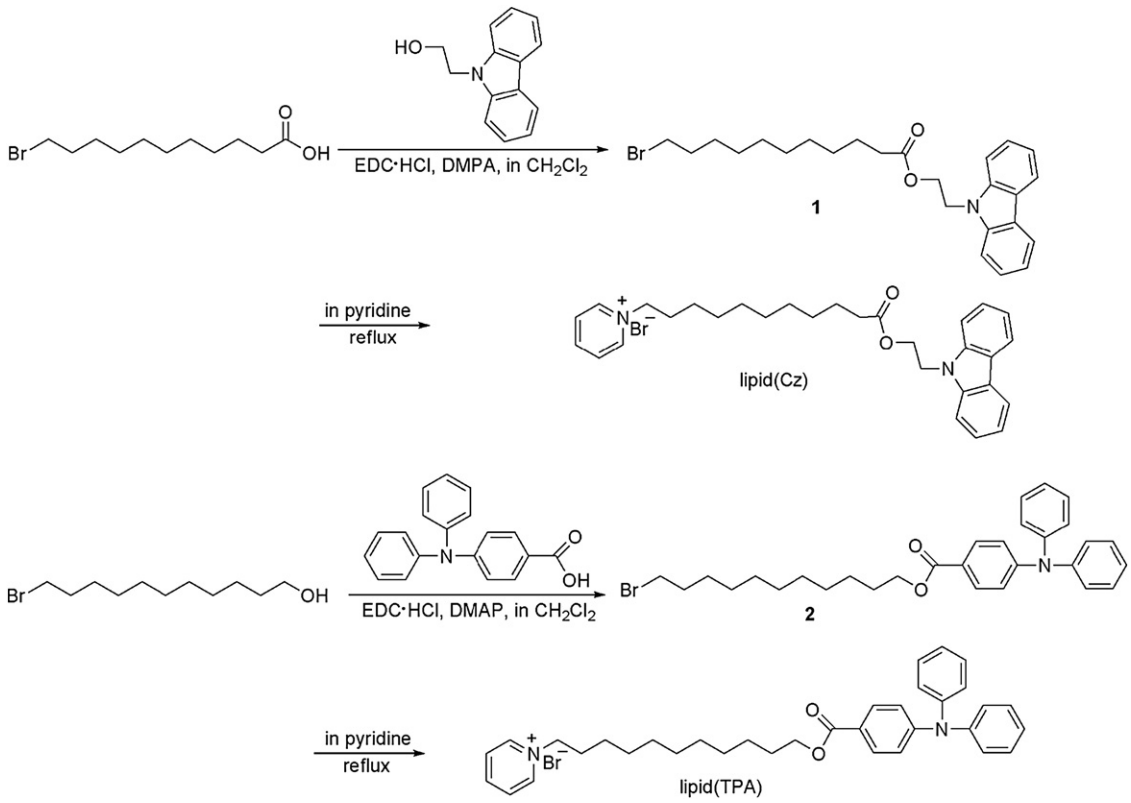
2. Experimental section

2.1. Materials

Sodium salts of DNA from the salmon testes (>95%) were donated from Japan Chemical Feeding Company, and used without further purification. According to the data of the company, the weight-average molecular weight of the DNA sample is 6.6×10^6 (ca. 30 000 bp) (tested by electrophoresis). 4-Dimethylaminopyridine (DMAP; Wako), 11-bromoundecanoic acid (Aldrich), 12-bromo-1-dodecanol (TCI), 9*H*-carbazol-9-yl-ethanol (Aldrich) were purchased and used without further purification. *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC·HCl; Eiweiss) was offered by Tokuyama Co. Ltd. 4-(Diphenylamino)-benzoic acid was synthesized according to the literature [15].

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 observed on JASCO FT/IR-4100, V-550, and FP750 spectrophotometers, respectively. CD spectra were recorded on a JASCO J-820 spectropolarimeter. Melting points (mps) were measured on a Yanaco micro melting point apparatus. Elemental analysis was conducted at the Kyoto University Elemental Analysis Center. Cyclic voltammograms were measured on an HCH Instruments ALS600A-n electrochemical analyzer. The measurements were carried out with a glassy carbon rod as a working electrode coupled with a Pt plate counter electrode and a Ag/AgCl reference electrode, with a solution of a polymer (1 mM) and tetrabutylammonium perchlorate



Scheme 2. Synthetic routes of lipid(Cz) and lipid(TPA).

(TBAP; 0.1 M) in $CHCl_3$. Thermal gravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 thermal analyzer. The content of Na ion was determined by inductively coupled plasma (ICP) emission spectrometry using a Shimadzu ICP-1000 IV spectrometer; DNA–lipid samples were dissolved in 2 N HCl.

2.3. Synthesis of lipids [16]

Scheme 2 illustrates the synthetic procedures of 9*H*-carbazol-9-yl-ethoxy-11-oxoundecyl pyridinium bromide [lipid(Cz)] and 4-(diphenylamino)benzoyloxy-11-undecyl pyridinium bromide [lipid(TPA)].

Lipid(Cz) was prepared as follows: 11-bromoundecanoic acid (1.33 g, 5.0 mmol) was added to a solution of EDC·HCl (1.0 g, 5.2 mmol) and DMAP (60 mg, 0.50 mmol) in CH_2Cl_2 (45 mL) at room temperature. 9*H*-Carbazol-9-yl-ethanol (1.20 g, 5.7 mmol) was added to the solution, and the resulting mixture was stirred at room temperature overnight. The reaction mixture was washed with water (50 mL) three times, and the organic layer was dried over anhydrous $MgSO_4$. It was filtered, and the filtrate was concentrated on a rotary evaporator. The residual mass was purified by silica gel column chromatography eluted with *n*-hexane/ethyl acetate = 19/1 (volume ratio) to give 9*H*-carbazol-9-yl-ethoxy-11-oxoundecyl bromide (**1**) as a white solid. Yield 1.96 g (85%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.17$–1.24 (m, 12H, $6CH_2$), 1.40–1.47 (m, 2H, $-OCOCH_2CH_2-$), 1.80–1.87 (m, 2H, $-CH_2CH_2Br$), 2.14–2.18 (m, 2H, $-OCOCH_2-$), 3.37–3.41 (m, 2H, $-CH_2Br$), 4.44–4.56 (m, 4H, $-CH_2CH_2Cz$), 7.21–8.09 (m, 8H, Cz). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 24.6$, 28.1, 28.7, 28.9, 29.1, 29.2, 29.3, 32.8, 34.0, 41.6, 61.9, 108.5, 119.2, 120.4, 123.0, 125.7, 140.4, 173.6 ($-CO_2-$). Anal. Calcd for $C_{25}H_{32}BrNO_2$: C, 65.50; H, 7.04; N, 3.06. Found: C, 65.46; H, 7.04; N, 3.10.

The above-stated product **1** (1.50 g, 3.3 mmol) was dissolved in 50 mL of pyridine and stirred at reflux temperature for 2 days. After cooling to room temperature, the reaction mixture was concentrated on a rotary evaporator, and then poured into a large amount

Table 1
Preparation of DNA–lipid complexes

Lipid	Yield[a] (%)	Ratio of replaced Na^{+}[b] (%)	Mole ratio of phosphate to lipid[c]
Lipid(Cz)	90	98	1:1.10
Lipid(TPA)	92	97	1:0.83

[a] DNA–lipid complex is the insoluble part in water. The yield was determined according to Eq. (1).
[b] Determined by ICP.
[c] Calculated by P elemental analysis according to Eq. (3).

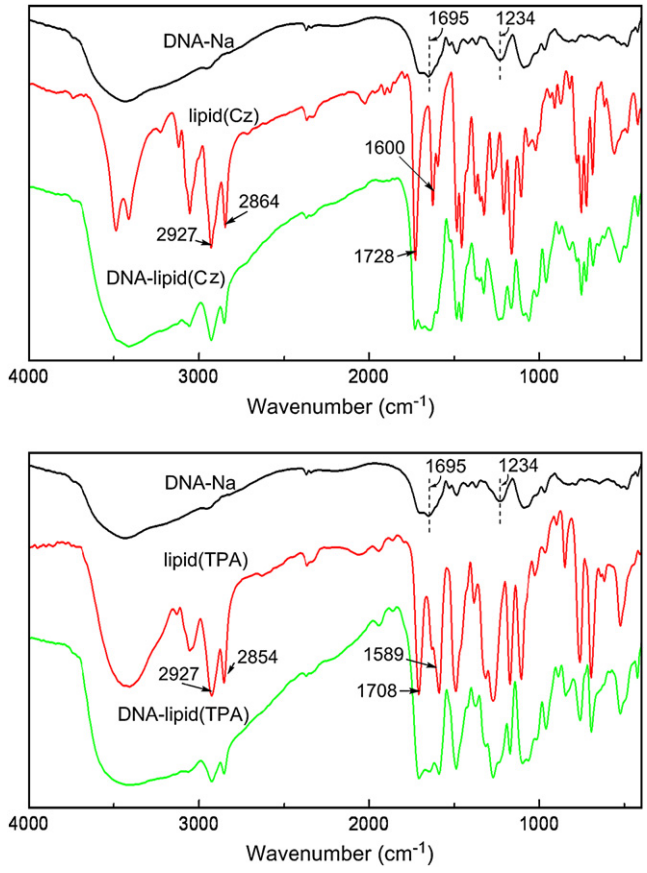


Fig. 1. IR spectra of DNA–Na, lipid(Cz), lipid(TPA), DNA–lipid(Cz), and DNA–lipid(TPA) (KBr pellet).

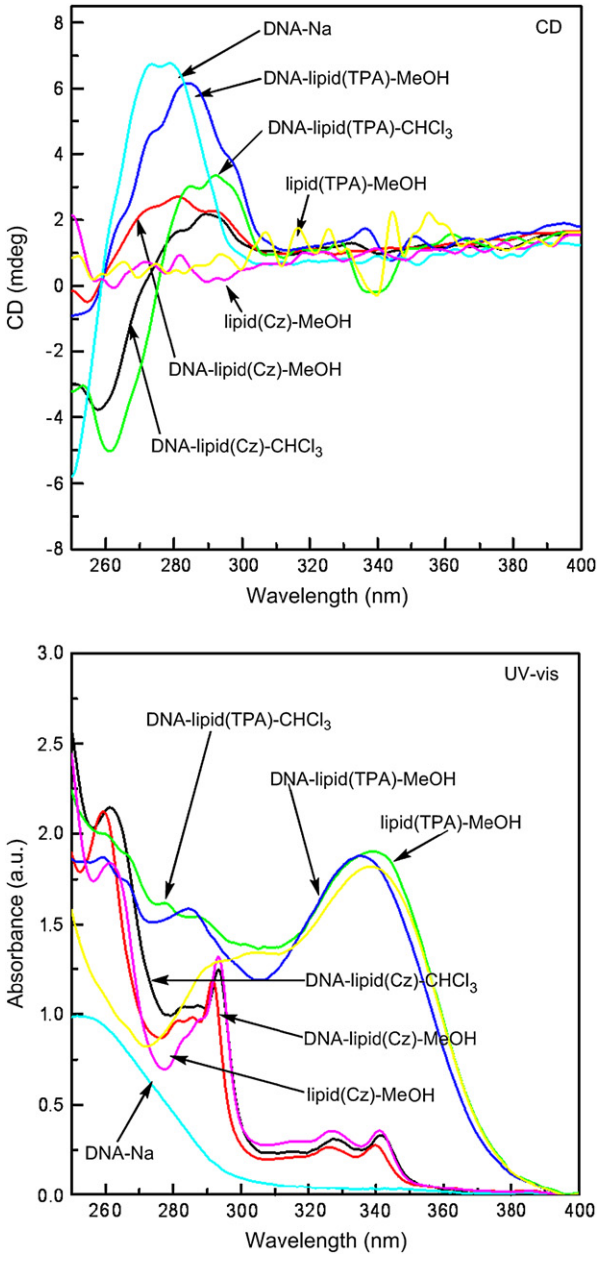


Fig. 2. CD and UV–vis spectra of lipid(Cz), lipid(TPA), DNA–lipid(Cz) and DNA–lipid(TPA) in $CHCl_3$ and methanol ($c = 0.025$ mg/mL) and DNA–Na in water ($c = 0.04$ mg/mL) at 22 °C.

of diethyl ether to precipitate lipid(Cz). The white crystals in this step were dried in vacuum: yield 1.2 g (61%, 2.0 mmol); mp 87–89 °C; IR (KBr): 3486, 3413, 3054, 2927, 2846, 1728, 1627, 1600, 1485, 1458, 1326, 1211, 1164, 752, 721, 559 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.12$ (s, 12H, $6CH_2$), 1.29 (s, 2H, $COCH_2CH_2$), 1.41 (d, 2H, pyridine–CH_2CH_2), 2.14 (m, 2H, –$OCOCH_2$), 4.43–4.56 (m, 4H, –CH_2CH_2Cz), 4.89 (m, 2H, pyridine–CH_2), 7.20–8.08 (m, 8H, Cz), 8.84–9.42 (m, 5H, pyridine). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 24.4$, 25.8, 28.6, 28.7, 28.8, 28.9, 29.0, 31.8, 33.8, 41.6, 50.2, 61.7, 108.5, 119.1, 120.2, 122.8, 125.7, 128.3, 140.2, 144.8, 144.9, 173.4. Anal. Calcd for $C_{30}H_{37}N_2O_2Br$: H, 6.94; C, 67.03; N, 5.21. Found: C, 67.16; H, 6.84; N, 5.10.

Lipid(TPA) was synthesized in a manner similar to that of lipid(Cz). Compound **2**: yield 88%, pale yellow solid. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.24$–1.28 (m, 12H, $6CH_2$), 1.41–1.45 (m, 2H, –$OCOCH_2CH_2$), 1.80–1.87 (m, 2H, –CH_2CH_2Br; m, 2H, –CH_2CH_2–O–CO–TPA), 3.37–3.41 (m, 2H, –CH_2Br), 4.28 (m, 2H, –CH_2OCO–TPA), 6.98–7.86 (m, 14H, TPA). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 26.0$, 28.1, 28.7, 28.8, 29.2, 29.4, 29.5, 32.8, 34.0, 50.2, 64.7, 120.0, 122.5, 124.3, 125.7, 129.5, 130.7, 130.9, 145.4, 150.3 165.6. Anal. Calcd for $C_{30}H_{36}BrNO_2$: C, 68.96; H, 6.94; N, 2.68. Found: C, 69.01; H, 7.12; N, 2.64.

Lipid(TPA): yield 57%, pale grey solid; mp 75–77 °C. IR (KBr): 3409, 3054, 2927, 2854, 1708 ($\nu_{C=O}$), 1589, 1489, 1315, 1272, 1173, 1107, 760, 694, 524 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.24$–1.28 (m, 12H, $6CH_2$), 1.41–1.45 (m, 2H, –$OCOCH_2CH_2$), 1.80–1.87 (q, 2H, pyridine ring–CH_2CH_2; m, 2H, –CH_2CH_2–O–CO–TPA), 3.39 (m, 2H, pyridine $^+CH_2$), 4.28 (m, 2H, –CH_2OCO–TPA), 6.98–7.86 (m, 14H, TPA), 8.10 (m, 2H, pyridine ring), 8.56–8.60 (t, 1H, pyridine ring), 8.98–9.00 (d, 2H, pyridine ring). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 26.0$, 28.1, 28.7, 28.8, 29.2, 29.4, 29.5, 32.8, 34.0, 50.2, 64.7, 120.0, 122.5, 124.3, 125.7, 129.5, 130.7, 130.9, 146.7, 146.8, 148.8, 151.9, 166.4. Anal. Calcd for $C_{36}H_{42}BrNO_2$: C, 71.9; H, 7.05; N, 2.33. Found: C, 72.01; H, 7.32; N, 2.34.

2.4. Synthesis of DNA–lipid complexes [12,13]

A small amount of lipid (2.0 mmol) in THF was added slowly into double-distilled H_2O to form a uniform solution. An aqueous solution (200 mL) of DNA–Na from the salmon testes (0.50 g) was added dropwise into the aqueous lipid solution (the feed mole ratio of phosphate to lipid was 1.50). Immediately, the formed DNA–lipid complex precipitated out from the aqueous solution. After mixing for 24 h, the precipitate was collected by filtration, washed with

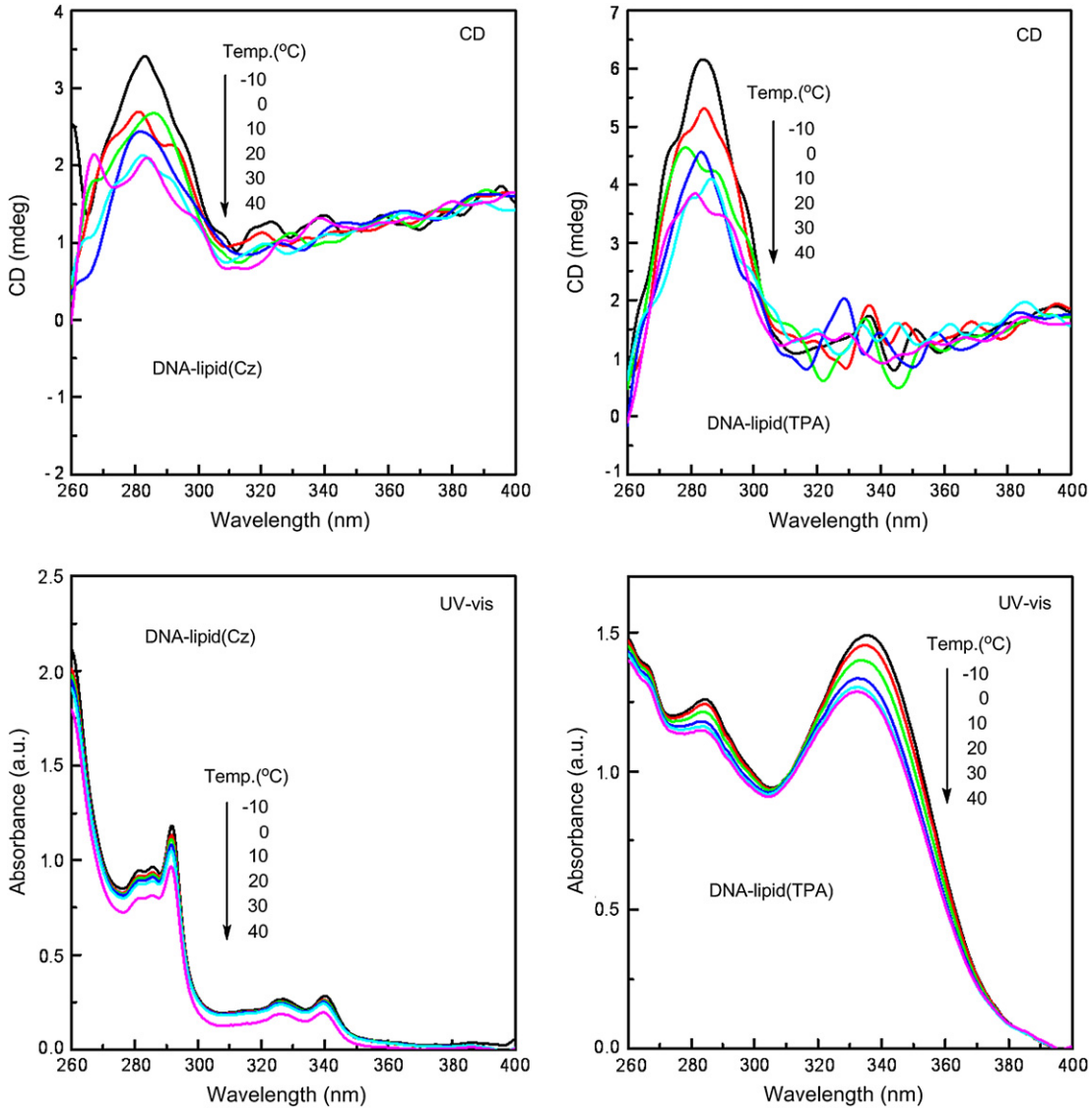


Fig. 3. Temperature-variable CD and UV–vis spectra of DNA–lipid(Cz) and DNA–lipid(TPA) measured in a range of −10 to 40 °C in MeOH ($c = 0.025$ mg/mL).

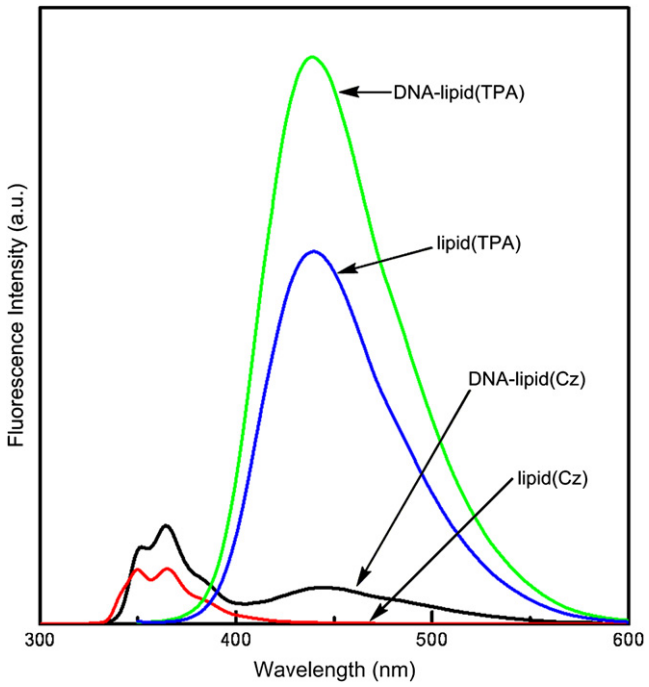


Fig. 4. Fluorescence spectra of lipid(Cz), lipid(TPA), DNA–lipid(Cz) and DNA–lipid(TPA) measured in $CHCl_3$ at 22 °C. DNA–lipid(Cz) excited at 343 nm, $\Phi = 5.7\%$; lipid(Cz) excited at 343 nm, $\Phi = 4.4\%$; DNA–lipid(TPA) excited at 335 nm, $\Phi = 76.4\%$; lipid(TPA) excited at 335 nm, $\Phi = 55.3\%$. The intensities have been normalized based on the concentration of the carbazole ($c = 0.0025$ mg/mL).

H_2O to remove free DNA, and then dried in a vacuum oven at 50 °C for 24 h. The white DNA–lipid complex was dissolved in chloroform and reprecipitated in THF two times. The obtained DNA–lipid complex was examined by elemental analysis to decide the actual composition of phosphate anion and the cationic lipid in the DNA–lipid complex.

DNA–lipid(Cz): IR (KBr): 3413, 3058, 2927, 2850, 1731, 1689, 1639, 1485, 1458, 1238, 1165, 1060, 1014, 960, 752, 528 cm^{-1}. Anal. Calcd for DNA–lipid(Cz) complex with 1:1 ratio of phosphate anion to cationic lipid(Cz): C, 61.36; H, 6.60; N, 10.10; P, 3.88. Found: C, 61.09; H, 6.70; N, 9.34; P, 3.40.

DNA–lipid(TPA): IR (KBr): 3413, 2923, 2854, 1708, 1647, 1589, 1489, 1273, 1173, 1099, 960, 845, 760, 694, 525 cm^{-1}. Anal. Calcd for DNA–lipid(TPA) complex with 1:1 ratio of phosphate anion to cationic lipid(Cz): C, 63.77; H, 6.58; N, 9.35; P, 3.59. Found: C, 63.82; H, 6.55; N, 9.26; P, 3.73.

2.5. Calculation of the yield of DNA–lipid complex

We define the yield of DNA–lipid complex as the ratio of the actual weight of DNA–lipid complex to the theoretical weight of DNA–lipid complex based on DNA–Na. The yield of DNA–lipid complex was calculated based on the following equation.

$$\text{yield}\ (\%) = \frac{W_{\text{DNA-lipid}} \times 100}{W_{\text{DNA-Na}}\left(1 + \frac{M_{\text{lipid}} - M_{\text{NaBr}}}{M_{\text{base}}}\right)} \quad (1)$$

where $W_{\text{DNA-lipid}}$ is the actual weight of DNA–lipid complex, $W_{\text{DNA-Na}}$ is the feed weight of DNA–Na, M_{lipid} and M_{NaBr} are the molecular weights of lipid and NaBr, respectively, M_{base} is the average molecular weight of base groups in the repeating unit of DNA–Na [the value is 347.91 calculated from the structures of base couple (according to the fragment sequence of the salmon DNA with an AT/GC ratio of approximately 56:44)] [17].

2.6. Determination of the actual mole ratios of phosphate to lipid in the DNA–lipid complexes

The actual mole ratio of phosphate to lipid in the DNA–lipid complexes was estimated from the amounts of phosphorus before and after complexation. Phosphorus was determined by elemental analysis. The actual percent phosphorus content in a DNA–lipid (P_a) was calculated based on the following equation:

$$P_a\ (\%) = \frac{P_0}{1 + \frac{N(M_{\text{lipid}} - M_{\text{NaBr}})}{M_{\text{base}}}} \quad (2)$$

where P_0 is the percent phosphorus content in DNA–Na (the value is 8.50% determined by elemental analysis), M_{lipid} and M_{NaBr} are the molecular weights of lipid and NaBr, respectively, M_{base} is the average molecular weight of base groups in the repeating unit of DNA–Na [the value is calculated to be 347.91 from the structure of base couples (according to the fragment sequence of the salmon DNA with an AT/GC ratio of approximately 56:44)] [17], and N is the actual mole ratio of lipid to phosphate in the DNA–lipid complexes. When solved for N, the equation becomes

$$N = \frac{P_0 - P_a \times M_{\text{base}}}{P_a \times \left(M_{\text{lipid}} - M_{\text{NaBr}}\right)} \quad (3)$$

3. Results and discussion

3.1. Synthesis of lipids

Scheme 2 illustrates the synthetic routes of the carbazole- and triphenylamine-containing lipids [lipid(Cz) and lipid(TPA)]. Lipid(Cz) was synthesized by the reaction of 11-bromoundecanoic acid with 9*H*-carbazol-9-yl-ethanol using EDC·HCl as a condensation agent, DMAP as a catalyst, followed by the reaction of the product with pyridine. Lipid(TPA) was prepared similarly by the condensation of the 12-bromo-1-dodecanol with 4-(diphenylamino)-benzoic acid and the subsequent reaction with pyridine. The lipids were identified by ^1H, ^{13}C NMR, and IR spectra besides elemental analysis.

3.2. Preparation of DNA–lipid complexes

Table 1 summarizes the conditions and results of preparation of DNA–lipid(Cz) and DNA–lipid(TPA) complexes. When the aqueous solution of DNA–Na was added into the aqueous lipid solutions, the DNA–lipid complexes immediately precipitated from the aqueous solution. After 24 h, the white flocculous products were easily isolated by filtration to afford DNA–lipids in good yields (90 and 92%). The ICP data revealed that the Na ion was almost completely replaced by the lipids. The formed DNA–lipids were completely soluble in $CHCl_3$, CH_2Cl_2, methanol and ethanol, while insoluble in water, THF, toluene, diethyl ether, and *n*-hexane. Elemental analyses showed that the obtained DNA–lipid complexes possessed 1:1.10 to 1:0.83 composition of a phosphate anion to the cationic amphiphile (in Table 1) [18].

3.3. Properties of DNA–lipid complexes

Fig. 1 shows the FTIR spectra of DNA–Na, lipid(Cz), and DNA–lipid(Cz) in the range of 4000–400 cm^{-1}. Judging from the absorption band at 1234 cm^{-1} (asymmetric stretching vibration of PO_2^-) in the spectrum of DNA–Na, the DNA adopts the B-form conformation [14]. The absorption at 1695 cm^{-1} is attributed to the hydrogen-bonded C=O stretching in the base pairs [thymine (T), guanine (G), and cytosine (C)]. The unsymmetrical shape of this

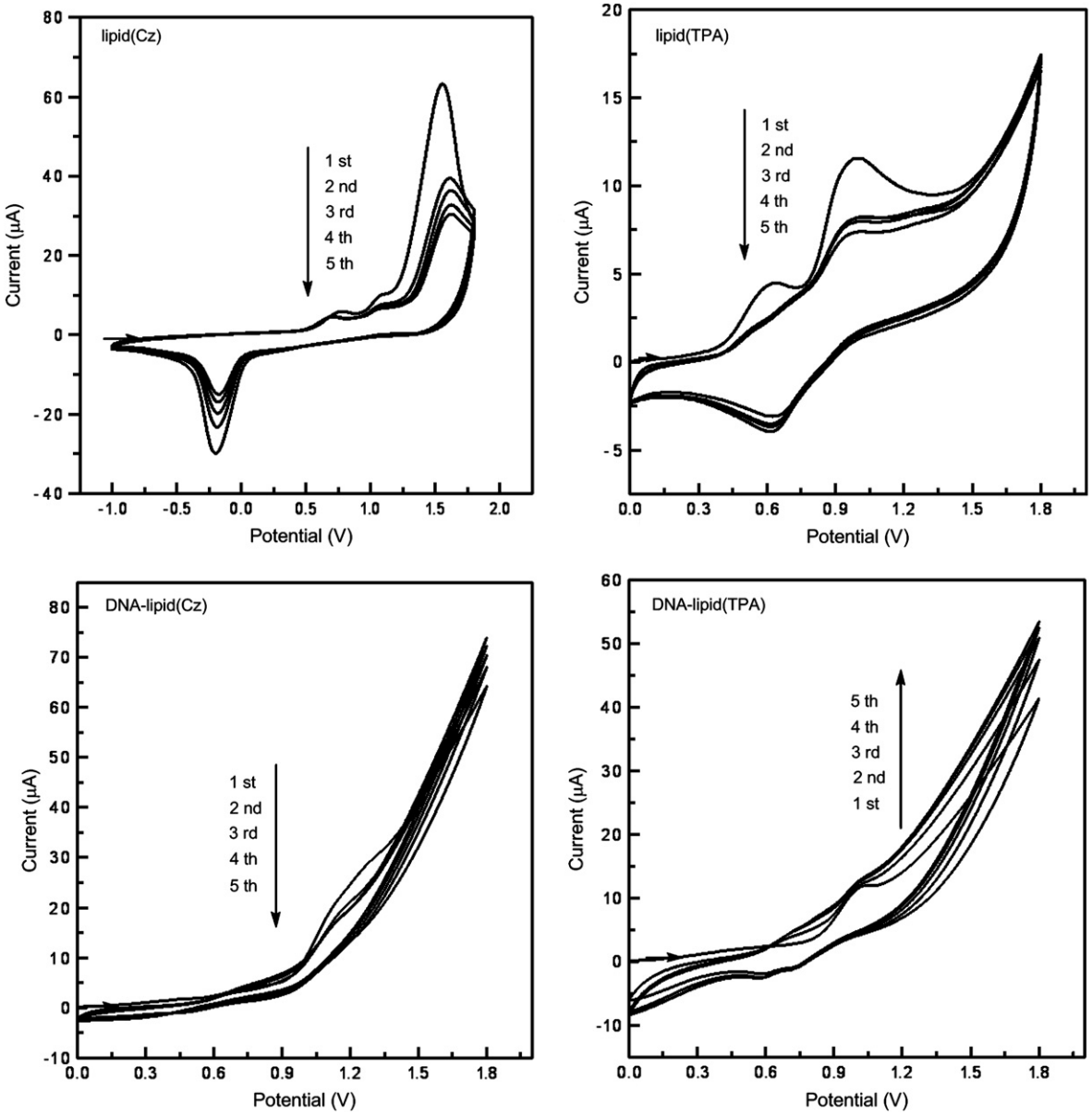


Fig. 5. Cyclic voltammograms of lipid(Cz), lipid(TPA), DNA–lipid(Cz) and DNA–lipid(TPA) measured at a scan rate of 0.1 V/s vs Ag/Ag^{+} in a solution of TBAP (0.2 M) in $CHCl_3$ ($c = 1$ mg/mL).

band is due to the C═N and C═C stretchings in the aromatic bases of DNA around 1640 cm^{-1}. In the spectrum of lipid(Cz) in Fig. 1, the absorptions at 2927 and 2846 cm^{-1} are assignable to asymmetric and symmetric $-CH_2$ stretching vibrations, respectively (see Scheme 1), the absorption at 1728 cm^{-1} to the non-hydrogen-bonded ester C═O stretching, and the one at 1600 cm^{-1} to the stretching of C═C in aromatic carbazole rings. The spectrum of the DNA–lipid(Cz) complex displays almost all the absorption bands of both lipid(Cz) and DNA–Na, indicating the presence of both lipid(Cz) and double-strand DNA in the complex. The spectrum of the DNA–lipid(TPA) also exhibits absorptions characteristic of both lipid(TPA) and DNA–Na.

The top part of Fig. 2 shows the CD spectra of lipid(Cz), lipid(TPA), DNA–lipid(Cz) and DNA–lipid(TPA) measured in $CHCl_3$ and methanol, along with the one of DNA–Na in water for comparison. Pristine DNA in an aqueous solution exhibits a positive Cotton effect at 270 nm and a negative Cotton effect at 245 nm, while lipid(Cz) and lipid(TPA) are of course CD inactive. On the other hand, both DNA–lipid(Cz) and DNA–lipid(TPA) display a large plus CD signal at 290 nm and a minus one at 260 nm in $CHCl_3$, while they show a large plus signal at 280 nm and no negative Cotton effect in a region of 245–260 nm in methanol. Thus it is evident that DNA–lipid(Cz) and DNA–lipid(TPA) adopt a double helical C-form conformation different from that of virgin DNA [6b]. In the UV–vis spectra, DNA–lipid(Cz) and lipid(Cz) exhibit almost the same absorption peaks at 294, 327, and 343 nm attributable to Cz. Further, DNA–lipid(Cz) possesses an obvious absorption peak at 263 nm attributable to DNA, while lipid(Cz) shows an absorption at 265 nm attributable to benzene of Cz. The UV–vis spectra of DNA–lipid(TPA) and lipid(TPA) show a strong and broad absorption band at 335 nm due to the benzenoid transition of phenyl group in triphenylamine. The absorptions of DNA–lipid(TPA) in the range of 250–400 nm also confirm that the lipid(TPA) moieties have been incorporated into the DNA. The CD signals and UV–vis absorptions of DNA–lipid(Cz) and DNA–lipid(TPA) were all slightly blue-shifted when the solvent was changed from $CHCl_3$ to methanol. It is assumed that the helical lipid(Cz) and lipid(TPA) arrays became disordered to decrease the

CD intensities in $CHCl_3$ due to aggregation in $CHCl_3$, leading to looser helical structure of DNA–lipid complexes in $CHCl_3$ than in methanol.

The temperature dependence of the CD and UV–vis spectra of DNA–lipid(Cz) and DNA–lipid(TPA) was examined (Fig. 3). When the measuring temperature was raised from −10 to 40 °C in methanol, the magnitude of Cotton effect decreased only slightly. This phenomenon resembles the aqueous DNA–Na solution which exhibited slight changes of Cotton effect in a temperature range of 10–90 °C in aqueous solution (the figure is not shown). It can be said that the helical structure of the DNA–lipids is thermally very stable in the measured temperature range.

Fig. 4 shows the fluorescence spectra of DNA–lipid(Cz) and DNA–lipid(TPA) along with the lipid(Cz) and lipid(TPA). A solution of lipid(Cz) emitted weak luminescence at 350 and 370 nm with fluorescence quantum yields (Φ) of 4.4% upon excitation at 343 nm, which should come from carbazole. DNA–lipid(Cz) fluoresced in a manner similar to lipid(Cz), while the Φ value of DNA–lipid(Cz) was slightly larger than that of the corresponding lipid(Cz) (5.7%). On the other hand, the solutions of lipid(TPA) and DNA–lipid(TPA) emitted strong luminescence at 440 nm with fluorescence quantum yields (Φ) of 55.3 and 76.4%, respectively, upon excitation at 335 nm, which is attributed to triphenylamine. The fluorescence quantum yields of DNA–lipid(Cz) and DNA–lipid(TPA) solutions were higher than those of the corresponding lipid(Cz) and lipid(TPA). The reason seems to be the differences in the chain stereoregularity and/or packing arrangements of the DNA complexes in solution. The double helical conformation of DNA complexes may improve the photoluminescence efficiency of Cz and TPA moieties in DNA complexes, but the concrete reason is unclear. No change of fluorescence spectra was observed in methanol.

Fig. 5 depicts the cyclic voltammetric (CV) curves of lipid(Cz), lipid(TPA), DNA–lipid(Cz), and DNA–lipid(TPA). The oxidation of DNA–lipid(Cz) initiated at 0.95 V in the first cycle, which was higher than that of lipid(Cz) (0.75 V). This result may indicate that carbazole moieties of the DNA–lipid complex synergize with the DNA main chain, resulting in low electron density at the nitrogen atom compared to that of the lipid(Cz). The oxidation of DNA–lipid(TPA) started at 0.85 V in the first scan, which was again higher than that of lipid(TPA) (0.60 V). As the CV scan was continued, DNA–lipid(Cz) and DNA–lipid(TPA) hardly exhibited oxidation and reduction peaks.

Fig. 6 depicts the TGA traces of DNA–Na, DNA–lipid(Cz) and DNA–lipid(TPA). The onset temperatures of weight loss of DNA–lipid(Cz) and DNA–lipid(TPA) were both 220 °C under air, which were higher than that of DNA–Na (the onset temperature of weight loss was 150 °C). DNA–lipid(Cz) and DNA–lipid(TPA) exhibited similar thermal stability to each other. They did not completely lose weight even at 900 °C, which is attributable to the formed phosphorus oxide.

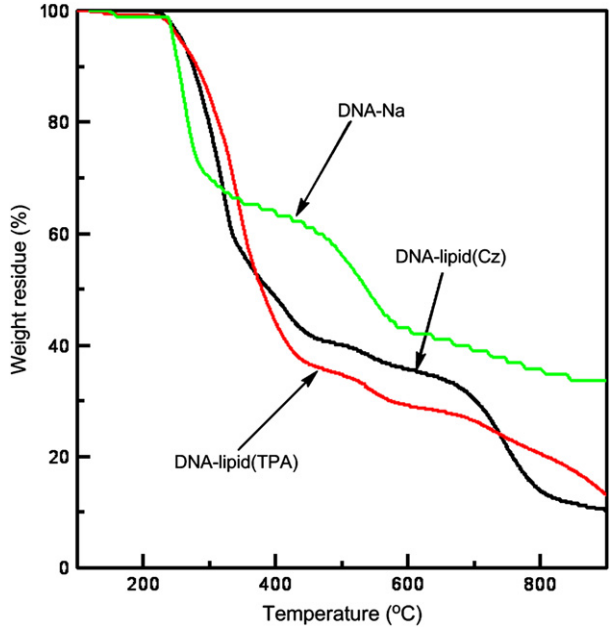


Fig. 6. TGA curves of DNA–Na, DNA–lipid(Cz) and DNA–lipid(TPA) measured at a heating rate of 10 °C/min in air.

4. Conclusions

Novel DNA–lipid complexes carrying carbazole and triphenylamine moieties were prepared by substituting sodium counter cations with cationic amphiphilic lipid(Cz) and lipid(TPA); the actual mole ratios of phosphate to lipid were 1:1.10 and 1:0.83, respectively. The DNA–lipid(Cz) and DNA–lipid(TPA) were soluble in common organic solvents including $CHCl_3$, CH_2Cl_2, methanol and ethanol, but insoluble in THF, toluene and aqueous solutions. CD spectroscopic studies revealed that DNA–lipid(Cz) and DNA–lipid(TPA) took predominantly double helical structure in $CHCl_3$ and methanol, and the helical structure was very stable against heating. The solution of DNA–lipid(Cz) and DNA–lipid(TPA) emitted fluorescence in 5.7 and 76.4% quantum yields, which were higher than those of the corresponding lipid(Cz) and lipid(TPA) (4.4 and 55.3%). The cyclic voltammograms of the DNA–lipid complexes indicated that the oxidation potentials of DNA–lipid(Cz) and DNA–lipid(TPA) were 0.95 and 0.85 V, respectively. The onset temperatures of weight loss of DNA–lipid(Cz) and DNA–lipid(TPA) were both 220 °C under air.

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