Front. Chem. China 2008, 3(4): 406–412
DOI 10.1007/s11458-008-0073-5

RESEARCH ARTICLE

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Interaction of water-soluble bridged porphyrin with DNA

Abstract A water-soluble porphyrin dimer (Por Dimer) containing eight positive charges, bridged by 4,4′-dicarboxy-2,2′-bipyridine, has been synthesized. With *Meso*-tetrakis(N-methyl-pyridium-4-yl)porphyrin (H_2TMPyP) as the reference compound, the water-soluble porphyrin dimer was investigated for its interaction with DNA by absorption, fluorescence, and circular dichroism (CD) spectroscopy. The apparent affinity binding constant ($K_{app} = 1.2 \times 10^6$) of Por Dimer binding to CT DNA was measured by a competition method with ethidium bromide (EB) (that of H_2TMPyP was 6.9×10^6). The cleavage ability of Por Dimer to pBR322 plasmid DNA was studied by gel electrophoresis. The results suggest that the binding modes of Por Dimer were complex and involve both intercalation and outside binding.

Keywords porphyrin dimmer, DNA, the apparent affinity binding constant, photocleavage

1 Introduction

Since porphyrins were covalently linked to form the first porphyrin dimer in 1972, bridged bisporphyrin compounds have become a focus in porphyrin chemistry [1–6]. The bridged reagents have a strong influence on the performance of the porphyrin dimers. The relative distance and position of the two porphyrin cycles are the major factors that decide the character of the bisporphyrin molecule [7]. Porphyrin dimers and oligomers have been studied widely in the field of mimic photosynthesis [8], molecular devices [9], magnetic materials [10] and nonlinear optical material [11].

The interaction of water-soluble cationic porphyrins and nucleic acids has been intensively studied because of their potential clinical applications in photodynamic therapy [12–16]. Porphyrin as a photosensitizer can localize in tumor cells and be phototriggered to produce singlet oxygen, cleaving DNA and damaging tumor cells. There are three major binding modes between the water-soluble porphyrins and DNA – intercalation, outside groove binding and outside stacking binding [17]. Each binding mode exhibits a unique characteristic in the spectrum measurement. The development of the oligonucleotide synthetic technique makes the study of the interaction between porphyrin dimer and DNA convenient. The results show that cationic porphyrins prefer to intercalate in the GC-rich regions of DNA at low [porphyrin]/[DNA base pairs] ratio and low ionic strength. When the [porphyrin]/[DNA base pairs] ratio and/or ionic strength increases, the binding mode becomes complex and involves both intercalation in GC-rich regions and outside binding at AT-rich sites [18,19].

The studies on the interaction of porphyrin dimer or oligomer with DNA are of interest in photodynamic therapy. The first clinical photosensitizer was a mixture of pophyrin oligomers which contain two to eight porphyrin units [20]. However, the interaction of porphyrin dimers with DNA was rarely studied [21]. In this paper, the synthesis of a water-soluble porphyrin dimmer (Por Dimer) containing positive charges, using 4,4′-dicarboxy-2,2′-bipyridine as the linker, is described. With H_2TMPyP (*Meso*-tetrakis(N-methylpyridium-4-yl)porphyrin) as the evaluating criterion, the interaction of the porphyrin dimer with CT (calf thymus) DNA, the apparent affinity binding constant, the binding mode and the ability to cleave plasmid DNA were investigated.

2 Experiments

2.1 General

All reagents and solvents were purchased from commercial sources and used with standard purification. Chromatographic separations were performed using silica gel G (200–300 mesh). The spectral measurements were

Translated from *Acta Chimica Sinica*, 2007, 65(22): 2597–2603

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performed at room temperature in a buffer solution (pH = 7.4, 0.05 M Tris-HCl, 0.1 M NaCl). All UV-visible spectra were obtained on a Shimadzu 1601 spectrophotometer. Fluorescence spectra were recorded on a Perkin Elmer LS-55 spectrometer. Circular dichroism was measured on a JASCO J-810 spectrometer. IR spectra were obtained on a Shimadzu FT-IR 3000 spectrometer. Proton NMR spectra were measured using a Varian Mercury-VX 300 spectrometer. Mass spectra were obtained on a TSQ 7000 instrument.

2.2 Synthesis

5-(4-Aminophenyl)-10,15,20-tripyridyl porphyrin was prepared according to the method described in Ref. [22]. The synthetic routes of the porphyrin dimer **1** and Por Dimer are shown in Scheme 1.

2.2.1 Synthesis of the porphyrin dimer 1

18.3 mg (0.075 mmol) 4,4′-dicarboxy-2,2′-bipyridine and 2 mL thionyl chloride were mixed and refluxed for three hours. The mixture was concentrated to dryness, and 110.7 mg (0.175 mmol) 5-(4-aminophenyl)-10,15,20-tripyridyl porphyrin, 0.3 mL triethylamine, and 15 mL dried chloroform were added and reacted at 70°C for 18 hours. The solution was concentrated and the residue was purified on a silica gel column using a mixture of chloroform and methanol as the eluent. The main fraction was collected and compound **1** was obtained by recrystallization from a mixture of chloroform and petroleum ether.

Yield, (45.1 mg, 40%). UV-vis (λ_{max}/nm, in $CHCl_3$): 420, 517, 553, 594, 652; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ: 9.06 (s, 2H, Py^3), 9.05–9.02 (m, 16H, H_β), 8.94 (d, $J = 8.1$ Hz, 4H, CONH-Ph_m), 8.90 (d, $J = 6.0$ Hz, 2H, Py^6), 8.83 (d, $J = 5.7$ Hz, 12H, Por-Py_o), 8.67 (d, $J = 6.6$ Hz, 2H, Py^5), 8.24 (d, $J = 8.1$ Hz, 4H, CONH-Ph_o), 8.13 (d, $J = 5.7$ Hz, 12H, Por-Py_m), −2.85(s, 4H, pyrrole-H); IR (KBr, cm^{-1}): 1654 (-CONH-); MS (FAB), m/z: 1472 $[M\text{-}1]^+$.

2.2.2 Synthesis of the Por Dimer

To a solution of the porphyrin dimer **1**, 14.7 mg (0.01 mmol) in 5 mL DMF, was added 2 mL methyl iodide, and the mixture was stirred at room temperature for 3 hours. After concentrating, 50 mL ether was poured into the mixture, and the precipitate was obtained with a centrifuge and dried under vacuum.

Yield, (24.5 mg, 94%). ^{1}H-NMR (DMSO-d_6, 300 MHz), δ: 11.24 (s, 2H, Py^3), 9.47–9.45 (m, 16H, H_β), 9.19 (br s, 6H, CONH-Ph_m, Py^6), 9.11(br s, 12H, Por-Py_o), 9.00–8.97 (m, 6H, Py^5, CONH-Ph_o), 8.18 (br s, 12H, Por-Py_m), 4.70(s, 24H, -CH_3), −2.99(s, 4H, pyrrole-H); MS (FAB), m/z: 1594 $[M\text{-}8I]^+$.

2.3 The ability to produce singlet oxygen

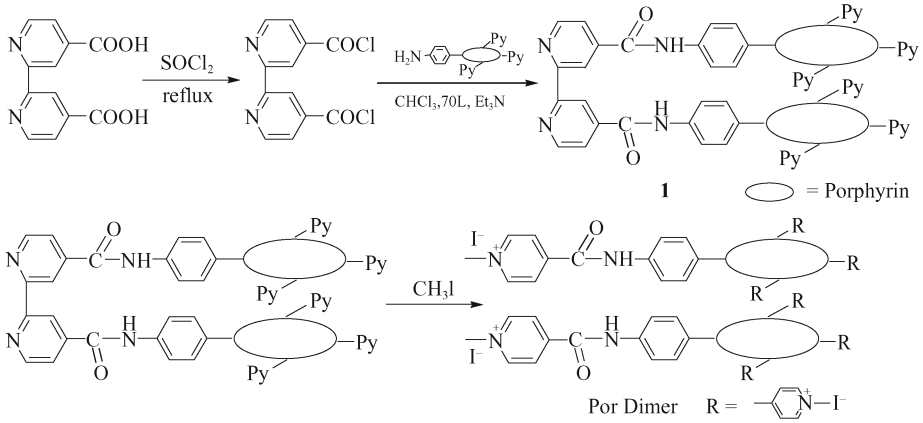
Measurement of singlet oxygen production was carried out by DPBF (1,3-diphenyl isobenzofuran) decomposition. Porphyrin (1.0×10^{-6} M) and DPBF (1.0×10^{-4} M) was dissolved in the buffer solution (pH = 7.4, 0.05 M Tris-HCl, 0.1 M NaCl) and irradiated under a high-pressure lamp (50 W) at a distance of 15 cm. DPBF concentration was measured by UV absorbance at 415 nm.

2.4 Spectral properties of the porphyrin-CT DNA interactions.

The spectral measurements were performed at room temperature in the buffer solution (pH = 7.4, 0.05 M Tris-HCl, 0.1 M NaCl). An extinction coefficient of 1.31×10^4 M^{-1} cm^{-1} at 260 nm was used to determine the CT DNA concentration in base pairs.

2.4.1 UV-vis absorption spectra

UV titrations were performed with the two porphyrins in solutions containing an increasing concentration of CT DNA. UV-vis absorption spectra were recorded within a



Scheme 1

range of 380–520 nm and the concentration of the porphyrins was 2 μmol/L.

2.4.2 Fluorescence spectra

Fluorescence emission spectra were recorded with the increase of CT DNA for the two porphyrins. Fluorescence spectra were recorded at 422 nm for excitation, 652 nm for emission and within a range of 550–750 nm. The concentration of the porphyrins was 1 μmol/L.

2.4.3 CD spectra

CD spectra were recorded within a range of 380–520 nm. The concentration of the porphyrins was 10 μmol/L and the concentration of CT DNA was 0 or 200 μmol/L ($r = 0$, 0.05).

2.5 Measurement of apparent binding constants

The apparent affinity binding constants were determined by a competition method with EB. The measurement was performed at room temperature in the buffer solution (pH = 7.4, 0.05 M Tris-HCl, 0.1 M NaCl). The binding constant of EB for DNA in the experimental conditions was 5.93×10^5 M^{-1}. Fluorescence spectra of EB binding to DNA were recorded at 540 nm for excitation and 610 nm for emission. This assay included the measurement of the fluorescence intensity of EB bound to CT DNA in the presence of the porphyrin.

2.6 Photocleavage abilities of the porphyrins to plasmid DNA

pBR322 plasmid DNA (1.0 μg) was mixed with the porphyrin solution (concentration of 2.0 or 0.5 μM) to form a solution (10 μL). All the experiments were performed in the buffer solution. The photo-inducing experiments were performed by illumination with 50 W high-pressure mercury lamp at 37°C. The distance from the filament of the mercury lamp to the sample was kept at 15 cm. The time of illumination was 12 min, DNA was analyzed by 0.9% agarose gel electrophoresis. The gel was incubated in a solution of ethidium bromide for 30 min and the DNA bands were filmed by a gel imaging instrument from Vilber Lourmat Bio Print.

3 Results and discussion

3.1 Measurement of the singlet oxygen production

It is known that DNA could be damaged by porphyrins after photoactivation owing to its ability to produce singlet oxygen. Therefore, it is necessary to ascertain the ability of the porphyrins to produce singlet oxygen so as to study its cleavage ability to DNA.

Measurement of singlet oxygen production was performed by measuring the reduction of absorbance of 1,3-diphenylisobenzofuran (DPBF) whose decomposition is caused by singlet oxygen [23,24]. A decrease of DPBF concentration was measured by absorbance at 415 nm. The slopes of the plots of bleached absorption of DPBF versus illumination time were proportional to the rate of production of singlet oxygen.

As shown in Fig. 1, there was no distinct difference for the rates of singlet oxygen production by Por Dimer and H_2TMPyP. Thus, the photocleavage ability of the two porphyrins to DNA was only related to their affinity to DNA and binding mode with DNA. The structure of H_2TMPyP is also shown in Fig. 1.

3.2 Spectral properties of the interaction of the porphyrins with CT DNA

3.2.1 UV-vis absorption spectra

Because of the presence of a conjugated rigid ring structure, porphyrin compounds have a unique absorbance peak in its UV spectra. This peak is often used to study the interaction of porphyrin and DNA [25,26].

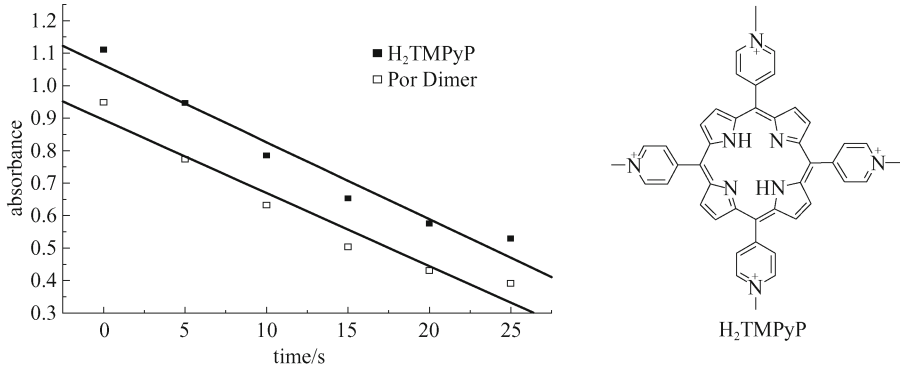


Fig. 1 Decomposition of DPBF by Por Dimer and H_2TMPyP; The structure of H_2TMPyP

As shown in Fig. 2, UV titrations were performed for the two porphyrins in solutions containing an increasing concentration of calf thymus DNA [27,28]. The red shift and intensity change of the Soret region with the increase of CT DNA suggested the binding of the porphyrin to CT DNA. The porphyrin dimer exhibited 37% hypochromism and 9 nm red shift of the Soret band. The data is summarized in Table 1.

3.2.2 Fluorescence spectra

Fluorescence spectroscopy is an important method for studying the interaction of small molecules and DNA [29,30]. Fluorescence emission spectra of the two porphyrins were recorded in the presence and absence of CT DNA. In the presence of CT DNA, both porphyrins showed a remarkable decrease in intensity of fluorescence emission as shown in Fig. 3. The data is summarized in Table 1.

3.2.3 CD spectra

CD spectroscopy is another useful method for studying the interaction between small molecules and DNA [31,32]. The sign of the induced CD spectra in the Soret band depends upon the binding mode of porphyrin-DNA [33,34]. In the case of duplex DNA, a positive induced CD band in the Soret region indicates groove binding and a negative induced CD band indicates intercalation [35]. The induced CD spectrum of Por Dimer bound to CT DNA at a [Por Dimer]/[DNA base pairs] ratio of 0 or 0.05 is shown in Fig. 4. The data is summarized in Table 1.

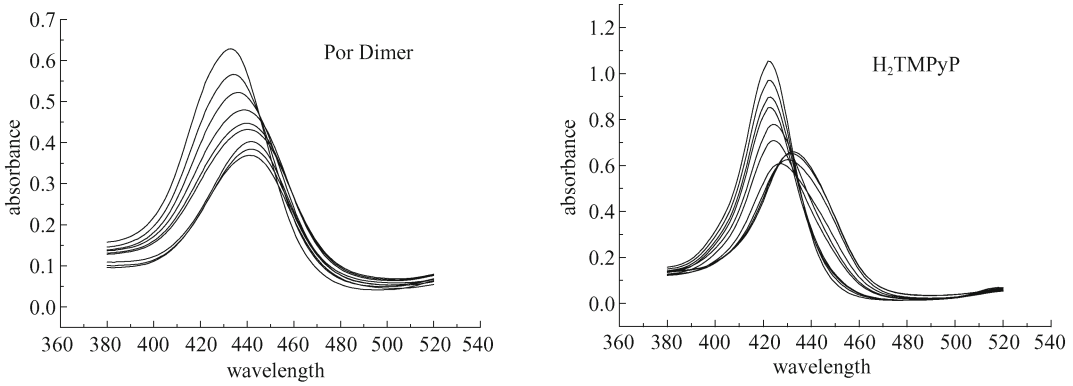


Fig. 2 UV-vis absorbance change when titration of the cationic porphyrins by CT DNA

Table 1 Data for the interaction of the two porphyrins with CT DNA

porphyrin	UV-vis on the soret band		fluorescence emission	CD in the soret region		K_{app}/L·mol$^{-1)}$
	hypochromicity H/%	red shift $\Delta\lambda$/nm	decrease of intensity/%	positive band/nm	negative band/nm	
Por Dimer	37	9	21	445	426	1.2×10^6
H_2TMPyP	39	10	37	–	–	6.9×10^6

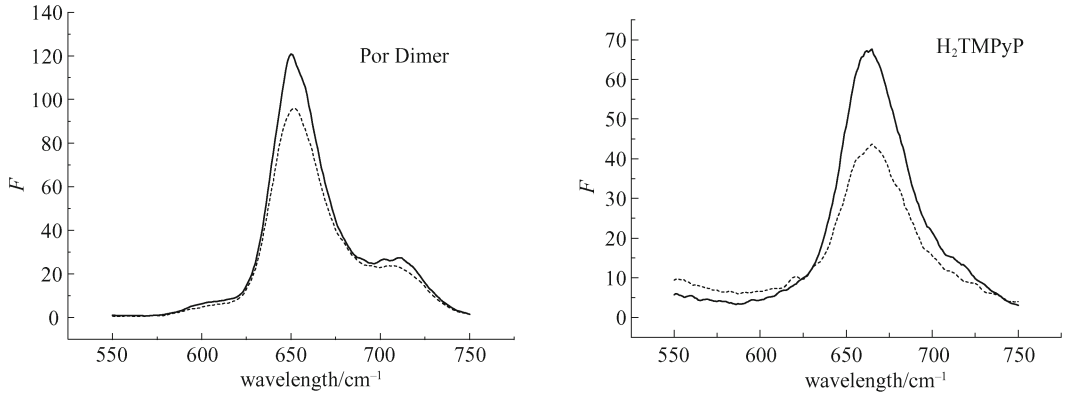


Fig. 3 Fluorescence emission spectra of the cationic porphyrins in the absence (——) and presence (·····) of CT DNA

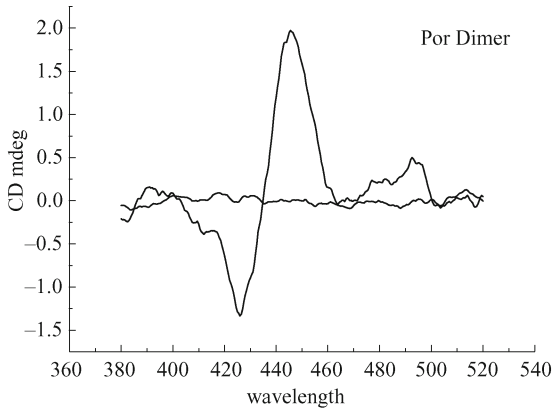


Fig. 4 Induced CD spectrum of Por Dimer bound to CT DNA, $r = 0, 0.05$

At a [Por Dimer]/[DNA base pairs] ratio of 0, no bands on the CD spectra were detected. When the ratio was changed to 0.05, a strong positive band at 445 nm and a weaker negative band at 426 nm appeared. Considering the hypochromic effect, the red shift in the UV-vis spectra and the decrease in intensity of fluorescence emission, it appears that the Por Dimer binds to DNA by outside binding. The bisignate nature of the induced CD, however, indicates that the binding modes of Por Dimer is complex and involves both intercalation and outside binding. The conformation of the molecule might play an essential role in the process of porphyrin dimer bonding to DNA.

3.3 Measurement of apparent binding constants

UV and fluorescence titration have been used to determine the binding constant of drugs for DNA [36,37] but both methods have disadvantages. A competition method with ethidium bromide (EB) was used to determine the apparent affinity binding constant (K_{app}) [38]. This method can be used for all compounds having a good affinity for DNA as it only measures the ability of a compound to prevent intercalation of EB into DNA.

When EB interacted with DNA, the equilibrium of dissociative EB and combined EB could be expressed by the Scatchard equation:

$$\frac{r_{EB}}{c_{EB}} = K_{EB}(n - r_{EB})$$

When EB competed with porphyrin for binding sites on DNA, the Scatchard equation becomes

$$\frac{r_{EB}}{c_{EB}} = \frac{K_{EB}}{1 + K_{app}c_{por}}(n - r_{EB})$$

where K_{EB} and K_{app} are the binding constants of EB and porphyrin to DNA, c_{EB} and c_{por} are the concentration of free EB and porphyrin, r_{EB} is the number of moles of bound EB by nucleotide and n is the combined number of moles of bound EB per mole of nucleotide. The constant of porphyrin, K_{app}, is estimated from this equation.

The Scatchard plots for the binding of EB to CT DNA in the presence of various porphyrins are shown in Fig. 5. The data is summarized in Table 1.

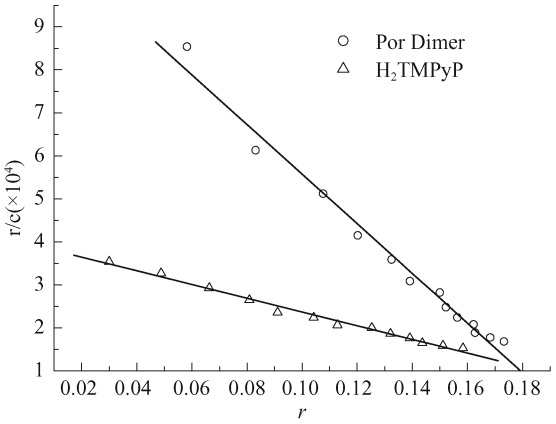


Fig. 5 Competition between porphyrins and EB for the binding site of CT DNA (Scatchard plot), r is the number of moles of EB bound per mole of DNA, c is the concentration of free EB

Our studies indicate that the binding ability of porphyrin with DNA should be improved with an increase of positive charges [8]. The results show that the value of K_{app} of H_2TMPyP is more that five times that of Por Dimer. This may be due to the different binding modes employed by the two molecules. It is likely that the conformation of Por Dimer plays a passive part in the electronegative environment and results in weaker affinity for CT DNA. Furthermore, the conformation of our target compound should be linear [39,40] as shown in Fig. 6.

This conformation caused only one porphyrin ring containing three positive charges to intercalate DNA and influence its affinity to DNA. Photocleavage of pBR322 plasmid DNA by the two porphyrins was carried out to verify this conclusion.

3.4 Photocleavage of plasmid DNA by the two porphyrins

As shown in Fig. 7, no cleavage of DNA occurred without irradiation whether in control experiments or in the presence of porphyrins. No cleavage was observed when only DNA was illuminated.

At high concentration (A in Fig. 7) of the two porphyrins, DNA was almost fully cleaved by both porphyrins, while at low concentration (B in Fig. 7), there was no cleavage by Por Dimer compared with complete cleavage by H_2TMPyP. These results are consistent with the K_{app} measured above.

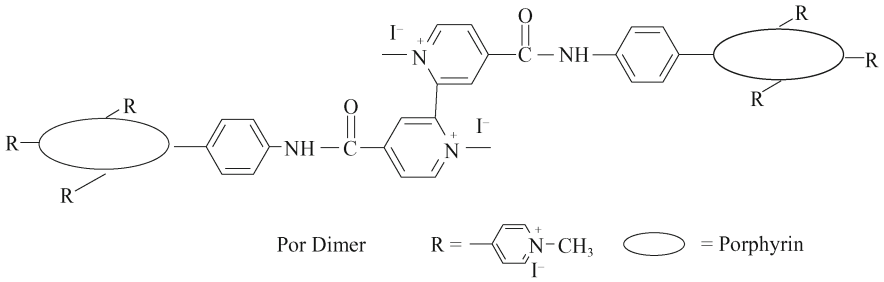


Fig. 6 Linear molecular structure of Por Dimer

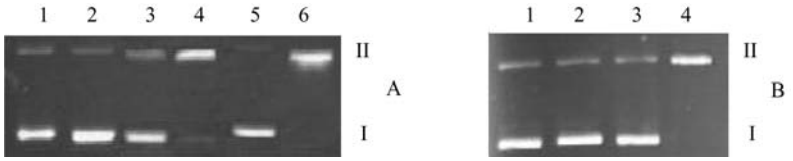


Fig. 7 Cleavage of supercoiled pBR322 DNA by the two porphyrins. Conditions: 10 μL reaction mixtures contained 1.0 μg of plasmid DNA, time of illumination was 12 min. A: Concentration of the two porphyrins was 2.0 μmol/L. Lane 1: DNA alone; lane 2: DNA alone + hν; lane 3: DNA + PorDimer; lane 4: DNA + PorDimer + hν; lane 5: DNA + H_2TMPyP; lane 6: DNA + H_2TMPyP + hν; B: Concentration of the two porphyrins was 0.5 μ mol/L. Lane 1: DNA alone; lane 2: DNA alone + hν; lane 3: DNA + PorDimer + hν; lane 4: DNA + H_2TMPyP + hν.

4 Conclusions

In this paper, a water-soluble bridged porphyrin containing eight positive charges was synthesized using 4,4′-dicarboxy-2,2′-bipyridine as the bridge. Cationic porphyrin binding with DNA and cleavage of DNA were investigated by UV-visible absorption, fluorescence and CD spectroscopy. The apparent affinity binding constant (K_{app}) was measured and cleavage of plasmid DNA by the porphyrins was observed. The DNA binding and plasmid DNA cleavage ability of the porphyrin dimer were in agreement with our estimates with reference to H_2TMPyP. The possible reason was the configuration and binding mode of the porphyrin dimer. The structure of the bridged porphyrin was probably too large to intercalate DNA and this influenced its DNA affinity.

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