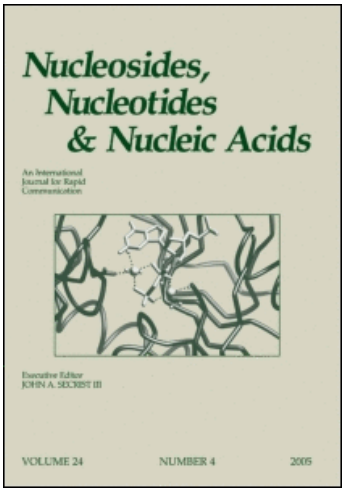


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# Conformational Changes of DNA by Photoirradiation of DNA-Bis($Zn^{II}$-Cyclen)-Azobenzene Complex

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# CONFORMATIONAL CHANGES OF DNA BY PHOTOIRRADIATION OF DNA-BIS($Zn^{II}$-CYCLEN)-AZOBENZENE COMPLEX

**Kenji Maie, Mitsunobu Nakamura, and Kazushige Yamana** □ *Department of Materials Science and Chemistry, University of Hyogo, Hyogo, Japan*

□ *Bis($Zn^{II}$-cyclen)-azobenzene derivative, which has two $Zn^{II}$-macrocyclic tetraamine complexes connected through azobenzene spacer, has been synthesized as a cross-linking agent for double stranded DNA in aqueous solution. The $Zn^{II}$-cyclen derivative selectively binds to A-T base pairs producing complexes between the $Zn^{II}$-cyclen moiety and the imide-deprotonated thymine with breaking A-T base pairs. The azobenzene spacer undergoes* cis/trans *photoisomerization in the complex between the $Zn^{II}$-cyclen derivative and the DNA duplex. The conformation of the DNA remarkably changed by photoisomerization of the azobenzene linker, when the $Zn^{II}$-cyclen derivative binds to the DNA duplex with an interstrand cross-linking manner.*

**Keywords** $Zn^{II}$-cyclen; Azobenzene; Photoisomerization; Conformational change



## INTRODUCTION

There is current interest in applications of DNA to the development of novel functional nano-materials.[1–4] The regulation of DNA structures or conformation by an external stimulus such as light is an important approach to extend the scope of the applications.[5–9] One such example is the changes of DNA hybridization by the covalently attached azo-dyes.[6–9] An attractive alternative approach to generate a photoregulation system involving DNA is the use of a photoresponsive receptor that can physically bind to DNA.

We have been interested in tetraaza-cyclododecane Zn(II) complexes ($Zn^{II}$-cyclen) and their derivatives, because the $Zn^{II}$-cyclen can strongly bind to DNA via the coordination of the Zn atom with the thymine base nitrogen and the hydrogen bonds between the carbonyl group of thymine and the NH groups of $Zn^{II}$-cyclen.[10–14] It is therefore anticipated that a designed

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This article is dedicated to Professor Eiko Ohtsuka on the occasion of her 70th birthday.
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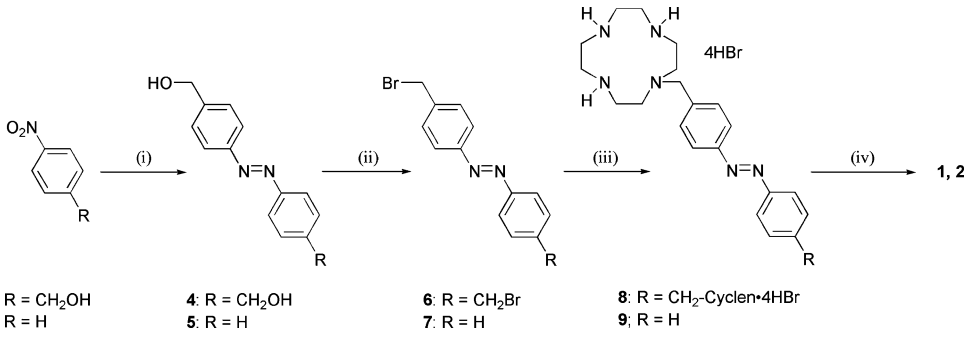



**SCHEME 1** *Reagents and conditions:* (i) 4-nitorobenzyl alcohol, Zn powder, NaOH aq, ethanol, reflux 2h; (ii) $Br_2$, triphenyl phosphine, dry acetonitrile, 60°C, 1h; (iii) cyclen, chloroform, 40°C, 12h, HBr; (iv) $Zn(ClO_4)_2 \bullet 6H_2O$, ethanol.

molecule such as two $Zn^{II}$-cyclens connected with an azobenzene moiety may act as a photoresponsible cross-linking agent for a DNA. In this report, we describe the synthesis of the ($Zn^{II}$-cyclen)-azobenzene derivatives and their binding to DNA. The conformational changes of the DNA-(bis-$Zn^{II}$-cyclen)-azobenzene complexes were observed by photo-irradiation.



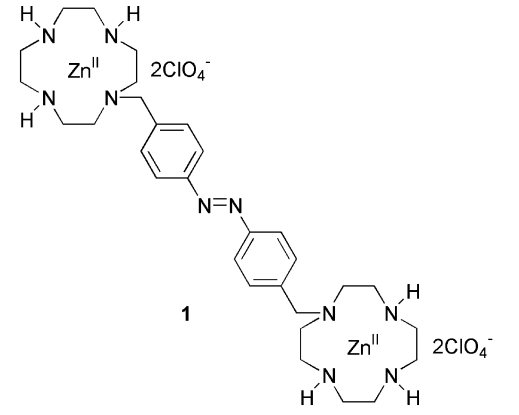
## RESULTS AND DISCUSSION

### Synthesis of ($Zn^{II}$-Cyclen)-Azobenzene Derivatives

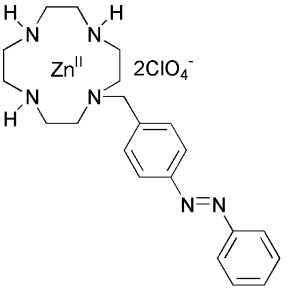
According to Scheme 1, bis($Zn^{II}$-cyclen)-azobenzene **1**, mono-($Zn^{II}$-cyclen)-azobenzene **2**, and $Zn^{II}$-cyclen **3**, whose chemical structures are shown in Chart I, were prepared. The reductive coupling of 4-nitrobenzyl alcohol under the basic conditions afforded the 4,4′-hydroxymethyl azobenzene **4**. After the conversion of the hydroxyl group to the bromine function, the reaction of **6** with excess amount of cyclen yielded the bis-cyclen **8**. The mono-cyclen **9** was obtained in a similar procedure by using 4-hydroxymethyl azobenzene **5** that was obtained from the coupling reaction between 4-nitrobenzyl alcohol and 4-nitrobenzene. The zinc complexes **1** and **2** were obtained as orange crystals from an ethanol solution of **8** and **9** treated with an equimolecular amount of $Zn(ClO_4)_2 \bullet 6H_2O$. $Zn^{II}$-cyclen **3** was prepared from acid free cyclen by treating with $Zn(ClO_4)_2 \bullet 6H_2O$.

### Binding of ($Zn^{II}$-Cyclen)-Azobenzene Derivatives to Double-Helical DNA

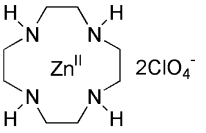
We first examined the binding of ($Zn^{II}$-cyclen)-azobenzene derivatives **1,2**, and $Zn^{II}$-cyclen **3** to the DNA duplexes (**I–III**), where **I** and **II** have thymine bases at the defined positions, while **III** has no thymine base (Chart I). Therefore, with bis($Zn^{II}$-cyclen)-azobenzene **1**, the duplexes **I** and




**1**




**2**




**3**

**I:** 5'-GGT TGA AGG-3'
3'-CCA ACT TCC-5'

**II:** 5'-GGT TGT TGG-3'
3'-CCA ACA ACC-5'

**III:** 5'-GCG CGC GC-3'
3'-CGC GCG CG-5'

**II** may be expected to form interstrand and intrastrand cross-links, respectively. Figure 1 shows the duplex melting curve for **I** and **II** in the presence and absence of **1**. The *Tm* values obtained from the melting studies are summarized in Table 1. The duplex **I** melted at 33°C in the absence of **1**, while the addition of an equimolecular amount of **1** to the duplex **I** lowered the $T_m$ to 28°C. Similar destabilization took place for **II** in the presence of **1**. The $T_m$ (35°C) of the native DNA **II** decreased to 24°C upon addition of an equimolecular amount of **1**. In contrast, the mono($Zn^{II}$-cyclen)-azobenzene **2** and $Zn^{II}$-cyclen **3** barely affected the $T_m$s of **I** and **II** under similar conditions. Since it is known that the binding of Zn-cyclen derivatives to thymine-containing DNA duplexes results in the breakage of A-T base pair,[11–13] our observations that the significant destabilization of the DNA duplexes occurred only with the bis-Zn-cyclen **1**, not with the mono-cyclen derivatives, appeared to be consistent with the efficient breakage of at least

**TABLE 1** $T_m$ of Double Helical DNA ($7.16 \times 10^{-6}$ mol dm$^{-3}$) in the Presence of Cyclen Derivatives[a]

| DNA duplex | $T_m$/°C | **1** [**1**]/$10^{-6}$ mol dm$^{-3}$ | $T_m$/°C | **2** [**2**]/$10^{-6}$ mol dm$^{-3}$ | $T_m$/°C | **3** [**3**]/$10^{-6}$ mol dm$^{-3}$ | $T_m$/°C |
|---|---|---|---|---|---|---|---|
| I | 33 | 7.16 | 28 | 7.16 | 30 | 7.16 | 31 |
| II | 35 | 7.16 | 24 | 7.16 | 31 | 7.16 | 32 |
| III | 42 | 7.16 | 42 | | | | |
| | | 35.80 | 41 | | | | |

[a]UV-melting curves monitored at 260 nm were measured with increasing temperature from 0 to 80°C at a rate of 0.5°C/min.

two A-T base pairs in the duplex DNA. The thermal denaturation studies thus strongly suggested the cross-linking of our bis-cyclen compound with multi-thymine-containing DNAs. In the case of intrastrand cross-link of **1** on DNA, the observed destabilization of DNA is reasonable. Although the interstrand cross-link generally acts as a stabilizer of duplex DNA, the duplex destabilization observed for DNA **I** may be due to the significant energy loss from the base pair breakage and the structural constraint owing to the rigid aromatic linker.

Since it has been reported that Zn-cyclen derivatives could coordinate phosphate anions such as the 4-nitorophenyl phosphate dianion in aqueous solution,[14] the binding of **1** to **III** was also examined in order to clarify that **1** bound only to the thymine base without coordinating with the phosphate anion in a DNA main chain. The duplex **III** exhibited typical transition with the $T_m$ at 42°C, and the even addition of excess amounts of **1** did not reduce the $T_m$. Therefore, little or no coordination of **1** occurs to the phosphate anion of the DNA main chain in our experimental conditions.



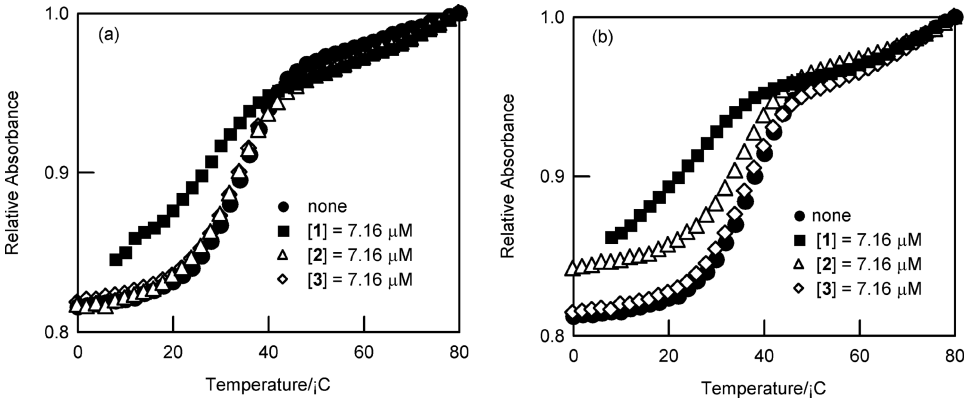



**FIGURE 1** UV melting curves of **I** ($7.16 \times 10^{-6}$ mol dm$^{-3}$) (a) and **II** ($7.16 \times 10^{-6}$ mol dm$^{-3}$) (b) in the presence ($7.16 \times 10^{-6}$ mol dm-3) and absence of compound **1–3** monitored at 260 nm in 0.1 mol dm$^{-3}$ $NaNO_3$ and 0.01 mol dm$^{-3}$ HEPES, adjusted to pH 7.4.

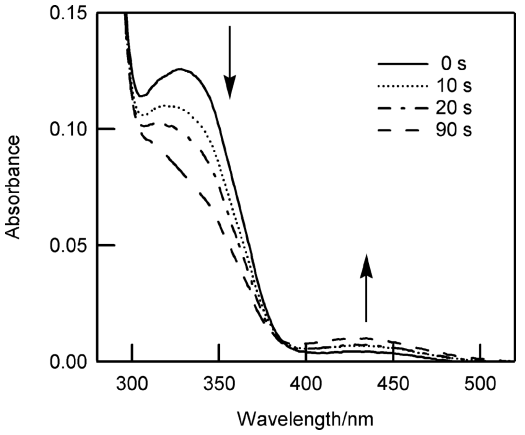



**FIGURE 2** Absorption spectral change of **1** ($7.16 \times 10^{-6}$ mol $dm^{-3}$) in the complex with **I** ($7.16 \times 10^{-6}$ mol $dm^{-3}$) during UV-irradiation in 0.1 mol $dm^{-3}$ $NaNO_3$ and 0.01 mol $dm^{-3}$ HEPES, adjusted to pH 7.4.



## Photoisomerization of Bis($Zn^{II}$-Cyclen)-Azobenzene Bound to Double-Helical DNA

We next measured the changes in absorption spectra for the complex of **1** with double-helical DNA under the UV-illumination conditions. The results are shown in Figure 2. The decrease in the absorption intensity at 330 nm and the increase of the intensity at 425 nm were observed with the isosbestic point at 386 nm. These spectral changes are well consistent with the *trans* →*cis* photoisomerization of an azobenzene derivative. Under the photo-stationary state that was reached within the short period (1 min) of the irradiation, the *trans* to *cis* isomer ratio was estimated in ca. 20:80. By the visible light irradiation, the absorption spectrum went back to the original spectrum obtained before the UV-irradiation. These results prove that the reversible photoisomerization of **1** occurs in the complex with a DNA duplex. The photoisomerization of **1** and **2** in the complexes were found to be similarly effective compared to those of **1** and **2** in the absence of DNAs. We could not evaluate the stability of the complexes possessing the *cis*-form of **1** and **2** by thermal denaturing studies, because of the rapid *cis* →*trans* thermal isomerization.

## Conformational Changes in DNA-Bis($Zn^{II}$-Cyclen)-Azobenzene Complex by Photo Irradiation

The DNA **I** and **II** forms a B-form duplex that shows typical CD signal in pH 7.4, 0.1 mol $dm^{-3}$ $NaNO_3$ and 0.01 mol $dm^{-3}$ HEPES aqueous solution with positive CDs at 275 and 266 nm, respectively (Figures 3a and 3b). Unfortunately, the CD signal below 250 nm was perturbed by the HEPES buffer under the conditions. Upon the addition of **1** to **I**, the CD signal at

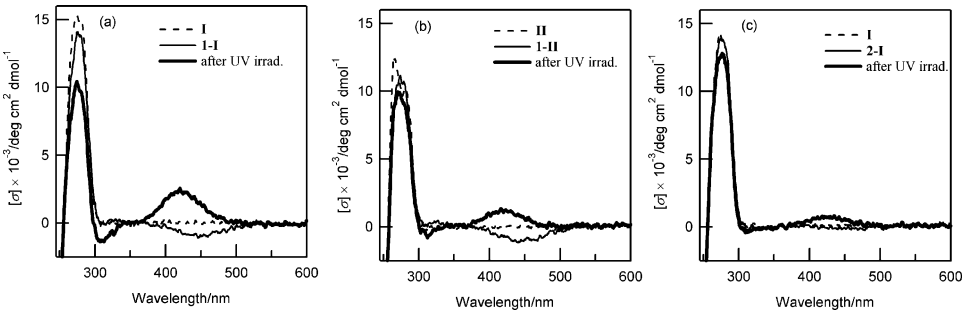



**FIGURE 3** Circular dichroism spectra of (a) **I** ($7.16 \times 10^{-6}$ mol dm$^{-3}$) in the absence and the presence ($7.16 \times 10^{-6}$ mol dm$^{-3}$) of **1**, (b) **I** ($7.16 \times 10^{-6}$ mol dm$^{-3}$) in the absence and the presence ($7.16 \times 10^{-6}$ mol dm$^{-3}$) of **2**, and (c) **II** ($7.16 \times 10^{-6}$ mol dm$^{-3}$) in the absence and the presence of **1**, in 0.1 mol dm$^{-3}$ $NaNO_3$ and 0.01 mol dm$^{-3}$ HEPES, adjusted to pH 7.4.

275 nm slightly decreased in intensity accompanied with a negative induced CD around 450 nm due to azobenzene chromophore. With the *trans* →*cis* photoisomerization of **1** in **1-I** complex, remarkable changes in CD spectrum were induced. The positive CD signal at 275 nm decreased from $[\sigma] = 13,700$ deg cm$^2$ dmol$^{-1}$ to 9,900 deg cm$^2$ dmol$^{-1}$, and the negative-induced CD signal around 451 nm disappeared with appearance of positive induced CD signal around 420 nm, indicating **1** is capable of modulating the duplex helicity upon photoirradiation (Figure 3a). Similar CD profiles were observed for **II** in the presence of **1**. The negative induced peak around 450 nm due to azobenzene chromophore was inverted to positive peak around 420 nm by photoirradiation; however, the decrease of the intensity for the positive peak at 266 nm was not as large as those observed in **1-I** (Figure 3b). On the other hand, upon addition of **2** to **I**, the positive peak at 275 barely changed and no induced peak appeared around 450 nm. Photoisomerization of **2** in **2-I** reduced the positive peak at 275 nm slightly and induced the weak positive peak around 420 nm (Figure 3c). These results provide that the $Zn^{II}$-cyclen-azobenzene derivatives bind to **I** and **II** producing a complex, and that the photoisomerization of the derivatives in the complex changes the conformation of the complex. Especially, **1** is capable of modulating the duplex structure effectively with photoirradiation in **1-I** system. The reverse of the induced CD signal in the region of 450 nm for **1-I** upon photoirradiation would be caused by the changes of the transition moment of the azobenzene backbone in *trans* → *cis* isomerization, and by the conformational change of the complex; i.e., the *cis*-azobenzene backbone, which is not planer structure, would be located out of duplex.

## SUMMARY

The $Zn^{II}$-cyclen-azobenzene derivatives are capable of binding to the DNA duplex–containing thymine bases at appropriate positions. The

reversible isomerization of the $Zn^{II}$-cyclen-azobenzene occurs in the complex with change in the global conformation by photoirradiation. When the bis ($Zn^{II}$-cyclen) derivative binds to a DNA duplex in interstrand manner, remarkable conformational changes take place with the *cis/trans*-photoisomerization of the azobenzene chromophore.

## EXPERIMENTAL

### General Methods

Melting points were measured with a Yanaco micro melting point apparatus and were uncorrected. Furthermore, $^1$H NMR spectra were recorded on a JEOL JNM-EX270 (270 MHz) spectrometer, in which chemical shifts were determined on the basis of a residual peak of solvent (2.49 for DMSO-$d_6$, or 7.26 for $CDCl_3$). Absorption spectra were recorded on a Hitachi U-3500 spectrophotometer, and CD spectra were obtained on a JASCO 720WI spectrophotometer.



### Preparation of Materials

*[4-(4-Hydroxymethyl-phenylazo)-phenyl]-methanol* **4**. Zinc powder (4.2 g, 0.064 mol) was slowly added to a mixture of 4-nitrobenzyl alcohol (5.0 g, 0.032 mol) and sodium hydroxide (6.4 g) in ethanol (100 mL) with stirring. The mixture was refluxed for 2 h and then filtered while hot. The precipitate was washed with ethanol and the filtrate was evaporated. The residue was suspended into 6M hydrochloric acid to remove excess zinc powder and $Na_2ZnO_2$. Crude **4** was then obtained by filtration from the suspension. Recrystallization with methanol gave 1.5 g of pure **4** with 39% yield. $^1$H NMR (DMSO) $\delta = 4.70$ (d, $J_{HH} = 5.61$ Hz, 4H), 5.49 (t, $J_{HH} = 5.61$ Hz, 2H), 7.62 (d, $J_{HH} = 8.58$ Hz, 4H), 7.95 (d, $J_{HH} = 8.58$ Hz, 4H). Mp: 230–231°C.

*(4-Phenylazo-phenyl)-methanol* **5**. The title compound was prepared by reaction of 4-nitorobenzyl alcohol (2.0 g, 0.014 mol) and nitrobenzene (1.6 g, 0.014 mol) according to the same procedure as **4**. Silica gel column chromatography with ethyl acetate ($R_f = 0.6$) gave 0.8 g (27%) of pure 5. $^1$H NMR ($CDCl_3$, $Me_4Si$) $\delta = 1.93$ (broad, 1H), 4.89 (s, 2H), 6.83 (d, 8.0 Hz, 2H), 7.19 (d, $J_{HH} = 8.0$ Hz, 2H), 7.24 (dd, $J_{HH} = 8.0$, 7.5 Hz, 1H), 7.56 (d, $J_{HH} = 8.0$ Hz, 2H), 7.97 (d, $J_{HH} = 7.5$ Hz, 2H).

*Bis-(4-bromomethyl-phenyl)-diazene* **6**. Bromine (0.33 g, 0.004 mol) was added to a solution of triphenyl phosphine (1.05 g, 0.004 mol) in dry acetonitrile (30 ml), and to this solution was added the solution of **4** (0.5 g, 0.002 mol) in acetonitrile (10 ml) while vigorously stirring. The reaction mixture was heated at 60°C for 1 h while stirring. The precipitate was subsequently filtered and recrystallized with ethyl acetate (0.59 g, 80%). $^1$H NMR ($CDCl_3$,

$Me_4Si$) $\delta = 4.56$ (s, 4H), 7.55 (d, $J_{HH} = 8.2$ Hz, 4H), 7.89 (d, $J_{HH} = 8.2$ Hz, 4H). Mp: 228–230°C.

*(4-Bromomethyl-phenyl)-phenyl-diazene* **7**. The title compound was prepared from 0.5 g of 5 according to the same procedure as **6**. Recrystallization with ethyl acetate gave 0.48 g of pure **7** (75%). $^1$H NMR ($CDCl_3$, $Me_4Si$) $\delta = 4.79$ (s, 2H), 7.06 (d, 8.5 Hz, 2H), 7.72 (d, $J_{HH} = 7.0$ Hz, 2H), 7.77 (dd, $J_{HH} = 7.0$, 7.5 Hz, 1H), 8.13 (d, $J_{HH} = 8.5$ Hz, 2H), 8.14 (d, $J_{HH} = 7.5$ Hz, 2H). Mp: 103–105°C.

*Bis-[4-(1,4,7,10-tetraaza-cyclododec-1-ylmethylzinc)-phenyl]-diazene octahydrobromic acid salt ([8]• 8HBr).* To a solution of cyclen (1.8 g 0.011 mol) in chloroform (40 ml) was added a solution of **6** (0.5 g 0.0014 mol) in chloroform (15 ml) with stirring at room temperature. The reaction mixture was heated for 12 h at 40°C, and then washed with two portions of water to remove excess cyclen. Chloroform was removed under reduced pressure. The residue was dissolved in ethanol, after which 40% hydrobromic acid was added to the ethanol solution followed by filtration to remove unreacted **6**. The title compound was purified by recrystallization with ethanol (1.1 g, 68%). $^1$H NMR ($D_2O$) $\delta = 2.86$ (t, $J_{HH} = 5.50$ Hz, 8H), 2.92 (broad, 6H), 3.06 (t, $J_{HH} = 5.5$ Hz, 8H), 3.08 (m, 16H), 3.85 (s, 4H), 7.50 (d, $J_{HH} = 10.0$ Hz, 4H), 7.82 (d, $J_{HH} = 10.0$ Hz, 4H).

*Phenyl-[4-(1,4,7,10-tetraaza-cyclododec-1-ylmethyl)-phenyl]-diazene tetrahydrobromic acid salt ([9]• 4HBr).* The title compound was prepared from **7** (0.4 g, 0.0015 mol) according to the same procedure as **8**. Crude [**9**] • *4HBr* was recrystallized with ethanol (0.76 g, 73%). $^1$H NMR ($D_2O$) $\delta = 2.83$ (t, $J_{HH} = 5.50$ Hz, 4H), 2.92 (broad, 3H), 3.18 (t, $J_{HH} = 5.50$ Hz, 4H), 3.25 (m, 8H), 3.97 (s, 2H), 7.02 (d, 8.4 Hz, 2H), 7.34 (d, $J_{HH} = 7.0$ Hz, 2H), 7.59 (dd, $J_{HH} = 7.0$, 7.5 Hz, 1H), 7.64 (d, $J_{HH} = 8.4$ Hz, 2H), 7.93 (d, $J_{HH} = 7.5$ Hz, 2H).

*Bis-[4-(1,4,7,10-tetraaza-cyclododec-1-ylmethylzinc)-phenyl]-diazene* **1**. An aqueous solution of the hydrobromic acid salt of **8** (1.1 g) was passed through anion exchange resin. Acid free **8** (0.47 g) was given after evaporation. $Zn(ClO_4)_2 \bullet 6H_2O$ in ethanol was added to a solution of **8** (0.47 g) in ethanol. The precipitate was filtered and recrystalized with 0.1 M $NaClO_4$ aqueous solution (0.62 g, 67%). $^1$H NMR ($D_2O$) $\delta = 2.81$ (m, 32H), 3.16 (broad, 6H), 4.02 (s, 4H), 7.51 (d, $J_{HH} = 8.50$ Hz, 4H), 7.83 (d, $J_{HH} = 8.50$ Hz, 4H).

*Phenyl-[4-(1,4,7,10-tetraaza-cyclododec-1-ylmethylzinc)-phenyl]-diazene* **2**. An aqueous solution of the hydrobromic salt of **9** (0.76 g) was passed through anion exchange resin. Acid free **9** (0.39 g) was given after evaporation. $Zn(ClO_4)_2 \bullet 6H_2O$ in ethanol was added to a solution of **9** (0.39 g) in ethanol. The precipitate was filtered and recrystallized with 0.1 M $NaClO_4$ aqueous solution (0.46 g, 73%). $^1$H NMR (DMSO) $\delta = 2.62$ (t, $J_{HH} = 8.0$ Hz, 4H), 2.67 (t, $J_{HH} = 8.0$ Hz, 4H), 2.72 (m, 8H), 3.00 (broad, 3H), 3.95 (s, 2H), 7.45 (d,

7.5 Hz, 2H), 7.58 (d, $J_{HH} = 9.0$ Hz, 2H), 7.61 (dd, $J_{HH} = 9.0$, 7.5 Hz, 1H), 7.87 (d, $J_{HH} = 7.5$ Hz, 2H), 7.90 (d, $J_{HH} = 7.5$ Hz, 2H).

### Preparation of Oligonucleotide Solution for UV Melting Measurements

Oligonucleotide solutions were prepared using a buffer containing 0.1 M $NaNO_3$ and 0.01 M HEPES, adjusted to pH 7.4. Oligonucleotide concentrations were determined by absorbance at 260 nm and the calculated single-strand extinction coefficients based on a nearest neighbour model.[24] Prior to conducting the melting experiments, the solutions were heated to 80°C, kept there for 5 min, then gradually cooled down to room temperature. All duplex melting curves by UV spectra were measured with increasing temperature from 0 to 80°C at a rate of 0.5°C/min.

### Photoirradiation Procedure

An aerated sample solution charged in a quartz cell (10 mm × 10 mm) connected to a Pyrex tube was irradiated using a 300-W, water-cooled (20–25°C) high-pressure mercury lamp. For the UV irradiation process, a $Ni(NO_3)_2/Co(NO_3)_2$ solution in a 10-mm-thick doughnut-type Pyrex cell was used as a band-pass filter (band-pass region; 330–390 nm). For the visible light irradiation, a $K_2CrO_4/CuSO_4$ solution in a 10-mm-thick doughnut-type Pyrex cell was used as a cut off filter (cut off below 400 nm).[25] The quantum yields were measured as follows. A 3-$cm^3$ buffer solution of **1** saturated with argon gas in a quartz cell was irradiated within 10% conversion. Actinometry was carried out using benzophenone and benzhydrol solution.[25] The product yield was determined by absorption spectra.



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