

# Effect of solvent on the photocontrolled coordination of aza analogues of 1-(9-anthryl)-2-phenylethene to a zinc porphyrin

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## Abstract

The axial coordination of aza analogues of 1-(9-anthryl)-2-phenylethene to zinc 5,10,15,20-tetratolylporphyrin (ZnTTP) was investigated. *E*-1-(9-Anthryl)-2-(*n*-pyridyl)ethenes ( $n=2, 3$  and 4) (*E*-*n*-APyE), the *Z* isomers ( $n=2$  and 4) (*Z*-*n*-APyE) and *E*-1-(9-anthryl)-2-(2-pyrazinyl)ethene (*E*-APzE) were tested as aza analogues of 1-(9-anthryl)-2-phenylethene. *E*-2-APyE, *Z*-2-APyE and *E*-APzE did not form a complex with ZnTTP. ZnTTP formed a complex with *E*-3-APyE, but complexation of ZnTTP with *Z*-3-APyE could not be observed because *Z*-3-APyE was not available. *E*-4-APyE and *Z*-4-APyE showed a considerable difference in their ability to form a complex with ZnTTP. In order to examine the effect of the solvent polarity, the results in dichloromethane were compared with those in toluene. The extent of coordination of *E*-4-APyE to ZnTTP in dichloromethane was significantly reduced due to the *E*→*Z* photoisomerization of *E*-4-APyE on UV irradiation. However, because the photoisomerization of *E*-4-APyE was very inefficient in toluene, the extent of coordination of *E*-4-APyE to ZnTTP in toluene remained unchanged on UV irradiation for up to 2 h. Therefore a change in solvent affected the photoresponsiveness of the system. © 1997 Elsevier Science S.A.

**Keywords:** Absorption spectrum; Aza analogues of 1-(9-anthryl)-2-phenylethene; Photocontrolled coordination; Solvent effect; Zinc 5,10,15,20-tetratolylporphyrin

## 1. Introduction

The basic challenge of photochemistry is the design and construction of a photochemical molecular device [1–3]. Photochemical molecular devices can be divided into two classes: artificial energy conversion devices [4,5] and information processing devices [6]. Natural systems provide the origin of such devices, e.g. photosynthesis (energy conversion device) and vision (information processing device) [7]. The photoresponsive chemical system responsible for vision is 11-*cis*-retinal and the corresponding reaction is the photoisomerization of 11-*cis*-retinal to all-*trans*-retinal. Photochemical *cis*–*trans* isomerization has received considerable attention due to its potential application in artificial information processing devices.

Azobenzene derivatives have been extensively used as photocontrolling chromophores [8–13], e.g. photoresponsive azobiscrowns [10]. The *E* isomer of azobis(benzo-15-

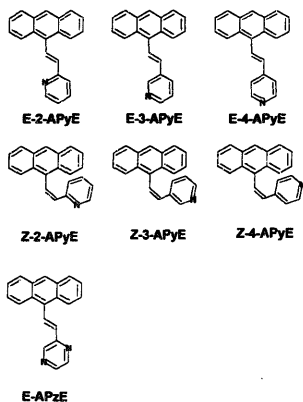
crown-5) is isomerized by UV light to the *Z* isomer and the latter is isomerized thermally to the *E* isomer. The *E* isomer exhibits high selectivity and extractability for  $\text{Na}^+$ , and the *Z* isomer efficiently extracts  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  ions [11]. Vögtle et al. [12] have reported photoswitchable catenanes in which the azobenzene unit is converted from the *E* form into the *Z* form by UV irradiation and reverts to the *E* form by heating or on irradiation with visible light.

A metalloporphyrin-1-phenyl-2-(*n*-pyridyl)ethene system has been reported to be photoresponsive, and is expected to be applied as a photoswitch [14]. 1-Phenyl-2-(*n*-pyridyl)ethene derivatives undergo *E*–*Z* isomerization on UV irradiation [15]; the reverse reaction occurs on irradiation with visible light in the presence of a metalloporphyrin [16]. 1-Phenyl-2-(*n*-pyridyl)ethene derivatives show considerable differences between the *E* and *Z* isomers in the degree of complexation with metalloporphyrins. Therefore the coordination of 1-phenyl-2-(*n*-pyridyl)ethene to a metalloporphyrin is controlled by its photoisomerization.

Aza analogues of 1-(9-anthryl)-2-phenylethene (9-APe), including 1-(9-anthryl)-2-(*n*-pyridyl)ethenes ( $n=2, 3$  and 4) (*n*-APyE) [17,18] and 1-(9-anthryl)-2-(2-pyrazinyl)ethene (APzE) [19], are a family of aza analogues of

Abbreviations: *E*-*n*-APyE, *E*-1-(9-anthryl)-2-(*n*-pyridyl)ethenes ( $n=2, 3$  and 4); *Z*-*n*-APyE, *Z*-1-(9-anthryl)-2-(*n*-pyridyl)ethenes ( $n=2$  and 4); *E*-APzE, *E*-1-(9-anthryl)-2-(2-pyrazinyl)ethene; ZnTTP, zinc 5,10,15,20-tetratolylporphyrin

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Scheme 1.

diarylethenes similar to 1-phenyl-2-(*n*-pyridyl)ethenes, but exhibit one-way *Z* → *E* adiabatic photoisomerization in non-polar solvents. The *Z* isomers are photochemically converted into the *E* isomers, but the reverse reaction, i.e. *E* → *Z* isomerization, is not observed. As the medium polarity is increased, the photoisomerization of 2-APyE, 4-APyE and APzE changes from a one-way mode to a two-way mode: *E* → *Z* and *Z* → *E* photoisomerization reactions are observed.

In this paper, the complexation of aza analogues of 9-APe (Scheme 1) to a zinc porphyrin and the effect of UV irradiation on the complexes are investigated. Moreover, from the viewpoint of solvent-dependent photoisomerization behaviour, it is determined whether or not the solvent contributes to the factors which make the chemical system photoresponsive. It is expected that the presence of the bulky anthryl group in *n*-APyEs and APzE may lead to considerable differences between the *E* and *Z* isomers in the extent of complexation to the zinc porphyrin. The degree of complexation of aza analogues of 9-APe to a zinc porphyrin can be changed by *E* → *Z* photoisomerization which is dependent on the solvent polarity. In non-polar solvents, the degree of complexation remains unchanged on UV irradiation because no *E* → *Z* photoisomerization occurs. However, on UV irradiation of a solution of a ZnTTP-*E*-*n*-APyE (or ZnTTP-*E*-APzE) com-

plex in a polar solvent, it is expected that efficient *E* → *Z* photoisomerization will result in the liberation of *n*-APyE (or APzE) from the complex due to the large difference between the *E* and *Z* isomers in the degree of coordination of *n*-APyE (or APzE) to the zinc porphyrin (Scheme 2). A chemical system which is photoresponsive in polar solvents and non-photoresponsive in non-polar solvents is suggested.

## 2. Experimental details

### 2.1. Materials

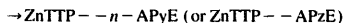
Dichloromethane and toluene were freshly prepared over  $P_2O_5$  in a dry nitrogen atmosphere. The preparation of *n*-APyE [17,18] and APzE [19] has been described elsewhere. 5,10,15,20-Tetratolylporphyrin (TTP) was prepared by a standard method [20]. Zinc 5,10,15,20-tetratolylporphyrin (ZnTTP) was prepared by stirring a dichloromethane solution of free-base TTP with an excess of zinc acetate at room temperature under Ar, and purifying the resulting ZnTTP by column chromatography on silica gel using dichloromethane as eluent.

### 2.2. Instrumentation

UV-visible absorption spectra were recorded on a Hitachi U-321097 spectrophotometer. An Aminco-Bowman Series 2 luminescence spectrometer was used for steady state fluorescence studies.

### 2.3. Complexation of ZnTTP with *n*-APyE and APzE

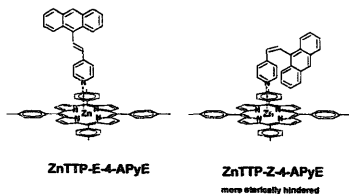
The formation constants for ZnTTP-*n*-APyE and ZnTTP-APzE complexes were measured in dichloromethane or toluene at room temperature by the spectrophotometric titration method using the equation derived by Radzki and Giannotti [21]



$$1/(A_0 - A_1) = 1/(A_0 - A_1) + [1/(A_0 - A_1)] \\ \times (1/K) \times (1/[S])$$

where  $A_0$  is the absorbance of free ZnTTP when  $[S] = 0$ ,  $A_1$  is the absorbance of the sample solution with *n*-APyE (or APzE) concentration  $[S]$  and  $A_1$  is the absorbance of ZnTTP completely complexed with *n*-APyE (or APzE) when the concentration of *n*-APyE (or APzE) is very high.

All spectra were taken at a ZnTTP concentration of about  $1 \times 10^{-5}$  M. *n*-APyE (or APzE) was added to the solution of ZnTTP and its concentration was adjusted in the range  $2 \times 10^{-5}$  to  $2.5 \times 10^{-4}$  M. The mixture was stirred for 5 min at room temperature under Ar.



Scheme 2.

The  $K$  values for ZnTTP-*n*-APyE (or ZnTTP-APzE) complexes were determined using the absorbances at 550 nm ( $\beta$  band in the Q band region).

#### 2.4. Photolysis

A solution of ZnTTP ( $1 \times 10^{-5}$  M) and *n*-APyE (or APzE) ( $1.5 \times 10^{-4}$  M) in dichloromethane or toluene was irradiated at 350 nm using a Southern New England RPR 100 photochemical reactor equipped with an RMA-500 merry-go-round unit and 16 RPR 3500 Å fluorescent lamps. The change in the degree of complexation on *E-Z* isomerization of *n*-APyE (or APzE) on irradiation was followed using the UV-visible absorption spectrum.

### 3. Results and discussion

#### 3.1. Complexation of ZnTTP with *n*-APyE and APzE

Zinc porphyrin forms pentacoordinated complexes with coordinating ligands [22]. On complexing zinc porphyrin with an axial ligand, two effects are often observed in the UV-visible spectrum: a red shift of the entire spectrum relative to that of zinc porphyrin and an increase in the  $\epsilon_a/\epsilon_\beta$  ratio of the two visible bands. Thus we can use the wavelength shift and intensity ratio of the visible bands as a measure of the degree of complexation.

The UV-visible absorption spectrum of ZnTTP in dichloromethane shows a Soret band around 430 nm and Q bands around 549 nm ( $\beta$  band) and 588 nm ( $\alpha$  band). The Q band maxima and intensity ratios of ZnTTP in dichloromethane in the presence of *n*-APyEs and APzEs are summarized in Table 1. The Q band maxima, intensity ratios  $\epsilon_a/\epsilon_\beta$  and fluorescence maxima of ZnTTP in dichloromethane do not show any appreciable change in the presence of *E*-2-APyE, *Z*-2-APyE or *E*-APzE relative to those of pure ZnTTP,

Table 1  
Q band absorption maxima, intensity ratios  $\epsilon_a/\epsilon_\beta$  and fluorescence maxima of ZnTTP in dichloromethane in the presence of *n*-APyEs and APzEs<sup>a</sup>

<i>n</i> -APyE	$\lambda_{\text{max}}^{\text{Q}}$ (nm)		Intensity ratio $\epsilon_a/\epsilon_\beta$	$\lambda_{\text{max}}^{\text{fluo}}$ (nm)	
	$\beta$ band	$\alpha$ band			
Pure ZnTTP	549	588	0.25	599	647
Pure ZnTTP <sup>b</sup>	551	590	0.23	599	651
<i>E</i> -2-APyE	549	588	0.25	599	647
<i>Z</i> -2-APyE	549	588	0.24	599	647
<i>E</i> -3-APyE	562	603	0.60	609	649
<i>E</i> -4-APyE	563	604	0.61	611	653
<i>E</i> -4-APyE <sup>b</sup>	563	604	6.54	612	657
<i>Z</i> -4-APyE	559	603	0.53	608	644
<i>Z</i> -4-APyE <sup>b</sup>	553	601	0.34	603	651
<i>E</i> -APzE	549	588	0.26	599	647

<sup>a</sup> In dichloromethane, ZnTTP =  $1 \times 10^{-5}$  M and *n*-APyE (or APzE) =  $2.5 \times 10^{-5}$  M at room temperature. Fluorescence spectra were measured at an excitation wavelength of 550 nm.

<sup>b</sup> In toluene.

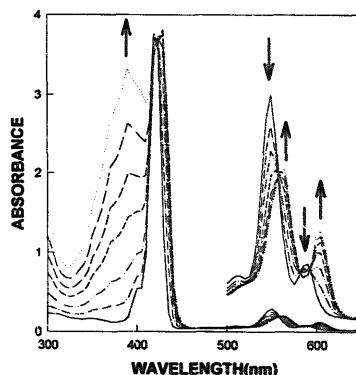


Fig. 1. UV-visible absorption spectra of ZnTTP-*E*-4-APyE in dichloromethane at room temperature. The concentrations of *E*-4-APyE were  $0$ ,  $2 \times 10^{-5}$ ,  $5 \times 10^{-5}$ ,  $1 \times 10^{-4}$ ,  $1.5 \times 10^{-4}$ ,  $2 \times 10^{-4}$  and  $2.5 \times 10^{-4}$  M. The concentration of ZnTTP was  $1 \times 10^{-5}$  M.

indicating a lack of complexation. As shown in Table 1, the complexation of ZnTTP with *E*-3-APyE results in a red shift of the Q band maxima from 549 and 588 nm to 562 and 603 nm and an increase in the intensity ratio  $\epsilon_a/\epsilon_\beta$  from 0.25 to 0.60 with a red shift of the fluorescence maxima. On complexation of ZnTTP with *E*-4-APyE (see Fig. 1 and Table 1), similar trends are observed, i.e. a red shift in the Q band maxima from 549 and 588 nm to 563 and 604 nm and an increase in the intensity ratio  $\epsilon_a/\epsilon_\beta$  from 0.25 to 0.61. On coordination of *Z*-4-APyE to ZnTTP, the change in the UV-visible absorption spectrum is somewhat different as shown in Fig. 2 and Table 1. The Q band maxima are shifted from

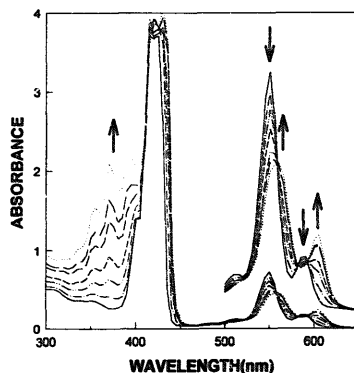


Fig. 2. UV-visible absorption spectra of ZnTTP-*Z*-4-APyE in dichloromethane at room temperature. The concentrations of *Z*-4-APyE were  $0$ ,  $2 \times 10^{-5}$ ,  $5 \times 10^{-5}$ ,  $1 \times 10^{-4}$ ,  $1.5 \times 10^{-4}$ ,  $2 \times 10^{-4}$  and  $2.5 \times 10^{-4}$  M. The concentration of ZnTTP was  $1 \times 10^{-5}$  M.

Table 2  
Formation constants ( $K$ ) of ZnTTP-*n*-APyE (or APzE) complexes<sup>a</sup>

Ligand	$K$ ( $10^3 \text{ M}^{-1}$ )		$K(E)/K(Z)$
	E	Z	
2-APyE	0	0	–
3-APyE	10.2	Not available	–
4-APyE	14.1	3.5	4.0
4-APyE <sup>b</sup>	13.3	3.8	3.5
APzE	0	Not available	–

<sup>a</sup> In dichloromethane, ZnTTP =  $1 \times 10^{-5}$  M and *n*-APyE =  $2 \times 10^{-5}$ – $2.5 \times 10^{-4}$  M at room temperature.

<sup>b</sup> In toluene.

549 and 558 nm to 559 and 603 nm; the  $\alpha$  band maximum is considerably red shifted, but the  $\beta$  band maximum is only slightly changed especially at low concentrations of Z-4-APyE (up to  $1 \times 10^{-4}$  M). The intensity ratio  $\epsilon_{\alpha}/\epsilon_{\beta}$  is increased from 0.25 to 0.53 and the degree of change is smaller than that of E-4-APyE. These results indicate a lesser degree of coordination of Z-4-APyE than E-4-APyE to ZnTTP.

Because both the E and Z isomers of 4-APyE are available and E-4-APyE and Z-4-APyE form a coordination complex with ZnTTP, the complexation of ZnTTP with E-4-APyE and Z-4-APyE was further investigated in toluene (as well as dichloromethane) and the results are shown in Table 1. The complexation of ZnTTP with E-4-APyE and Z-4-APyE results in a red shift of the Q band maxima and an increase in the intensity ratio in toluene similar to the observations in dichloromethane.

The formation constants ( $K$ ) of ZnTTP-*n*-APyE complexes were determined using the spectrophotometric titration method as described in Section 2 and are summarized in Table 2. The  $K$  value for E-4-APyE is slightly greater than that of E-3-APyE and much greater than that of Z-4-APyE.

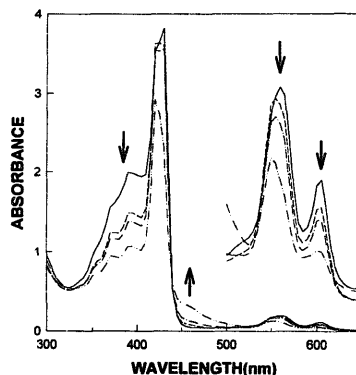


Fig. 3. UV-visible absorption spectral changes of a dichloromethane solution of ZnTTP ( $1 \times 10^{-5}$  M) and E-4-APyE ( $1.5 \times 10^{-4}$  M) as a function of the irradiation time (0, 0.5, 1 and 2 h) at 350 nm.

### 3.2. Photocontrolled coordination of 4-APyE to ZnTTP in dichloromethane

On UV irradiation, *n*-APyEs undergo photochemical E-Z isomerization, which is affected by the solvent polarity. In non-polar solvents, one-way Z  $\rightarrow$  E photoisomerization is observed for all *n*-APyEs ( $n = 2, 3$  and 4) and APzE. However, 2-APyE and 4-APyE, in polar solvents, undergo E  $\rightarrow$  Z photoisomerization as well as Z  $\rightarrow$  E photoisomerization, whereas only one-way Z  $\rightarrow$  E photoisomerization is observed for 3-APyE even in polar solvents [18].

Of the aza analogues of 9-APE examined, 4-APyE shows a large difference in the degree of coordination to ZnTTP between the E and Z isomers. Therefore the coordination of 4-APyE to ZnTTP is expected to be controlled by the pho-

Table 3  
Effect of UV irradiation on the Q band absorption maxima, intensity ratios and fluorescence maxima of ZnTTP-E-4-APyE in dichloromethane and toluene<sup>a</sup>

Irradiation time (h)	$\lambda_{\text{max}}^{\text{Q}}$ (nm)		Intensity ratio $\epsilon_{\alpha}/\epsilon_{\beta}$	$\lambda_{\text{max}}^{\text{FL}}$ (nm)	
	$\beta$ band	$\alpha$ band			
In dichloromethane					
Pure ZnTTP		549		599	647
Complex	0	562	0.58	608	652
	0.5	554	0.48	611	650
	1.0	554	0.46	611	653
	2.0	551	0.38	614	653
In toluene					
Pure ZnTTP		551	0.23	599	651
Complex	0	563	0.53	612	652
	0.5	562	0.53	612	652
	1.0	562	0.53	612	652
	1.0	562	0.53	612	652
	2.0	563	0.55	612	652

<sup>a</sup> Concentrations of ZnTTP =  $1 \times 10^{-5}$  M and E-4-APyE =  $1.5 \times 10^{-4}$  M were employed at room temperature. The fluorescence spectra were measured at an excitation wavelength of 550 nm.

toisomerization of 4-APyE induced by UV irradiation. Furthermore, the photoisomerization of 4-APyE depends on the solvent polarity. The combined use of an appropriate solvent and UV irradiation has the potential to control the coordination of 4-APyE to ZnTTP.

When a dichloromethane solution of ZnTTP ( $1 \times 10^{-5}$  M) and E-4-APyE ( $1.5 \times 10^{-4}$  M) is irradiated by 350 nm UV light, the UV-visible absorption changes as a function of the irradiation time; these changes are represented in Fig. 3 and Table 3. After irradiation for 2 h, the Q band maxima are blue shifted from 562 and 604 nm to 551 and 602 nm and the intensity ratio  $\epsilon_a/\epsilon_b$  between the Q band maxima is reduced from 0.58 to 0.38. The absorption intensity in the region between 350 and 400 nm, corresponding to the absorption of E-4-APyE, is decreased due to the E  $\rightarrow$  Z photoisomerization of E-4-APyE. These UV spectral changes indicate that, on UV irradiation, the coordination complex absorbing at longer wavelength changes gradually to uncomplexed ZnTTP. It is inferred that the extent of coordination is decreased and 4-APyE is liberated from ZnTTP by the dissociation of the ZnTTP-E-4-APyE complex induced by E  $\rightarrow$  Z photoisomerization.

When a dichloromethane solution of ZnTTP ( $1 \times 10^{-5}$  M) and Z-4-APyE ( $1.5 \times 10^{-4}$  M) is irradiated by 350 nm UV light, the UV-visible absorption changes as a function of the irradiation time; these changes are represented in Fig. 4 and Table 4. After irradiation for 2 h, the Q band maxima (from 552 and 603 nm to 551 and 602 nm), the intensity ratio  $\epsilon_a/\epsilon_b$  between the Q band maxima (from 0.42 to 0.37) and the fluorescence maxima show little change (decrease in the total intensity). The absorption intensity in the region between 350 and 400 nm is slightly decreased, indicating no appreciable Z  $\rightarrow$  E photoisomerization of Z-4-APyE or decomposition of ZnTTP on prolonged irradiation. If Z  $\rightarrow$  E photoisomerization of Z-4-APyE occurs, the absorption intensity in the region between 350 and 400 nm should increase because the absorbance of E-4-APyE is greater than

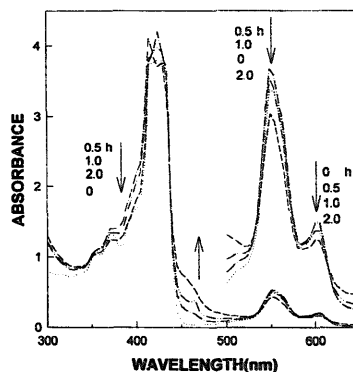


Fig. 4. UV-visible absorption spectral changes of a dichloromethane solution of ZnTTP ( $1 \times 10^{-5}$  M) and Z-4-APyE ( $1.5 \times 10^{-4}$  M) as a function of the irradiation time (0, 0.5, 1 and 2 h) at 350 nm.

that of Z-4-APyE in this spectral region. When visible light of 450 nm is used instead of UV light of 350 nm, similar results are obtained.

### 3.3. Effect of irradiation on the coordination complex of ZnTTP with 4-APyE in toluene

When a toluene solution of ZnTTP ( $1 \times 10^{-5}$  M) and E-4-APyE ( $1.5 \times 10^{-4}$  M) is irradiated with 350 nm UV light for 2 h, the Q band maxima and intensity ratio  $\epsilon_a/\epsilon_b$  remain unchanged as shown in Table 3. In non-polar solvents, such as toluene, E-4-APyE does not undergo photoisomerization. Therefore UV irradiation cannot produce the dissociation of the ZnTTP-E-4-APyE complex. In the case of Z-4-APyE, UV irradiation does not result in a change in the Q band maxima and intensity ratio  $\epsilon_a/\epsilon_b$  as shown in Table 4.

Table 4

Effect of UV irradiation on the Q band absorption maxima, intensity ratios and fluorescence maxima of ZnTTP-Z-4-APyE in dichloromethane and toluene<sup>a</sup>

Irradiation time (h)	$\lambda_{\text{max}}^{\text{Q}}$ (nm)		Intensity ratio $\epsilon_a/\epsilon_b$	$\lambda_{\text{max}}^{\text{fl}}$ (nm)	
	$\beta$ band	$\alpha$ band			
In dichloromethane					
Pure ZnTTP	549	588	0.25	599	647
Complex					
0	552	603	0.42	599	647
0.5	551	602	0.38	602	647
1.0	551	602	0.36	596	647
2.0	551	602	0.37	602	647
In toluene					
Pure ZnTTP	551	590	0.23	599	651
Complex					
0	552	594	0.27	605	651
0.5	550	592	0.34	599	649
1.0	550	590	0.37	601	649
2.0	553	601	0.34	604	652

<sup>a</sup> Concentrations of ZnTTP =  $1 \times 10^{-5}$  M and Z-4-APyE =  $1.5 \times 10^{-4}$  M were employed at room temperature. The fluorescence spectra were measured at an excitation wavelength of 550 nm.

#### 4. Conclusions

Of the aza analogues of 9-APE tested, the coordination of 4-APyE to zinc porphyrin is controlled by the E → Z photoisomerization of E-4-APyE in polar solvents as shown by the considerable difference between the E and Z isomers in the degree of complexation of 4-APyE to zinc porphyrin. However, in non-polar solvents, UV irradiation does not affect the coordination of E-4-APyE to ZnTTP because E-4-APyE cannot undergo E → Z photoisomerization in non-polar solvents.

The ZnTTP-E-4-APyE complex is a chemical system which is photoresponsive in polar solvents and non-photoresponsive in non-polar solvents. It is shown that the combined use of an appropriate solvent and UV irradiation has the potential to control such a chemical system, which is expected to be applied as a photoswitch for chemical reaction on a metalloporphyrin complexed with 4-APyE.

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