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Efficient catalysis of the photoisomerization of stilbene derivatives by zinc porphyrin complexation

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Abstract

Very high quantum yields have been obtained for the *cis–trans* photoisomerization of 1-(1-naphthyl)-2-(4-pyridyl)ethylene (NPE) using zinc(II)-5,15-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (ZnP) as sensitizer and catalyst. The quantum yield was found to increase with the concentration of the zincporphyrin to a maximum of about 85. At higher concentrations of the porphyrin the quantum yield decreases. The increase in quantum yield at low ZnP concentrations is explained as being due to energy transfer processes. Triplet energy is transferred from a complex of *trans*-isomer and ZnP to a ground state complex of *cis*-isomer and ZnP. Formation of excimers and exciplexes is probably responsible for the decrease in quantum yield at high concentrations of ZnP. Ligand exchange in complexes seems to have only a minor effect on the quantum yields. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Catalysis; *cis–trans* isomerization; Complexation

1. Introduction

cis–trans photoisomerizations are important processes, which by now are fairly well understood, and it is a challenge to try to make them as efficient as possible. We have recently shown that catalysis of triplet state *cis–trans* isomerizations is possible [1,2]. In this type of catalysis the excited states of the reactant, the product and the catalyst are all involved and the catalyst acts as a chain carrying species within a quantum chain process. There are a number of criteria that have to be fulfilled for this catalysis to be efficient. The shape of the potential energy surface in the triplet excited state is important and the isomerization has to proceed according to either an adiabatic or a dual mechanism. Adiabatic photoisomerizations occur exclusively on the excited state surface [3,16]. The *trans*-isomer corresponds to the energy minimum on the excited state surface and this makes a quantum chain process possible. In adiabatic photoisomerizations the excited state energy minimum corresponds to an intermediate (the p*-state) where the double bond is twisted 90° from its normal planar geometry. The reaction starts on the excited state surface but when the perpendicular geometry is reached intersystem crossing to the ground state occurs making a quantum chain process impossible [3,16]. For olefins, isomerizing according to a dual mechanism, deactivation of the excited state takes place from both p* and the excited *trans* conformer since an equilibrium between molecules in these two states is established [3,16]. Hence, a quantum chain process can be achieved in this case as well. In the chain process energy is transferred from the triplet excited *trans*-isomer to a ground state *cis*-isomer. Since the energy level of the donor is slightly lower than that of the acceptor this energy transfer step is endothermic. When a catalyst is added energy can first be transferred from the triplet excited *trans*-isomer to the catalyst in its ground state and then from the triplet excited catalyst to a ground state *cis*-isomer. This procedure has proved to be more efficient if the lifetime of the catalyst is much longer than the lifetime of the product in the triplet state. The triplet energy of the catalyst should be in between those of the *trans*- and *cis*-isomers, preferably about 1.5 kcal above the triplet energy of the *trans*-isomer [4]. It is also an advantage if the catalyst can be used as a sensitizer [2].

There are a few examples in the literature of *cis–trans* photoisomerizations being catalyzed within a complex [5–8]. Whitten et al. [7] performed such studies on stilbenes with metalloporphyrins as sensitizers and catalysts. In this case a cage–encounter complex was used to explain the results. They also investigated the possibility of catalyzing photoisomerizations of azastilbenes with metalloporphyrins [5–7]. Quantum yields for *cis–trans* isomerizations of some of the azastilbenes substantially exceeded unity, which is remarkable considering the fact that the triplet energy of the

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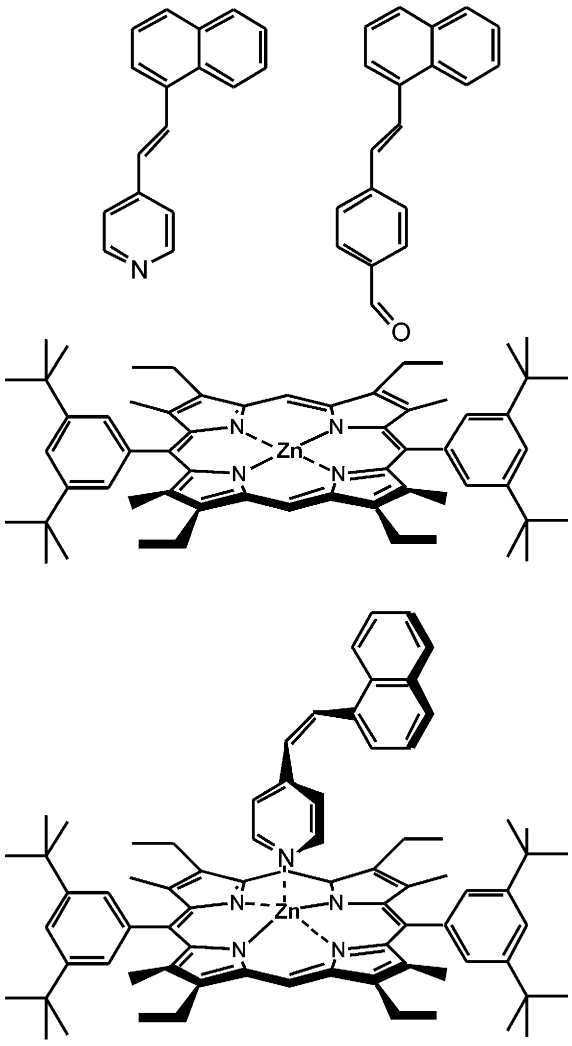

Fig. 1. ZnP, NPE, 1-naphthyl-2-(4′-benzaldehyde)ethylene (NBE) and a tentative complex between ZnP and NPE.

azastilbene is far above that of the metalloporphyrin. A mechanism involving reversible energy transfer of triplet excitation between porphyrin and azastilbene ligand within the exciplex coupled with rapid ligand exchange was put forward as a possible explanation for the results.

In this paper, a study of *cis–trans* photoisomerizations catalyzed by zinc(II)-5,15-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (ZnP) is presented. 1-(1-Naphthyl)-2-(4-pyridyl)ethylene (NPE) and 1-(1-naphthyl)-2-(4-(formyl)phenyl)ethylene (NFPE) are used as olefins and we discuss what mechanism is most likely for the catalysis of the quantum chain process (Fig. 1).

2. Experimental details

2.1. 1-(1-Naphthyl)-2-(4-pyridyl)ethylene

(1-Naphtalenemethyl)triphenylphosphonium chloride was synthesized from 1-chloromethylnaphtalene (16.98 g, 96 mmol) and triphenylphosphine (24.97 g, 95 mmol). The reactants were mixed in xylene (110 ml) and refluxed for 7.5 h. The reaction mixture was cooled for 1 h and then poured into a Büchner funnel. The colorless crystals obtained (36.25 g, 95%) were washed with ice-cooled ether.

A Wittig reaction was used to prepare 1-naphthyl-2-(4-pyridyl)ethylenes. (1-Naphtalenemethyl)triphenylphosphonium chloride (3.8 g, 8.7 mmol) and 4-pyridinecarboxaldehyde (0.93 g, 8.7 mmol) were dissolved in ethanol (80 ml). The mixture was cooled to −40°C and kept under a slow stream of nitrogen. Lithium ethoxide, made by adding Li (0.48 g, 69 mmol) to ethanol (99.5%, 75 ml), was added slowly during 18 h. The reaction was then quenched with brine and extracted three times with ether. The combined ether fractions were washed with water and dried with sodium sulfate. After evaporation of the solvent the crude product was purified by flash chromatography on silica gel with a mixture of ether and pentane (80:20) as the eluent. *cis*- and *trans*-isomers were separated by preparative HPLC using ether–pentane (80:20) as the eluent and a medium-polar column packed with Spherisorb S10CN. The isomeric purities were >99.5%.

2.2. 1-(1-Naphthyl)-2-(4-(formyl)phenyl)ethylene

1-(1-Naphthyl)-2-(4-bromophenyl)ethylene (NBPE) was synthesized by a Wittig reaction under similar conditions as for NPE. 4-Bromobenzyltriphenyl-phosphonium bromide (4.95 g, 9.7 mmol) and naphthalenealdehyde (1.51 g, 9.7 mmol) were mixed in dry DMF (100 ml). Lithium ethoxide in ethanol, made by adding Li (0.54 g, 78 mmol) to ethanol (99.5%, 60 ml), was used as the base. After 51 h the reaction was quenched with brine (50 ml) and the mixture was extracted three times with ether. The combined ether fractions were washed with water and dried over magnesium sulfate and the solvent was evaporated off. Purification using column chromatography (silica gel) with methylene chloride as the eluent was performed. The first band contained a colorless mixture of *Z*-NBPE and *E*-NBPE (85%).

NBPE (1 g, 3.23 mmol) was placed in a dried round bottomed flask fitted with a septum and a magnetic stirrer bar and the flask was filled with argon three times. Dry ether ($50\,\mathrm{cm}^3$) was added under a stream of argon and the mixture was stirred until the solids were dissolved. The reaction flask was then placed in an ice bath and *n*-buthyllithium (3.35 ml, 1.45 M) was added by a syringe, and the solution instantly became dark red. After 30 min distilled DMF (3.75 ml) was added by a syringe to the flask and the solution turned yellow. The ice bath was removed and the reaction left for 1 h with constant stirring. Diluted hydrochloric acid ($50\,\mathrm{cm}^3$, 2 M) was added after removing the septum and the mixture was stirred for a few minutes to assure complete quenching. The mixture was extracted with ether ($5\times 40\,\mathrm{cm}^3$) and dried over sodium sulfate. After evaporation of the solvent the residual was subjected to flash chromatography on silica gel with pentane–ether (80:20) as the eluent. The *trans*-fraction was recrystallized from ethanol (99.5%) and the *cis*-fraction was purified using preparative HPLC with pentane–ether (80:20) as the eluent and a medium-polar column packed with Spherisorb S10CN. The isomeric purities were >99.5%.

2.3. Zinc(II)-5,15-(3,5-di-tert-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin

The zincporphyrin used was a gift of Jerker Mårtensson and the synthesis is described in Ref. [9].

2.4. Isomerization measurements

Solutions of (*Z*)-NPE/(*Z*)-NFPE and ZnP in toluene were irradiated at 546 nm in an optical bench arrangement from Applied Photophysics, using a 150 W xenon arc lamp and a monochromator. Samples with the nonmetallated porphyrin and (*Z*)-NPE in toluene were irradiated at 509 nm using the same equipment. The isomerizations were followed by analytical HPLC with a medium-polar column, Spherisorb CN 5μ. Methylene chloride was used as the eluent in the case of NPE and pentane–ether (80:20) was used for NFPE. Quantum yields were determined using ferrioxalate actinometry. All samples were degassed with five freeze- pump-thaw cycles.

3. Results

3.1. Isomerizations of NPE with varying ZnP concentrations

Isomerizations of *cis*-NPE (2×10^{-3} M) to *trans*-NPE were studied using ZnP (5×10^{-6}–1.13×10^{-4} M) as both sensitizer and catalyst with toluene as the solvent. The samples were irradiated at 546 nm where the light is absorbed only by the porphyrin. Prolonged irradiations of samples 2×10^{-3} M in *cis*-NPE and 3×10^{-5} M in ZnP led to a photostationary state of 99% *trans*. Fig. 2 shows that the efficiency of the isomerization increases with increasing concentration of ZnP. A maximum in the quantum yield is reached at a certain concentration and then at higher concentrations the isomerization rate rapidly falls off.

3.2. Isomerizations of NPE with varying concentrations of nonmetallated porphyrin

Isomerizations of *cis*-NPE (2×10^{-3} M) to *trans*-NPE were also studied using the corresponding nonmetallated porphyrin. Four samples with varying concentrations of porphyrin (5×10^{-6}, 1×10^{-5}, 5×10^{-5} and 1×10^{-4} M) were irradiated at 509 nm where NPE does not absorb. No concentration effect on the efficiency of isomerization could be detected and quantum yields were lower than 0.03 in all cases.

3.3. Addition of pyridine to solutions of cis-NPE and ZnP

The effect of pyridine on *cis–trans* isomerizations of *cis*-NPE (2×10^{-3} M) with ZnP (5×10^{-5} M) was investigated. Three samples with varying concentrations of pyridine (2×10^{-3}, 2×10^{-2} and 0.2 M) were prepared. Table 1 shows that the isomerization efficiency decreases with increasing concentration of pyridine.

Table 1
Quantum yields for the isomerization of NPE in the presence of pyridine (the concentration of *cis*-NPE is 2×10^{-3} M and the concentration of ZnP is 5×10^{-5} M)

Concentration of pyridine (M)	Φ
2×10^{-3}	11.9
2×10^{-2}	0.25
2×10^{-1}	0.04

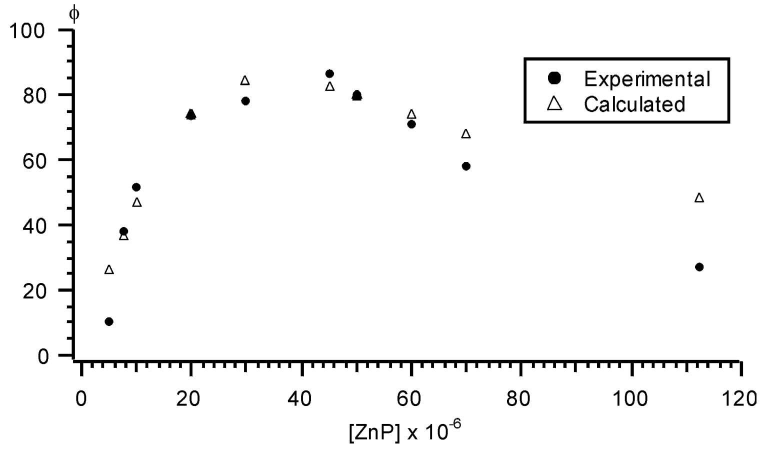

Fig. 2. Experimentally obtained quantum yields for the isomerization of *cis*-NPE as a function of ZnP concentration and the quantum yields calculated according to Eq. (19). The concentration of *cis*-NPE at It = 0 is 2.0 mM.

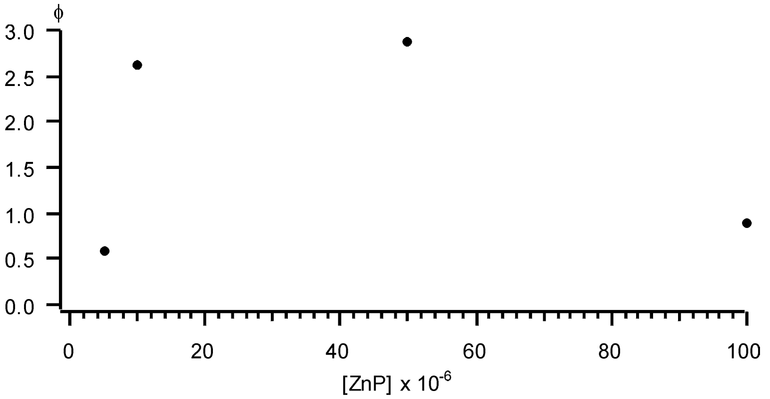

Fig. 3. Experimentally obtained quantum yields for the isomerization of *cis*-NBE as a function of ZnP concentration. The concentration of *cis*-NPE at It = 0 is 2.0 mM.

3.4. Equilibrium constants

In order to compare the strength of bonding between ZnP and ligand the equilibrium constants of NPE and pyridine were investigated. To solutions of ZnP (3.5×10^{-6} M) in toluene small samples of pyridine and *trans*-NPE, respectively, were added and the absorption spectra recorded. The equilibrium constant of pyridine with ZnP was determined to approximately 2100 and that of *trans*-NPE to 7800.

3.5. Isomerizations of NPE with varying NPE concentration

Isomerizations of *cis*-NPE ($2 \times 10^{-4}, 2 \times 10^{-3}, 2 \times 10^{-2}$ M) to *trans*-NPE were studied using ZnP (3×10^{-5} M) as catalyst and sensitizer. In Table 2 it is shown that the quantum yield increases up to a *cis*-NPE concentration of 2×10^{-3} M. Between 2×10^{-3} and 2×10^{-2} M there is only a slight difference in quantum yield. Absorption spectra show that at a *cis*-NPE concentration of 2×10^{-4} M there is plenty of uncomplexed porphyrin present, which lowers the quantum yield. For *cis*-NPE concentrations of 2×10^{-3} and 2×10^{-2} M full complexation is achieved and the quantum yields are thus similar in both cases.

3.6. Isomerizations of NFPE with varying ZnP concentrations

Isomerizations of *cis*-NFPE to *trans*-NFPE were investigated under the same conditions as isomerizations of NPE. Solutions of *cis*-NFPE (2×10^{-3} M) and ZnP (5×10^{-6}–1×10^{-4} M) were irradiated at 546 nm where NFPE does not absorb the light. Fig. 3 shows that, similar as for NPE, the efficiency of the isomerization is first increased with increasing concentration of ZnP and then the rate falls at higher concentrations. However, in this case the maximum in the quantum yield is much lower, about 3, as compared to around 85 for NPE. Samples of *Z*-NFPE (2×10^{-3} M) and ZnP (5×10^{-6}–1×10^{-4} M) were also irradiated at 416 nm with similar results.

Table 2
Quantum yields for the isomerization of NPE for various concentrations of *cis*-NPE (the concentration of ZnP is 3×10^{-5} M)

Concentration of *cis*-NPE (M)	Φ
2×10^{-4}	31
2×10^{-3}	77
2×10^{-2}	83

4. Discussion

As can be seen in Fig. 2 the efficiency of the isomerization depends strongly on the concentration of ZnP. At low ZnP concentrations the quantum yield increases with increasing ZnP concentration. A maximum of about 85 is reached at a ZnP concentration of about 4.5×10^{-5} M and then the isomerization rate falls off. Whitten et al. [7] reached a lower quantum yield, about 7, with the same *cis*-isomer but with a slightly different porphyrin. However, they never varied the concentration of the porphyrin, and it seems likely that they could have obtained a higher quantum yield by optimizing the concentration of the catalyst. The shape of the curve in Fig. 2 raises many questions as to what reactions can account for the increase and decrease of the quantum yields at various ZnP concentrations. Clearly, energy transfer directly from triplet excited ZnP to a ground state *cis*-NPE can be excluded because ZnP has a triplet energy of about 40 kcal/mol [10] and *cis*-NPE above 50 kcal/mol [7]. This energy difference is too large for simple energy transfer to occur. Instead a complex between ZnP and *cis*-NPE is needed to explain the results. For solutions of *cis*-NPE and ZnP in toluene it is clear from the absorption spectra that such a complex is present in the ground state since the electronic transitions are red-shifted. Further evidence for the importance of a complex is obtained from the results of isomerizations with nonmetallated porphyrin. In this case there is no possibility of forming a complex and as expected almost no isomerization occurs. The strength of the binding of ligand to porphyrin also seems important for the catalysis and the ligand has to bind quite strongly to the porphyrin. The equilibrium constant for ZnP-*trans*-NPE was estimated to 7800 and for *cis*-NPE with ZnP this value is probably somewhat lower due to less conjugation and some minor effects from sterical hindrance. For pyridine-ZnP the equilibrium constant was estimated to 2100 and when pyridine was added to solutions of *cis*-NPE and ZnP the isomerization efficiency was found to decrease with increasing concentration of pyridine due to less possibilities for *cis*-NPE to bind to ZnP. In contrast, NFPE binds very weakly to the porphyrin. No ground state complex is observed in the absorption spectra and the efficiency of the isomerization is greatly reduced.

An ion chain process is in principle possible as an alternative to a quantum chain process to rationalize the efficient photoisomerization. Excited zincporphyrins would then donate electrons to the olefins, which would then undergo isomerization. A radical process could also be possible. Studies have shown that in covalently linked donor–acceptor molecules singlet radical ion pairs can recombine leading to triplet formation [11]. A recent study on the compound C_{60}–ZnTPP showed that charge-recombination in toluene yielded C_{60}–^{3*}ZnTPP as an intermediate which then via an intramolecular triplet–triplet energy transfer resulted in the lower lying fullerene triplet ($^{3*}C_{60}$–ZnTPP) [12]. However, an ion chain or radical process can probably be excluded in this case. Generation of free ions in the nonpolar solvent toluene is expected to be quite inefficient. Furthermore, Whitten et al. [7] found that the isomerization process was less efficient in polar solvents and no radicals were detected when the solutions were irradiated in an esr cavity.

Whitten et al. [7] argued that a rapid ligand exchange is necessary for achieving high quantum yields. They state that 10^3–10^4 exchanges should occur during the triplet lifetime of the porphyrin. This is probably not completely true since the results show that in the beginning the quantum yield increases with increasing concentration of ZnP. If a rapid ligand exchange were the major factor a high quantum yield should be obtained already at low concentrations of ZnP and an increase would not occur. The dominant factor is probably instead energy transfer between complexes. Triplet energy is transferred from the *trans*-isomer–ZnP complex to a ground state complex of *cis*-isomer and ZnP. The triplet energy difference between the two complexes should be quite small and the energy transfer between them fast enough. Increasing the concentration of ZnP, and hence also of complexes, will increase the efficiency of the isomerization. However, Fig. 2 shows that the efficiency of the isomerization decreases considerably at higher concentrations of ZnP. A possible explanation is the formation of triplet excimers and triplet exciplexes from zinc porphyrins with or without ligand. The triplet energies of these excimers and exciplexes should be somewhat lower than those of the simple complexes and the triplet lifetimes much shorter making isomerization within the excimers and exciplexes unlikely as well as slowing down the energy transfer [13]. If a large part of the triplet excited molecules will form excimers and exciplexes instead of leading to isomerization the quantum chain process will ultimately be destroyed. The possible processes involved in the catalysis are shown in Fig. 4.

4.1. Reaction model

In order to test the relevance of the conclusions above a theoretical model has to be produced. On the basis of the discussion above we have selected reactions (1)–(18) as the important processes, which should be considered when modeling the isomerization of *cis*-isomers (*Z*) to *trans*-isomers (*E*) by metalloporphyrins (MP).

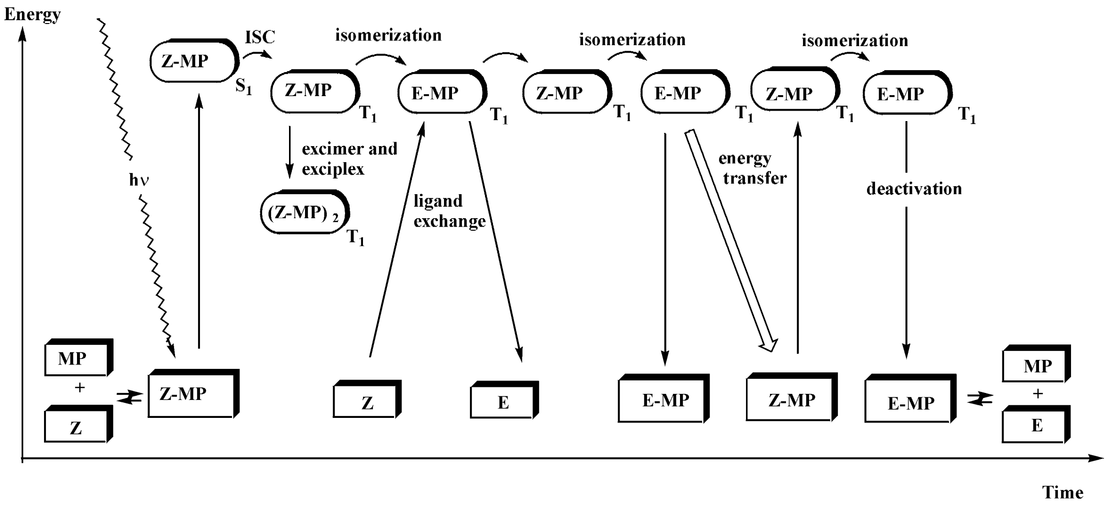

Fig. 4. Simplified scheme for the photocatalysis of a stilbene derivative (*Z* or *E*) by an MP. Excitation, intersystem crossing (ISC), isomerization, ligand exchange in the excited state, excimer and exciplex formation, energy transfer and deactivation are shown.

Excitation:

$$\text{MP} \to {}^1\text{MP}^* \to {}^3\text{MP}^* \quad (1-\alpha)I \tag{1}$$

$$Z\text{-MP} \to {}^1Z\text{-MP}^* \to {}^3Z\text{-MP}^* \quad \alpha I \tag{2}$$

Energy transfer:

$$E\text{-MP}^* + Z\text{-MP} \to Z\text{-MP}^* + E\text{-MP} \quad k_3 \tag{3}$$

$$\text{MP}^* + Z\text{-MP} \to Z\text{-MP}^* + \text{MP} \quad k_4 \tag{4}$$

$$E\text{-MP}^* + \text{MP} \to E\text{-MP} + \text{MP}^* \quad k_5 \tag{5}$$

Deactivation:

$$\text{MP}^* \to \text{MP} \quad k_6 \tag{6}$$

$$E\text{-MP}^* \to E\text{-MP} \quad k_7 \tag{7}$$

$$(Z\text{-MP})_2{}^* \to 2Z\text{-MP} \quad k_8 \tag{8}$$

$$(\text{MP})_2{}^* \to 2\text{MP} \quad k_9 \tag{9}$$

$$(Z\text{-MP-MP})^* \to Z\text{-MP} + \text{MP} \quad k_{10} \tag{10}$$

Excimer- and exciplex formation:

$$Z\text{-MP}^* + Z\text{-MP} \to (Z\text{-MP})_2{}^* \quad k_{11} \tag{11}$$

$$\text{MP}^* + \text{MP} \to (\text{MP})_2{}^* \quad k_{12} \tag{12}$$

$$Z\text{-MP}^* + \text{MP} \to (Z\text{-MP-MP})^* \quad k_{13} \tag{13}$$

$$\text{MP}^* + Z\text{-MP} \to (\text{MP-}Z\text{-MP})^* \quad k_{14} \tag{14}$$

Isomerization:

$$Z\text{-MP}^* \to E\text{-MP}^* \quad k_{15} \tag{15}$$

Dissociation of zincporphyrin complexes:

$$E\text{-MP} \to E + \text{MP} \quad k_{16} \tag{16}$$

Equilibrium:

$$\text{MP} + Z \leftrightarrows Z\text{-MP} \quad K \tag{17}$$

Ligand exchange:

$$E\text{-MP}^* + Z \to Z\text{-MP}^* + E \quad k_{18} \tag{18}$$

In reaction (1) and (2) intersystem crossing is believed to be efficient and $\Phi_{\text{ISC}} \approx 1$. The excited states are in all cases ((3)–(18)) the triplet excited states.

Using steady-state approximations for the intermediates the following expression for the rate of isomerization can be derived from the reactions above:

$$\frac{\text{d}[E]}{I\,\text{d}t} = \frac{k_{15}A(B\alpha + k_4[Z\text{-MP}](1-\alpha))}{ABC - k_4k_5k_{15}[\text{MP}][Z\text{-MP}] - k_{15}B(k_3[Z\text{-MP}] + k_{18}[Z])} \tag{19}$$

where

$$A = k_3[Z\text{-MP}] + k_5[\text{MP}] + k_7 + k_{18}[Z]$$

$$B = k_4[Z\text{-MP}] + k_6 + k_{12}[\text{MP}] + k_{14}[Z\text{-MP}]$$

$$C = k_{11}[Z\text{-MP}] + k_{13}[\text{MP}] + k_5$$

$$\alpha = \frac{K[Z]}{1+K[Z]}$$

$$[Z\text{-MP}] = \frac{K[Z][\text{MP}^{\text{total}}]}{1+K[Z]}$$

$$[\text{MP}] = \frac{[\text{MP}^{\text{total}}]}{1+K[Z]}$$

The following constants were used to fit a theoretical curve to the experimental values (Table 3).

The result is presented in Fig. 2, which shows that the theoretical curve follows the experimental values quite well. However, a discrepancy is seen at high concentrations of ZnP where the isomerization rate falls more rapidly than predicted by Eq. (19). Eq. (19) contains much information about the relative importance of reactions (1)–(18) and as the discussion below will show some reactions are more relevant for the catalysis than others.

4.2. Isomerization

Within the triplet excited complex the *cis*-isomer must undergo isomerization without loss of excitation energy. This is probably done the way Whitten et al. [7] describe by reversible energy transfer. Triplet energy is transferred from ZnP to *cis*-NPE whereupon isomerization occurs and reverse energy transfer then regenerates the triplet excited ZnP bound to *trans*-NPE. This mechanism is possible if the triplet energy difference between the porphyrin and the ligand is not too large. An energy difference of about 10 kcal/mol should result in a small amount of ligand excited triplets and a rate constant for energy transfer that is high enough for olefin triplet states to be formed during the lifetime of the porphyrin triplet. The approximate triplet energy difference between the *trans*-isomer and the porphyrin is 10 kcal/mol but the triplet energy of the *cis*-isomer is a few kcal/mol higher than that of the *trans*-isomer. The triplet energy difference within a complex of *cis*-NPE and ZnP is thus greater making the energy transfer from porphyrin triplet to *cis*-NPE much

Table 3
Constants used in Eq. (19)

k_3	k_4	k_5	k_6	k_7	k_{11}	k_{12}	k_{13}	k_{14}	k_{15}	k_{18}	K
5.5×10^9	9.0×10^9	2.0×10^9	4000	1000	1.0×10^7	1.0×10^7	1.0×10^7	1.0×10^7	60000	10^6	5500

slower. However, the triplet state of the *cis*-isomer should rapidly relax to a twisted geometry of lower energy and excitation to this distorted triplet might take place instead. The triplet energy difference would then become feasible for energy transfer to occur.

Reaction (15) describes the isomerization and the value of k_{15} is decisive for how high the quantum yields can be. Increasing the value of k_{15} increases the quantum yield and displaces the maximum towards higher concentrations of ZnP. However, a value of k_{15} of about 5–6 $\times 10^4$ seems reasonable. If a Boltzmann distribution is considered, a value of $e^{-\Delta E/RT} \approx 5.2 \times 10^{-8}$ is obtained using a triplet energy difference of 10 kcal/mol. With a normal isomerization rate of 10^{12}, k_{15} will then be about 5×10^4. Hence, as can be seen from the Boltzmann distribution, the efficiency of the isomerization is very dependent on the triplet energy difference. Increasing the triplet energy difference to 11 kcal/mol, which is considered to be the case for the excimers and exciplexes, will reduce the value of k_{15} substantially with almost no isomerization as a result.

4.3. Ligand exchange

Reaction (18) includes the ligand exchange. However, the value of k_{18} has to exceed 10^7 to affect the quantum yields to any great extent. If the value of k_{18} is increased above that value the shape of the curve will be altered. With a very high value of k_{18} a maximum in the quantum yield will be reached already at the lowest concentration of ZnP and then the quantum yield will decrease at higher ZnP concentrations. If only ligand exchange is considered and energy transfer and excimer- and exciplex formations are neglected the quantum yields will be independent of the ZnP-concentration. Eq. (19) then reduces to:

$$\frac{d[E]}{I\,dt} = a\left(1 + \frac{k_{18}[Z]}{k_7}\right) \tag{20}$$

Since the experimental values do not at all correlate with this equation ligand exchange as a major factor for catalysis can be excluded.

4.4. Energy transfer

Eq. (19) shows that energy transfer between complexes and between complex and ZnP can in fact explain the increase in quantum yield at low concentrations of ZnP. However, the energy transfer rates are not precisely known but $k_3 - k_5$ can be estimated using the Sandros equation [14]:

$$k_{\mathrm{et}} = \frac{k_{\mathrm{diff}}}{1 + \exp(-\Delta E/RT)}$$

An energy difference of 1 kcal/mol between triplet excited porphyrin and complex and a value of $1.1 \times 10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for k_{diff} [15] were used in the calculations.

4.5. Excimer- and exciplex formation

If excimer- and exciplex formations, reactions (11)–(14), were neglected in Eq. (19) the energy transfer reactions would make the quantum yields increase continuously with increasing ZnP concentration. Since the quantum yields reach a maximum and then decrease at higher ZnP concentrations energy transfer reactions alone cannot explain the results. Obviously excimer- and exciplex formations have to be considered as well in order to account for these phenomena. The rates of forming excimers and exciplexes ((11)–(14)) are not exactly known but are probably much slower than the energy transfer reactions. Reaction (11) is the most important of these reactions and a high value of k_{11} lowers the quantum yields substantially and moves the maximum towards lower concentrations of porphyrin.

4.6. Deactivation

Reactions (6)–(10) are deactivation processes and the most important of these is (7) where the triplet lifetime of E-MP* is crucial for obtaining high quantum yields. The lifetime of MP* is shorter than that of the complex [7] and does not affect the quantum yields to the same extent. Reactions (8)–(10) are all considered to be very fast [13].

In the model described above, the *trans*-isomer is considered to be strongly bonded to the zinc porphyrin also in the triplet state and hence there is time for energy transfer reactions between complexes to occur. If instead, the triplet excited complex would dissociate shortly after the isomerization, that is if reaction (16) would occur in the triplet state, the only important energy transfer reaction would be reaction (4). Reactions (7) and (8) can then be excluded as well as reactions (11) and (13) and reaction (18) would be slightly modified. This results in a much simpler expression for the rate of isomerization and the quantum yields will in this case increase continuously with increasing concentration of ZnP. Since these results do not correlate with the experimental findings this mechanism is unlikely.

5. Conclusion

Using metalloporphyrins is a very simple way of efficiently catalyzing *cis–trans* isomerizations where the porphyrin acts as both sensitizer and catalyst. In the case of catalysis through simple energy transfer between isomers and catalyst two slightly endothermic energy transfer steps are involved (from product to catalyst to *cis*-isomer). The energy difference between the isomers and catalyst is 1–2 kcal/mol and the triplet energy of the catalyst must be in between those of the *cis*- and *trans*-isomers. Catalysis within a complex on the other hand involves only one excitation energy transfer, which is less endothermic and thus more efficient. Furthermore, catalysis can occur although the triplet energy difference between the metalloporphyrin and *cis*-isomer is several kcal/mol. However, a prerequisite of an efficient catalysis through a complex is the possibility of strong binding between the metalloporphyrin and ligand.

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