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Synergistic effects in controlling excited-state photodimerisation using multiple supramolecular interactions†

Yolanda Vida Pol,[a] Rafael Suau,[a] Ezequiel Perez-Inestrosa[a] and Dario M. Bassani*[b]

[a] *Departamento de Quimica Organica, Facultad de Ciencias, Universidad de Malaga, Campus de Teatinos, E-29071 Malaga, Spain*

[b] *Groupe de Chimie Supramoléculaire, Biomimetisme et Nanosciences, LCOO, CNRS UMR 5802, Université Bordeaux I, 33405 Talence, France. E-mail: d.bassani@lcoo.u-bordeaux1.fr; Fax: 33 4000 6158; Tel: 33 4000 2827*

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The use of two independent binding sites, hydrogen-bonding and metal ion complexation, to accelerate and direct the photodimerisation of cinnamate chromophores demonstrates the operability of cooperative and synergistic effects on the excited state potential energy surface.

The self-assembly of photoactive architectures has proven to be a viable means of directing ground- and excited-state reactivity.[1] In this approach, suitable molecular or ion recognition motifs, such as hydrogen-bonding and metal chelating sites, are used to maintain and orient chromophores during the excitation and transformation processes. Systems incorporating two or more different binding sites possess the ability of responding to multiple inputs, and can be used to probe cooperativity and synergy on the excited state potential energy surface. In contrast to the many examples of multiple-input photoactive sensors and switches known to date,[2] examples of photochemical reactions sensitive to multiple chemical inputs are scarce.[3]

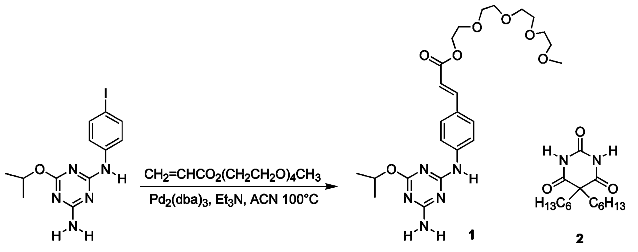
Compound **1** (Scheme 1) was prepared using Heck coupling methodology, and is designed to incorporate a hydrogen-bonding site and a metal ion-binding unit around a photoactive cinnamate chromophore. It was previously shown that, in the presence of barbituric acid derivatives such as **2**, hydrogen-bonded assemblies in which the photoactive cinnamate double bonds are placed in close proximity are formed.[4] The formation of such supramolecular architectures favours the ensuing photocyclisation reaction, which is accelerated and reflects the relative topology of the reactants within the assembly.

Irradiation of **1** (0.01 M in dichloromethane) results in fast *Z*–*E* isomerisation leading to a photostationary state enriched in the *Z* isomer. Upon prolonged irradiation, the inefficient formation of several photoproducts, attributed to photodimers (see below) is observed. Of the seven photodimers observed by HPLC, two are slightly favoured (accounting for *ca.* 50% of the total dimer formation). Under identical irradiation conditions, the presence of 0.5 eq of **2** induces a two-fold acceleration of the dimerisation efficiency, attributed to the formation of photoactive hydrogen-bonded assemblies.

The tetraethyleneglycol unit in **1** is apt to bind alkali metal ions in a fashion similar to well-known podand systems.[5] In the case of metal ions capable of binding two or more molecules of **1**, an enhancement in the rate of photodimerisation can be expected. This is indeed the case as the formation of photoproducts upon irradiation of **1** in the presence of **1** eq. KPF_6 proceeds *ca.* twice as fast as in the absence of added salt. Interestingly, the combination of **2** and K^+ gives a five-fold enhancement in dimerisation efficiency, consistent with an additive effect from both molecular receptor units in **1** working in unison. Chart 1 lists the effect of some group I and group II metal ions upon the dimerisation efficiency of **1** in the presence of 0.5 eq. of **2**. It is immediately apparent that the system is selective in response to the presence of selected metal ions, particularly Ba^{2+}. Compared to K^+, the smaller Na^+ ion gives a modest enhancement in photoreactivity. No discernable effect upon addition of quaternary ammonium salts could be detected, thus ruling out a purely electrostatic effect.

The considerable effect of Ba^{2+} on the photodimerisation efficiency of **1** can be rationalised by the formation of supramolecular assemblies in which two (or more) molecules of **1** are held together by simultaneously binding Ba^{2+} and **2**. Considering the **2** : **1** stoichiometry of the hydrogen bonding motif, it is plausible that the putative assembly is composed of **1**, **2**, and Ba^{2+} in a **2** : **1** : **1** ratio.[6] An energy-minimised (PM3 Hamiltonian) model of such a complex is shown in Fig. 1. Simultaneously binding both **2** and Ba^{2+} effectively locks two molecules of **1** into a face-to-face geometry, which is known to be particularly favourable towards photodimerisation. In contrast, if only one template is used, a greater number of geometrical isomers can be formed, and lowered reactivity is expected.

To quantify the effect of **2** and Ba^{2+} on the photodimerisation of **1**, the quantum yields for the formation of the two major photoproducts were determined in the presence and absence of the templates. The results summarised in Table 1 were obtained using a merry-go-round apparatus to ensure equal light exposure for all samples.‡ Samples were not degassed, as oxygen has no effect on the very short-lived cinnamate singlet excited state. As can be expected, the presence of either template exerts a positive influence on the photodimerisation process, albeit with differing selectivity towards specific photodimers. In the case of **2**, accrued selectivity for **3a**, whose quantum yield is nearly doubled, is observed. In contrast, although Ba^{2+} provides a much greater increase in the



Scheme 1 Synthesis of a photoactive cinnamate receptor possessing binding sites for metal ions and barbiturates such as **2**.

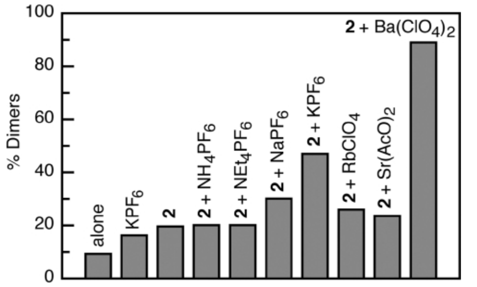


Chart 1 Proportion of dimers (determined by HPLC) formed upon irradiation of **1** (0.01 M in CH_2Cl_2 + 5% CH_3CN) in the absence and presence of **2** and selected ions (0.5 eq.).

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† Dedicated to Professor J.-M. Lehn on the occasion of his 65th birthday.

quantum yield for dimerisation, *ca*. 300-fold, the proportion **3a** : **3b** is unaltered. This may indicate that the principal effect of using non-directive ion chelation (as compared to hydrogen-bonding) is to increase the local concentration of reactants. The flexibility of the oligo(ethyleneoxide) tether may prevent orientational effects from being transferred from the metal coordination site to the photoactive centres.

Irradiations conducted in the presence of both templates are exceptionally fast. For comparison, under identical irradiation conditions where < 5% of dimers are formed in the absence of templates, the simultaneous presence of 0.5 eq. of **2** and Ba^{2+} affords nearly quantitative conversion to photodimers. The observed quantum yield for the formation of **3a** and **3b** are 0.10 and 0.026, over three orders of magnitude greater than what is obtained in the absence of templates. Such high quantum yields for the dimerisation of cinnamic acid derivatives are typically only observed in the solid or in fluid solutions in the absence of solvent.[7] Furthermore, the values reported in Table 1 likely underestimate the intrinsic dimerisation quantum yields as they are uncorrected for unbound **1** or absorption by the photochemically inert *Z* isomer. The latter accompanies the formation of photodimers during irradiation, but could not be sufficiently well separated from *E*-**1** for quantitative analysis.

Unlike previous studies of cinnamate dimerisation,[4] where photoisomerisation is much faster than intermolecular processes such as dimerisation, the dimerisation of **1** in the presence of **2** and Ba^{2+} is sufficiently fast to compete with isomerization. This complicates the accurate determination of dimerisation quantum yields, as it is no longer reasonable to assume that the photostationary states reached in the presence and absence of the templates are the same.

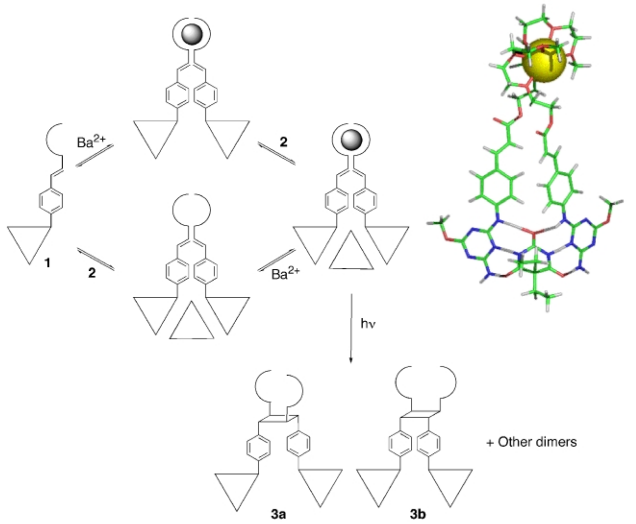

Fig. 1 Irradiation of the tetracomponent assembly formed between **1**, **2** and Ba^{2+} leads to enhanced formation of photodimers **3a** and **3b**. Top right: Energy-minimised (PM3) structure of an assembly formed between **1**, **2**, and Ba^{2+} (solid sphere).

Table 1 Quantum yields for the formation of photodimers **3a** and **3b**[a]

Product	Alone	$\mathbf{2}^{b}$	Ba^{2+b}	$\mathbf{2} + Ba^{2+c}$
3a	3.6×10^{-5}	6.4×10^{-5}	9.1×10^{-3}	9.6×10^{-2}
3b	3.7×10^{-5}	5.3×10^{-5}	1.0×10^{-2}	2.6×10^{-2}
3a/**3b**	1.0	0.2	0.9	3.7

[a] Determined in aerated CH_2Cl_2 (5% CH_3CN) solution. [**1**] = 0.01 M, 450 high pressure Hg-Xe lamp and quartz filter. [b] 0.005 M. [c] [**2**] = [Ba^{2+}] = 0.005 M.

The binding of cinnamoylaminotriazines to **2** has been previously investigated using ^1H NMR and is consistent with the stepwise formation of a 2 : 1 complex such as shown in Fig. 1. In contrast, binding isotherms obtained by NMR titration of **1** with **2** in the presence of 0.5 eq. Ba^{2+} can be fitted using a single association constant ($\log K = 4.47$). This behaviour is consistent with the pre-association of the aminotriazine moieties prior to the addition of **2**. The fact that the observed association constant is significantly higher than what is generally observed for such interactions is an indication that the aminotriazine moieties are already in a geometry conducive to binding **2**. Increasing the Ba^{2+} concentration beyond a 2 : 1 ratio (**1** : Ba^{2+}) results in a decrease of the photodimerisation efficiency, which eventually falls to what is observed in the absence of Ba^{2+}. This is interpreted by the formation of photochemically inert 1 : 1 (**1** : Ba^{2+}) assemblies.

The results obtained thus far are in agreement with the existence of cooperative effects on the ground-state association of **2** and Ba^{2+} to **1**. These also appear to hold true on the excited-state potential energy surface, as the presence of both templates results in a much greater enhancement of dimerisation than would be expected from a purely additive effect of the templates. Further evidence can be obtained from the electronic absorption and fluorescence emission spectra of **1**, both of which undergo a 5 nm bathochromic shift upon addition of Ba^{2+}. This implies that the metal cation remains bound upon excitation, a necessary condition for the observation of cooperative effects due to the presence of both **2** and Ba^{2+}. No significant increase in the lifetime of the singlet excited state of **1** is observed upon complexation, which remains below the temporal resolution of our instrumentation (*ca*. 0.3 ns). Such short lifetimes are typical of cinnamate derivatives, and exclude the possibility that the enhancement in dimerisation quantum yield upon binding Ba^{2+} is due to a significant increase in the singlet lifetime of **1**.

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Notes and references

‡ Irradiations were carried out in Pyrex tubes using a 450 W Hg-Xe lamp. For quantum yield determinations, 350 nm illumination from an optical bench equipped with a monochromator was used. Light flux was determined using Aberchrome actinometry.

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