Exclusive production of a cycloadduct from selective excitation of the charge-transfer complex between acenaphthylene and tetracyanoethylene in the crystalline state in contrast to failure of reaction in solution

Naoki Haga,*[a] Hiroyuki Nakajima,[a] Hiroaki Takayanagi[a] and Katsumi Tokumaru[b]

[a] *School of Pharmaceutical Sciences, Kitasato University, Minato-ku, Tokyo 108, Japan*
[b] *University of Tsukuba, Tsukuba, Ibaraki 305, Japan*

Selective excitation of the charge-transfer complex between acenaphthylene and tetracyanoethylene in the crystalline state exclusively affords a 1 : 1 [2 + 2] cycloadduct, in contrast to the excitation in solution, which gives no product.

Many electron donors and acceptors give charge-transfer (CT) complexes in solution and in the solid state, and their behaviour on photochemical irradiation has been investigated.[1,2] We now report that irradiation with light of wavelength longer than 500 nm of the crystalline CT complex between acenaphthylene **1** and tetracyanoethylene **2** affords a 1 : 1 [2 + 2] cycloadduct **3** of **1** and **2** as the sole product, whereas excitation in solution does not induce any reaction. To the best of our knowledge, this is the first observation of excitation of a CT complex leading to reaction in the crystal but not in solution.

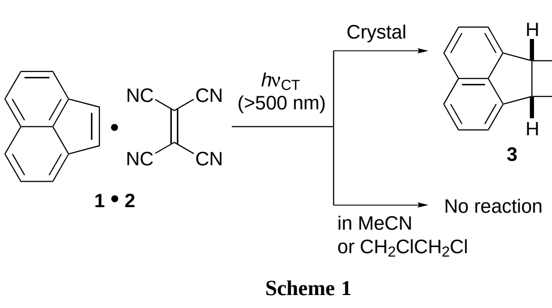
Mixing **1** and **2** in organic solvents immediately produces a tan–brown colour due to formation of their CT complex (with an absorption extending to 700 nm) in equilibrium with **1** and **2**. Evaporation of the solvent from an equimolar mixture of **1** and **2** in ethyl acetate affords crystals of a 1 : 1 CT complex **1·2** as tan–brown cubes (satisfactory elemental analysis, mp 103.0–105.0 °C, orthorhombic, space group $P2_1/n$).

X-Ray crystallographic diffraction of **1·2** indicates that molecules of **1** and **2** are stacked alternately with a distance of 4.0 Å between the **1** and **2** planes, with a dihedral angle of 0.8°. The alkenic parts of **1** and **2** are aligned with interatomic distances of 3.3–3.9 Å and a torsion angle of 62.2°.

On irradiation of crystalline **1·2** with light of wavelength longer than 500 nm at 20 °C, where neither **1** nor **2** was excited, **3** was isolated in a 80% yield (based on consumed **1**) as the sole product (Scheme 1).† The quantum yield for formation of **3** was *ca.* 4 (±1) × 10^{-3} under irradiation with 546.1 nm monochromatic light.[3]‡

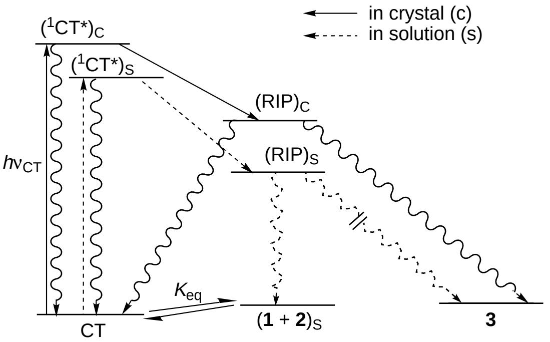
In contrast, irradiation of an equimolar (0.1 M) mixture of **1** and **2** in MeCN or dichloroethane with light of > 500 nm did not result in any reaction; however, irradiation with light of > 400 nm to excite **1** led to formation of **3** in low yield accompanied by larger amounts of the dimer of **1**.

A tan–brown fine powder prepared by pulverizing an equimolar mixture of **1** and **2** was irradiated with light of > 500 nm to give *ca.* 5% of **3** with larger amounts of the dimer of **1**. Formation of the dimer of **1** reflects the presence of two molecules of **1** in close proximity in the fine powder, whereas in the crystal the nearest two molecules of **1** are separated by more than 6 Å.



Scheme 1

Excitation of the CT complex can induce electron-transfer from **1** to **2**. The standard free energy change for this process,[4] ΔG^0, is estimated to be −132 kJ mol^{-1} in MeCN.§



Scheme 2

On excitation of the CT complex, the initially produced Frank–Condon excited CT state will rapidly change to a relaxed state or radical ion pair (RIP). In solution, the RIP is solvated and, therefore, much more stabilized than in the absence of solvents. The lack of reaction resulting from the CT excitation in solution indicates that the excited CT state and/or the RIP undergo facile deactivation and/or backward electron-transfer preceeding to charge separation in solution.[5] On the other hand, production of the cycloadduct from excitation of the CT complex crystal suggests that the fixed positions of **1** and **2**, separated by 3–4 Å in both the excited CT state and the resultant RIP in the crystal, might retard the deactivation and backward electron-transfer and enable them to undergo cycloaddition. Moreover, the absence of solvent molecules precludes stabilization of the RIP; therefore, this will also retard backward electron-transfer and enable the RIP to undergo cycloaddition (Scheme 2).

Finally it should be noted that the present results provide for the possibility of exclusive production of a cycloadduct *via* selective excitation of a crystalline CT complex when the proper conditions are met. Furthermore, the remarkable contrast in reactivity between the crystalline state and solution on CT excitation seems to indicate the important role of solvents for stabilization of the RIP. Full details of this present result will be published elsewhere.

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Footnotes

† A 40 mg sample of **1·2** placed between two disk glass filters was irradiated using a 400 W high pressure Hg lamp in a thermostat. The products (**3** and dimers of **1**) and unreacted **1** were isolated by column chromatography.

Compound **3** (ref. 6) and the dimers of **1** (ref. 7) were identified by comparison with authentic samples prepared by alternative methods.

‡ The quantum yield for the reaction was determined according to the method of Ito *et al.* (ref. 8).

§ The ΔG^0 was obtained based on the oxidation potential for **1** [1.58 V *vs.* SCE in MeCN (ref. 9)], the reduction potential of **2** [-0.2 V *vs.* Ag electrode in MeCN (ref. 10)] and the singlet excitation energy of **1** [257 kJ mol^{-1} (ref. 11)].

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