

Supporting Information

For

Examining the base stacking interaction in a dinucleotide context via reversible cyclobutane dimer analogue formation under UV irradiation

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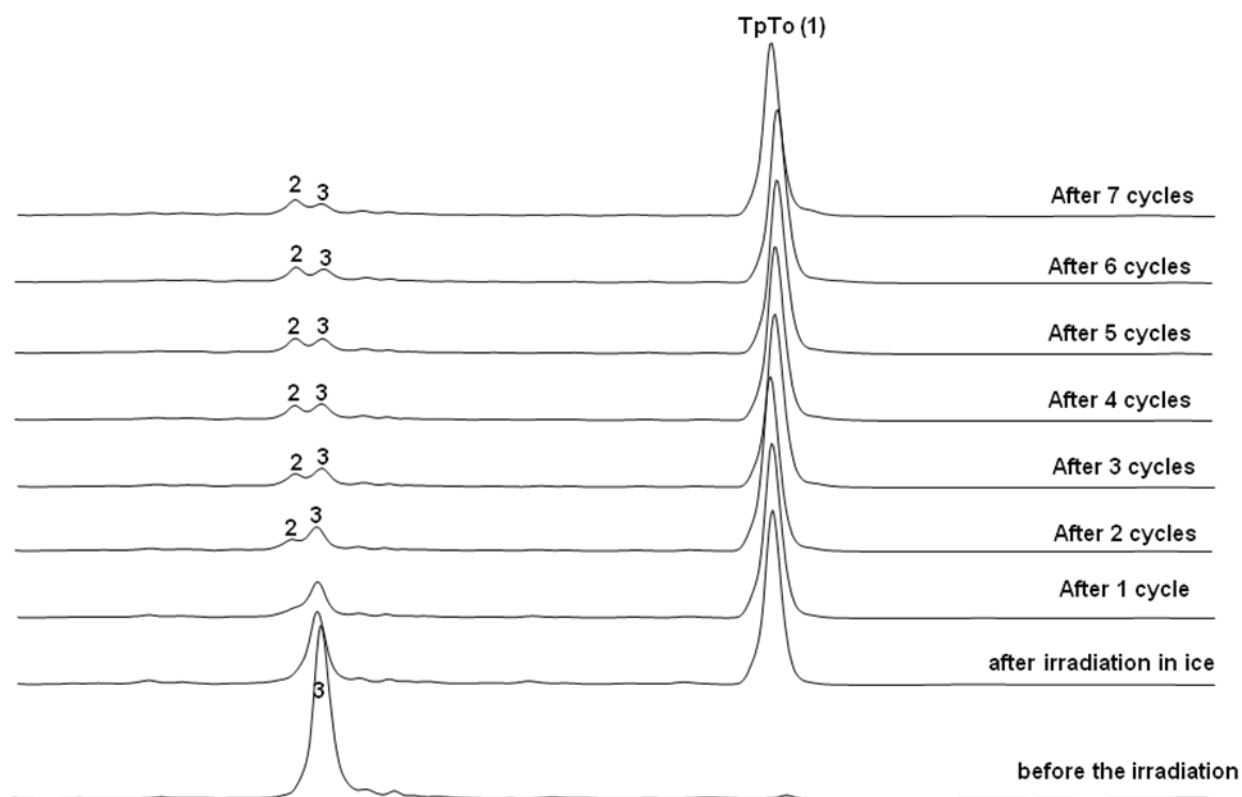


Figure S1. The HPLC chromatograph of the photoreaction of **3** after multiple irradiation-thaw-freeze cycles. No compound **2** was found before any cycle was applied due to the conformational trap in the resulting **1** under 77K. Such a conformational restraint was released after thawing the ice followed by re-freezing the solution. **2** was then observed after subsequent UV irradiation. After the seventh cycle, the ratio among **1**, **2** and **3** became very close to that obtained from the photoreaction of **1**.

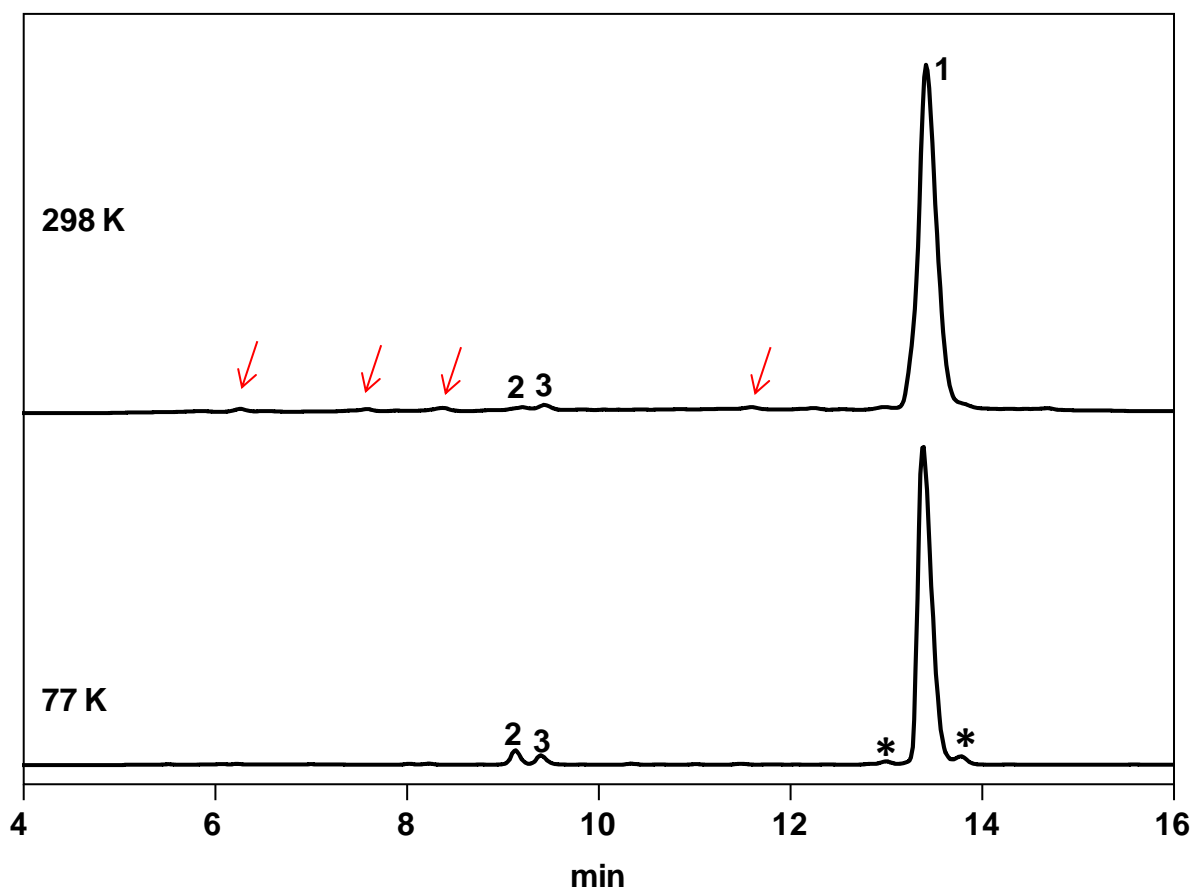
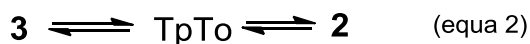


Figure S2. The HPLC chromatographs for the photoreaction of **1** at different temperature under 254 nm UVC light. Under the separation conditions employed, compound **2** eluted at 9.8 min, **3** at 10.0 min and the unreacted **1** at 14.0 min. Other products were found when the photoreactions were conducted at 298K as indicated by the peaks pointed by the red arrows. None of these peaks exhibits the same mass as **1**, suggesting them to be potential decomposition products. These peaks were thus not pursued and characterized. In contrast, the photolysis reaction at 77K is much cleaner; besides **2** and **3**, no other major products were detected (* impurities)

Quantum yield determination of photoreaction of **1** irradiated by 254 nm UV light at 77 K

Quantum yields during the photolysis of **1** were calculated according to a modified literature method.^[1] TpT and TpTo were co-dissolved in glycerol/H₂O (1 : 1) solution to make the final concentration to be 0.33 mM for both compounds. The photoreactions were carried out at 77K with the UV lamp 9.75 inches above the sample and the photoproducts separated and analyzed via HPLC.

As shown in the following two equations, the method adopted determines the quantum yields of **2** and **3** with respect to cyclobutane thymine dimer (T<>T) obtained for TpT photolysis. As shown in equation 1, two major products are produced in TpT photolysis: (6-4) photoproduct and *cis-syn* T<>T. Formation of the former species is irreversible; while formation of the later compound is reversible. Formation of **2** and **3** are reversible as well. Comparing the amount of *cis-syn* T<>T formed with those of **2** and **3** allows us to calculate the quantum yields of these T<>To species for both forward and backward reactions.



The quantum yields were calculated using the formulas below. For the symbols used, Φ and Φ^{-} represent the quantum yield for the formation and reversion of a photoproduct respectively. ϵ represents the extinction coefficient. When TpT or its photoproduct is involved, the extinction coefficient at 230 nm was used. When TpTo or T<>To is involved, the ϵ at 254nm was employed. ΔS is the peak area (integration) of a product generated at time t of the photoreaction in the HPLC chromatograph monitored at different wavelength. $\overline{\Delta S}$ is the mean value of a peak area at time t . Considering that no photoproduct is generated at time 0 and the linear region in the product formation is used in our calculation, the $\overline{\Delta S} = \Delta S \text{ measured at } t/2$, ΔS^* represents the peak area of a photoproduct when the reaction reaches equilibrium and the maximum amount of such a photoproduct is therefore produced. The subscript following each symbol indicates the specific compound associated. For instance, Φ_2 represents the quantum yield of **2**. ϵ_{TpT} represents the extinction coefficient of TpT at 230 nm and ϵ_2 represents the extinction coefficient of **2** at 254 nm.

$$\frac{\Phi_2}{\Phi_{\text{TPTCPD}}} = \frac{\Delta S_2/\varepsilon_2}{\Delta S_{\text{TPTCPD}}/\varepsilon_{\text{TPTCPD}}} \cdot \frac{\overline{\Delta S_{\text{TPT}}/\varepsilon_{\text{TPT}}}}{\overline{\Delta S_1/\varepsilon_1}} \cdot \frac{\rho_{\text{TPTCPD}}}{\rho_2};$$

$$\frac{\rho_{\text{TPTCPD}}}{\rho_2} = \frac{1 - \frac{\Delta S^*_{\text{TPT}}/\varepsilon_{\text{TPT}}}{\Delta S^*_{\text{TPTCPD}}/\varepsilon_{\text{TPTCPD}}} \cdot \frac{\overline{\Delta S_{\text{TPTCPD}}/\varepsilon_{\text{TPTCPD}}}}{\overline{\Delta S_{\text{TPT}}/\varepsilon_{\text{TPT}}}}}{1 - \frac{\Delta S^*_1/\varepsilon_1}{\Delta S^*_2/\varepsilon_2} \cdot \frac{\overline{\Delta S_2/\varepsilon_2}}{\overline{\Delta S_1/\varepsilon_1}}};$$

$$\frac{\Phi_3}{\Phi_{\text{TPTCPD}}} = \frac{\Delta S_3/\varepsilon_3}{\Delta S_{\text{TPTCPD}}/\varepsilon_{\text{TPTCPD}}} \cdot \frac{\overline{\Delta S_{\text{TPT}}/\varepsilon_{\text{TPT}}}}{\overline{\Delta S_1/\varepsilon_1}} \cdot \frac{\rho_{\text{TPTCPD}}}{\rho_3};$$

$$\frac{\rho_{\text{TPTCPD}}}{\rho_3} = \frac{1 - \frac{\Delta S^*_{\text{TPT}}/\varepsilon_{\text{TPT}}}{\Delta S^*_{\text{TPTCPD}}/\varepsilon_{\text{TPTCPD}}} \cdot \frac{\overline{\Delta S_{\text{TPTCPD}}/\varepsilon_{\text{TPTCPD}}}}{\overline{\Delta S_{\text{TPT}}/\varepsilon_{\text{TPT}}}}}{1 - \frac{\Delta S^*_1/\varepsilon_1}{\Delta S^*_3/\varepsilon_3} \cdot \frac{\overline{\Delta S_3/\varepsilon_3}}{\overline{\Delta S_1/\varepsilon_1}}};$$

$$\frac{\Phi_2 -}{\Phi_{\text{TPTCPD}} -} = \frac{\Phi_2}{\Phi_{\text{TPTCPD}}} \cdot \frac{\Delta S^*_1/\varepsilon_1}{\Delta S^*_2/\varepsilon_2} \cdot \frac{\Delta S^*_{\text{TPTCPD}}/\varepsilon_{\text{TPTCPD}}}{\Delta S^*_{\text{TPT}}/\varepsilon_{\text{TPT}}};$$

$$\frac{\Phi_3 -}{\Phi_{\text{TPTCPD}} -} = \frac{\Phi_3}{\Phi_{\text{TPTCPD}}} \cdot \frac{\Delta S^*_1/\varepsilon_1}{\Delta S^*_3/\varepsilon_3} \cdot \frac{\Delta S^*_{\text{TPTCPD}}/\varepsilon_{\text{TPTCPD}}}{\Delta S^*_{\text{TPT}}/\varepsilon_{\text{TPT}}};$$

Using these equations, the quantum yields were calculated. The reaction time t used for calculation is 2.5 minutes for reaction at 77K as they reflect a reaction time when a significant amount of photoproduct is produced while the reaction is still under the linear region. Furthermore, we found that using a shorter reaction time (for instance 1.25 minute) yields the same results. The determination was repeated three times and the average values are reported for the quantum yields.

At 77 K (in liquid N₂, frozen state)

$$\frac{\Phi_{\text{C}_2}}{\Phi_{\text{TPTCPD}}} = 1.80 \pm 0.10; \quad \frac{\Phi_{\text{C}_2^-}}{\Phi_{\text{TPTCPD}}^-} = 1.54 \pm 0.10; \quad \frac{\Phi_{\text{C}_3}}{\Phi_{\text{TPTCPD}}} = 1.05 \pm 0.05;$$

$$\frac{\Phi_{\text{C}_3^-}}{\Phi_{\text{TPTCPD}}^-} = 1.55 \pm 0.10$$

[1] C. Moriou, M. Thomas, M.-T. Adeline, M.-T. Martin, A. Chiaroni, S. Pochet, J.-L. Fourrey, A. Favre and P. Clivio, *The Journal of Organic Chemistry* **2007**, 72, 43-50.