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Photochemistry

Photochemical [2 + 4]-Dimerization Reaction from the Excited State

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 Dedicated to Professor John Porco on the occasion of his 60th birthday

Abstract: Aryl-maleimides undergo a novel [2 + 4]-photodimerization instead of the expected [2 + 2]-photodimerization under both direct irradiation with visible light and under sensitized energy transfer conditions. This new excited state reactivity in aryl-maleimides is deciphered through photochemical, photophysical, and spectroscopic studies. The stereochemistry of the photodimer depends on the type of non-bonding interactions prevalent during photodimerization which is in turn dictated by the substituents on the maleimide ring. More importantly, the stereochemistry of the photodimer formed is complementary to the product observed under thermal conditions.

Introduction

The utility of [2 + 2]-photodimerization across chemical sciences from synthesis to materials chemistry to biological systems is well documented.^[1–7] One of the main reasons for such widespread use across disciplines is both the simplicity of the reaction and the various ways one can carry out the reaction efficiently under different conditions with atom economy.^[8–11] [2 + 2]-Photodimerization upon direct irradiation from the singlet excited state is governed by orbital symmetry-initiated restrictions (*c.f.* Woodward–Hoffmann

rules).^[12] [2 + 2]-Photodimerization can also be accomplished by accessing the triplet excited state of the reactants through triplet energy transfer.^[8–11] To the best of our knowledge, [2 + 4]-photodimerization instead of [2 + 2]-photodimerization either by direct irradiation or by energy transfer has not been reported (Figure 1). In this report, we disclose that maleimides **1** can undergo [2 + 4]-photodimerization with visible light by both direct irradiation and by energy transfer mediated sensitization to form the photo-adduct **2** with very good conversions and isolated yields (Figure 1).

Photodimerization and [2 + 2]-photocycloaddition of excited chromophores have played a seminal role in the development of photochemistry and application related to light induced processes.^[1,7,13–17] As photodimerization is a bimolecular processes, the dynamics involved to manipulate the reactivity of excited chromophores undergoing the transformations have been subjected to in-depth investigations both in isotropic media and within supramolecular systems.^[7,18–21] The photochemistry of maleimides presents interesting opportunities for manipulating new modes of excited state reactivity.^[22–26] 3-Alkyl-substituted maleimides are known to undergo [2 + 2]-photodimerization and have been used for application in materials chemistry.^[27,28] In this report, we disclose the excited state reactivity of 3-aryl-substituted maleimides **1** towards [2 + 4]-photodimerization leading to tetralin derivative **2** instead of the traditional [2 + 2]-photodimerization or 6 π -photocyclization (Figure 1).^[27–30]

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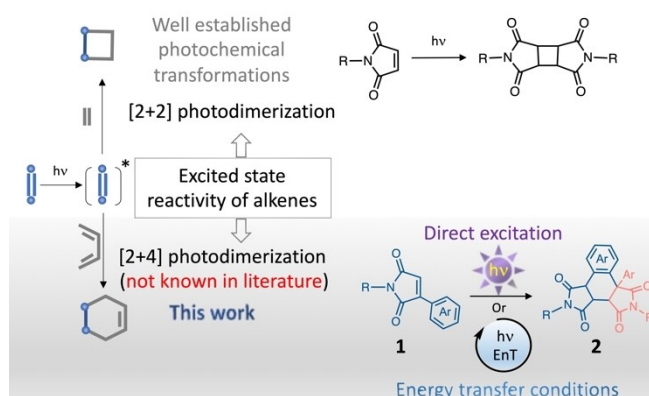


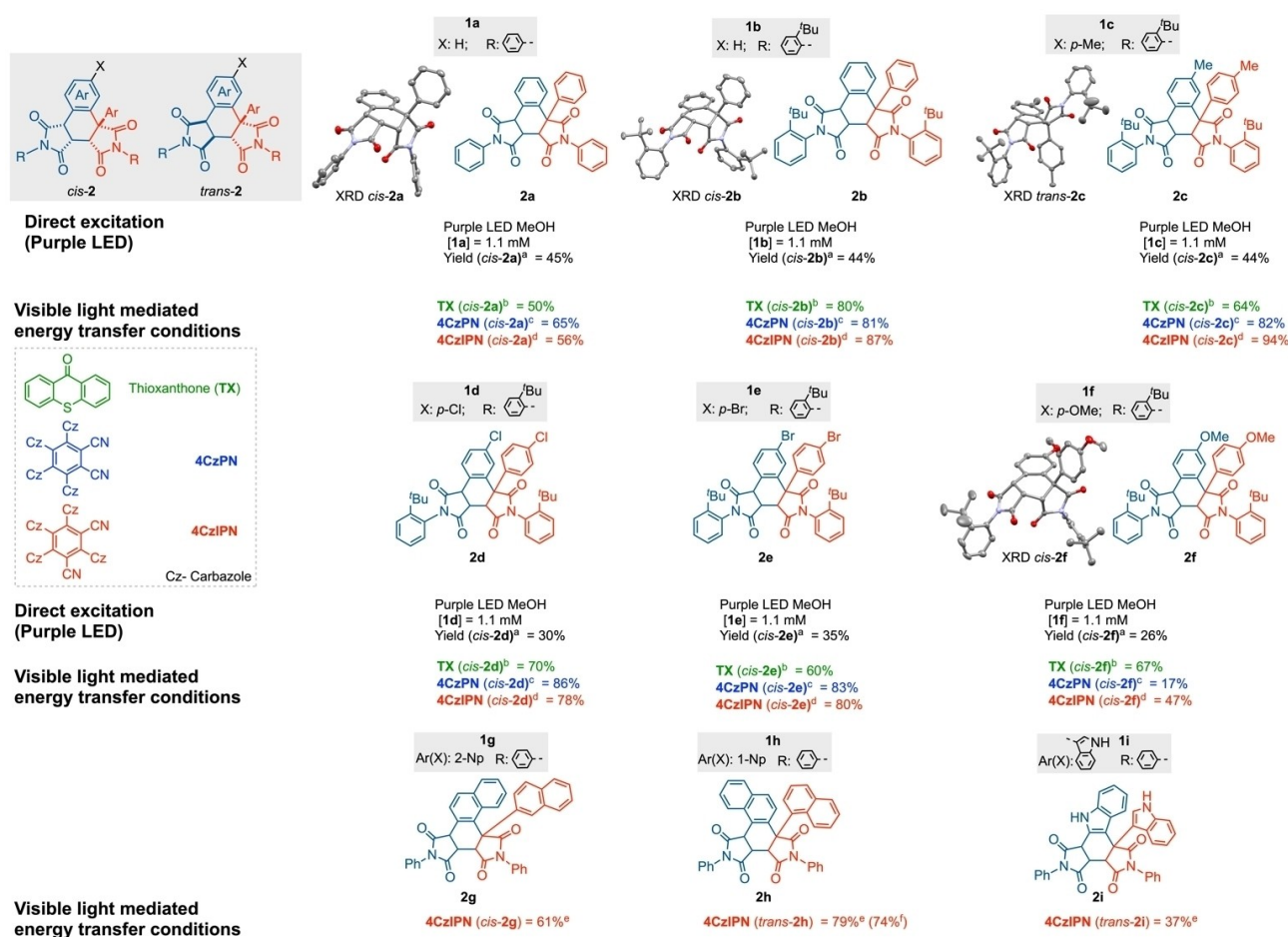
Figure 1. Photochemical reactivity of excited alkenes – [2 + 2]-photodimerization vs [2 + 4]-photodimerization.

Results and Discussion

We started our investigation by choosing maleimides **1a–b** (Scheme 1; Figure 1) as the model substrates that were synthesized using literature procedure^[29] and investigated their reactivity under direct irradiation (Scheme 1).^[31] Photoirradiation of maleimides **1** [1.1 mM] in methanol (MeOH) were performed under purple LED irradiation (≈ 390 nm) for 48 h that gave photoproduct **2**. The photoproduct structure was deciphered by Nuclear Magnetic Resonance (NMR) spectroscopy, High Resolution Mass Spectrometry (HRMS) and the structure was unambiguously established by single crystal X-Ray Diffraction (XRD).^[31] Crude NMR analysis revealed that photoproduct **2** was a mixture of *cis*- and *trans*-isomers based on the orientation of the succinimide rings. In 3-phenyl substituted substrates **1a–f**, the *cis*-isomer was observed as the major product with minor

amount of the *trans*-isomer (see below). The observation of *cis*-isomer under photochemical conditions is in stark contrast to thermal transformations of analogues substrates where the *trans*-product was preferred.^[32] Such a reversal in product selectivity in thermal and photochemical reaction is highly noteworthy.

In the case of parent N-phenyl maleimide derivative **1a**, under purple LED irradiations, the corresponding [2 + 4]-photodimerized photoproduct *cis*-**2a** was formed in 45 % isolated yield (Scheme 1). Purple LED irradiation of the *tert*-butyl derivative **1b** resulted in the corresponding [2 + 4]-photodimerized photoproduct *cis*-**2b** in 44 % yield (Scheme 1). The structure of the photoproduct was characterized by NMR spectroscopy, HRMS and single crystal XRD.^[31,33] The reaction was equally efficient with both electron rich and electron deficient maleimides. Electron rich maleimides **1c** and **1f** under direct purple LED



Scheme 1. [2 + 4]-Photodimerization of maleimide **1a–f** through direct excitation and under energy transfer mediated conditions with TX, 4CzPN and 4CzIPN as sensitizers. Yields of the major isomer is presented unless or otherwise noted. NMR yields are reported with triphenylmethane as the internal standard. [a] Maleimide **1a–f** [1.1 mM] through direct excitation at 390 nm LED in MeCN, NMR yields are reported. There were also some uncharacterized side products in negligible amounts. [b] Maleimide **1a–f** [1.1 mM] with TX = thioxanthone (20 mol %), irradiated at ≈ 420 nm for 5 hours in MeOH, isolated yields of the major isomer are reported. [c] Maleimide **1a–f** [1.1 mM] with 4CzPN = 3,4,5,6-tetra(9H-carbazol-9-yl)phthalonitrile (20 mol %), irradiated at 455 nm for 5 hours in MeCN, NMR yields are reported. [d] Maleimide **1a–i** [1.1 mM] with 4CzIPN = 3,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (20 mol %), irradiated at 455 nm for 4 hours in MeCN. NMR yields are reported for both 4CzPN and 4CzIPN. For clarity hydrogen atoms are not displayed in XRD structures of **2a–c** and **2f**. [e] NMR yields with triphenylmethane as an internal standard. [f] Isolated yield of the major isomer. The XRD structures CCDC numbers are 2241290 (**2a**), 2241309 (**2b**), 2241291 (**2c**), and 2241305 (**2f**).

irradiation gave the corresponding *cis*-photoproduct in yields of 44 % and 26 %, respectively. Electron deficient maleimides **1d** and **1e** under direct purple LED irradiation gave the corresponding *cis*-photoproduct in yields of 30 % and 35 %, respectively. Based on the direct irradiation yields of **1a–f**, it became clear that the newly observed [2+4]-photodimerization was tolerant to substituents on the maleimide ring.

Further, we evaluated the reaction under triplet energy transfer conditions. Based on the triplet energy of the maleimides (see below), we utilized three different sensitizers *viz.*, thioxanthone (**TX**), 3,4,5,6-tetra(9H-carbazol-9-yl)phthalonitrile (**4CzPN**) and 3,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (**4CzIPN**).^[11,34] By subjecting maleimides **1a–f** to photosensitized conditions under visible light irradiations (≈ 420 nm or ≈ 450 nm) resulted in excellent yields of the corresponding [2+4]-photodimerized product *cis*-**2a–f** (Scheme 1). With thioxanthone sensitization at ≈ 420 nm, the [2+4]-photodimerized product *cis*-**2** was obtained with isolated yields of 50 % for **1a**, 80 % for **1b**, 64 % for **1c**, 70 % for **1d**, 60 % for **1e** and 67 % for **1f** (Scheme 1). Carrying out the irradiation with blue LED (≈ 450 nm) with **4CzPN** as the sensitizer gave the [2+4]-photodimerized product *cis*-**2** (monitored by ¹H NMR spectroscopy) in 65 % yield for **1a**, 81 % yield for **1b**, 82 % for **1c**, 86 % for **1d** and 83 % for **1e**. A lower yield of 17 % was observed with maleimide **1f**. Sensitized transformations of maleimides **1a–i** with **4CzIPN** as the sensitizer under blue LED illumination resulted in the [2+4]-photodimerized product **2** (monitored by ¹H NMR spectroscopy) in 56 % yield for **1a**, 87 % yield for **1b**, 94 % for **1c**, 78 % for **1d**, 80 % for **1e** and 47 % for **1f**.

The scope of the reaction was also evaluated for maleimides **1g–i** featuring polyaromatic substituents. Visible light mediated sensitized irradiation of maleimides **1g–i** with **4CzIPN** as the sensitizer resulted in varying yields of the corresponding [2+4]-photodimer (Scheme 1). In the case of

2-naphthyl substituted maleimide **1g**, sensitized irradiation with **4CzIPN** led to 61 % yield of the photoproduct **2g**. Changing the substitution on the maleimide from 2-naphthyl to 1-naphthyl resulted in 79 % yield (74 % isolated yield) of the corresponding photoproduct **2h**. Sensitized irradiation of indole substituted maleimide **1i** led to 37 % yield of the photoproduct **2i**. A point to note is that in the case of maleimides **1a–g**, the *cis*-isomer **2** was observed as the major photoproduct (in the case of **1c** the minor *trans* isomer was crystallized and characterized by single crystal XRD), while for 1-naphthyl derivative **1h** and indole derivative **1i**, the *trans*-isomer **2** was observed as the major photoproduct.

Control studies were carried out to understand the [2+4]-photodimerization of **1** under both direct and sensitized irradiation conditions. [2+4]-Photodimerization was evaluated by changing the irradiation source for direct excitation from ≈ 350 nm to purple LED (Figure 2A). Thermal control at 50 °C with maleimide **1b** in methanol did not lead to corresponding [2+4]-product **2b** indicating that light is necessary for this transformations.^[31,35] Irradiation of maleimide **1b** at ≈ 350 nm (Rayonet irradiation) led to 54 % yield, while purple LED irradiations gave 44 % yield. Carrying out the photoreaction at same optical density of 0.2 of the maleimides **1b**, **1c** and **1e** in MeOH at 390 nm for 24 h resulted in 57 % yield for unsubstituted maleimide **1b** (conc. 0.33 mM), 60 % yield for bromo-maleimide **1e** (conc. 0.28 mM) and 73 % yield methyl-maleimide **1c** (conc. 0.2 mM) (Figure 2B). As the [2+4]-photodimerization of maleimides was efficient under sensitized irradiation conditions, we evaluated a) the effect of sensitizer loading and the effect of concentration of the maleimide (Figure 2C); b) solvent dependence of reactivity (Figure 2D). Varying the loading levels of thioxanthone for [2+4]-photodimerization of **1b** (1.1 mM) resulted in yields varying from 60–85 % (Figure 2-right). The optimum loading level was at 20 mol % of **TX**. As the observed reaction was a photodimerization process, we investigated the influence of concentration of

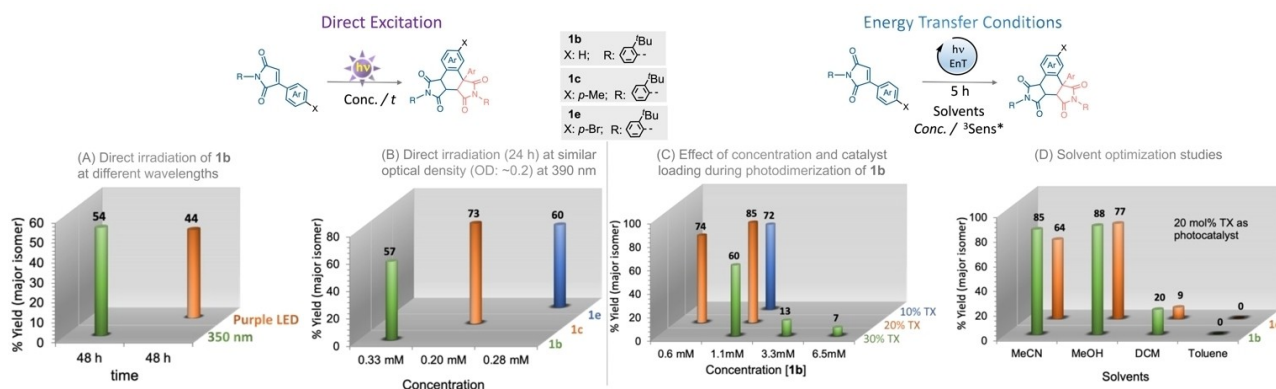


Figure 2. Control studies to understand [2+4]-photodimerization of maleimides by both direct irradiation and under energy transfer conditions. Reactions were performed at room temperature under N₂ atmosphere unless otherwise noted. The reported yields are based on ¹H NMR spectroscopy using triphenylmethane as internal standard (error ± 5 %). A) Direct irradiation of maleimide **1b** in methanol (MeOH) at ≈ 350 nm and with purple LED. B) Direct irradiation of maleimides **1b**, **1c** and **1e** in MeOH at an optical density of 0.2 at 390 nm. C) [2+4]-Photodimerization of maleimide **1b** at ≈ 420 nm in MeOH under triplet energy transfer conditions with various loading of thioxanthone as the sensitizer. D) Effect of solvents on [2+4]-Photodimerization of maleimides **1b** and **1c** at ≈ 420 with 20 mol % thioxanthone as the sensitizer. MeCN = Acetonitrile, MeOH = Methanol; DCM = Dichloromethane.

maleimides and observed that a concentration of 1.1 mM of **1b** gave the optimum yield with **TX** acting as the photosensitizer. Increasing the concentration of **1b** to 3.3 mM and 6.5 mM resulted in diminished yield of **2b**, 13 % and 7 % respectively (Figure 2-right). Lowering the concentration of **1b** below 1.1 mM to 0.6 mM with 20 mol % photosensitizer loading resulted in a slight decrease in yield from 85 % to 74 % (Figure 2C). This showed that the concentration of the maleimide **1b** employed is crucial for the observed [2+4]-photodimerization.

Based on the above concentration dependence of [2+4]-photodimerization, we employed 1.1 mM of **1b** with 20 mol % of thioxanthone as the photosensitizer to understand the impact of various solvents (Figure 2D). Varying the solvent for visible light mediated [2+4]-photodimerization of **1b** showed a clear solvent dependence of reactivity. The [2+4]-photodimerization of **1b** was highly efficient in polar protic methanol (88 % yield) and polar aprotic acetonitrile (85 % yield). There was a significant drop in the reaction yield when the reaction was carried out in dichloromethane (20 % yield). There was no observable [2+4]-photodimerization product in toluene. The solvent studies revealed that methanol is the ideal solvent for carrying out [2+4]-photodimerization of maleimides.

To gain more insights into the [2+4]-photodimerization of maleimides we performed detailed photophysical investigations. We utilized maleimides **1b** and **1f** as model systems as they have high (87 %) and low (32 %) yields with **4CzIPN** as the photosensitizer respectively (Scheme 1). Weak luminescence was observed in maleimides **1b** and **1f** even at 77 K that pointed to a very fast decay of the excited states which suggested inefficient intersystem crossing.^[36] As we anticipated the triplet energy of maleimides to be between 58–60 kcal/mol based on prior literature precedence,^[11,29,37] triplet energy transfer from **TX** ($E_T \approx 63$ kcal/mol), **4CzPN** ($E_T \approx 57$ kcal/mol) and **4CzIPN** ($E_T \approx 58$ kcal/mol), is likely albeit with different rates (*vide infra*).^[38,39] Having ascertained the excited state energy of the reactants and sensitizer, we evaluated the viability of

energy or electron transfer under sensitized conditions. By using the Rehm–Weller equation,^[40,41] we evaluated the viability of photo-induced electron transfer playing a role under sensitized conditions. Inspection of Table 1 revealed an endergonic electron transfer from excited sensitizer to maleimides for all three sensitizers. As the triplet energy of the sensitizer and the maleimides are close, one can anticipate energy transfer from the sensitizers to maleimides. A point of note is that in systems featuring isoenergetic excited state energies, electron transfer might occur albeit under slower rates under endergonic conditions.^[42] This necessitated establishing the formation of the transient species responsible for the observed reactivity using laser flash photolysis experiments (Figures 3).^[11] We chose **4CzIPN** as the triplet energy was in between that of **TX** and **4CzPN**.

Laser excitation ($\lambda_{ex}=355$ nm, pulse width: 7 ns) of argon-saturated solution of **4CzIPN** in acetonitrile which generated a transient absorption spectrum (Figure 3A, red). The transient absorption had distinct features with maxima around 300 nm, 470 nm and 820 nm (detection limit of the employed detector). Similarly, the formation of maleimide triplet was determined by laser excitation ($\lambda_{ex}=355$ nm, pulse width: 7 ns) of argon-saturated solution of **1b** (as well as **1f**) in acetonitrile generated a transient absorption spectrum (Figure 3A, blue). This transient with maximum at 400 nm was assigned to the triplet of maleimide **1b*** based on literature precedence.^[11] As the triplet transient of the **4CzIPN** photosensitizer (**4CzIPN***) and maleimide (**1b***) has signature features in their respective transient absorption spectra, the dynamics in a mixture of **1b** and **4CzIPN** can be monitored by the change in the intensity of the respective signals. To photoexcite **4CzIPN** selectively, we used 435 nm (generated from an OPO) for pulsed excitation where **1d** and **1f** are transparent at this wavelength. Pulsed laser excitation ($\lambda_{ex}=435$ nm) of **4CzIPN** in the presence of maleimide **1b** in argon saturated acetonitrile solution gave the triplet excited maleimide **1b*** ($\tau_{1b}^* = 13$ μ s). The generation of the **1b*** by energy transfer from **4CzIPN*** was

Table 1: Free energy for electron transfer under sensitized conditions.

Entry	Substrate	$E^\circ_{(A/A^-)} (V)$	$\Delta G^\circ_{et} (kcal/mol)^{[a,b]}$		
			TX	4CzPN	4CzIPN
1)	1a	−1.32	6.00	4.15	4.15
2)	1b	−1.37	7.15	5.30	5.30
3)	1c	−1.41	8.07	6.23	6.23
4)	1d	−1.30	5.53	3.69	3.69
5)	1e	−1.28	5.07	3.23	3.23
6)	1f	−1.44	8.76	6.92	6.92
7)	1g	−1.55	11.30	9.45	4.95
8)	1h	−1.33	6.22	4.38	4.38
9)	1i	−1.54	11.06	9.22	9.22

[a] ΔG°_{et} calculated by Rehm–Weller equation.^[40,41] $\Delta G^\circ_{et} = E^\circ_{(D^+/D)} - E^\circ_{(A/A^-)} - E_{0,0} - w$; ΔG°_{et} = free energy of electron transfer (V); E_{ox} or $E^\circ_{(D^+/D)}$ = oxidation potential of electron donor (ν s Ag/Ag⁺); E_{red} or $E^\circ_{(A/A^-)}$ = reduction potential of electron acceptor (ν s Ag/Ag⁺); $E_{0,0}$ = excitation energy (eV); w = Coulomb term (estimated to be −0.06 V in MeCN). For **TX**, $E_{0,0} = 2.51$ eV,^[38] ground state E_{ox} or $E^\circ_{(D^+/D)} = 1.39$ V (ν s Ag/AgNO₃). For **4CzPN**, $E_{0,0} = 2.45$ eV, ground state E_{ox} or $E^\circ_{(D^+/D)} = 1.24$ V (ν s Ag/AgNO₃). For **4CzIPN**, $E_{0,0} = 2.49$ eV, ground state E_{ox} or $E^\circ_{(D^+/D)} = 1.29$ V (ν s Ag/AgNO₃).^[39] [b] Refer to Supporting Information.

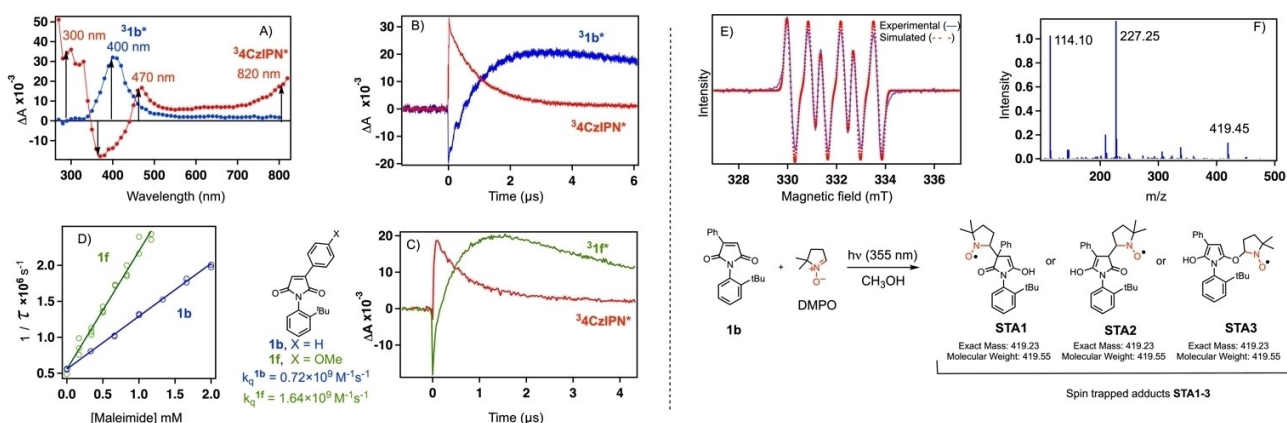


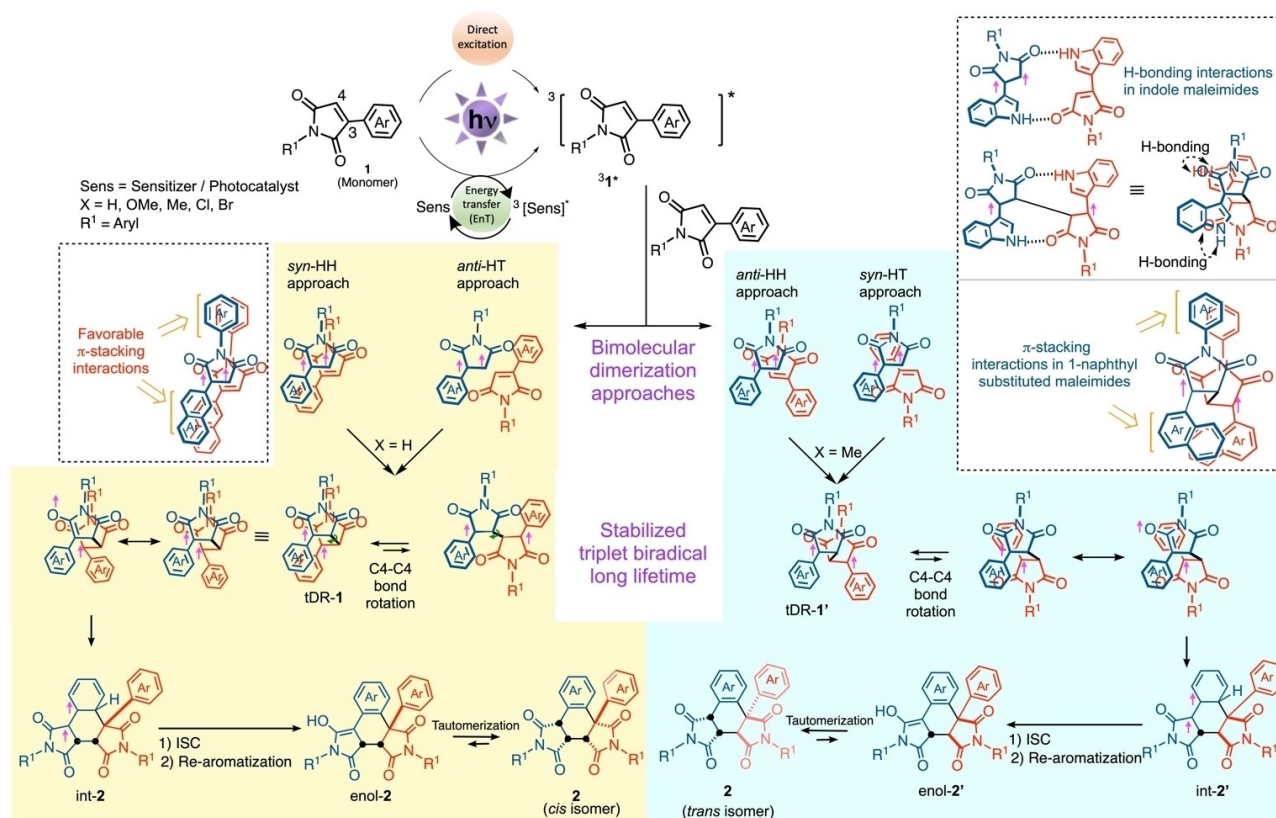
Figure 3. Photophysical and spectroscopic investigations to understand [2+4]-photodimerization of maleimides to establish the mechanism of energy transfer catalysis with **4CzIPN**. Left: Laser flash photolysis (LFP): A) Transient absorption spectra after pulsed laser excitation of **4CzIPN** (red) or **1b** (blue) monitored at the end of the laser pulse ($\lambda_{\text{ex}}=355$ nm, 7 ns pulse width) of argon saturated solutions in MeCN. B) Kinetic traces after pulsed laser excitation ($\lambda_{\text{ex}}=435$ nm) of **4CzIPN** in the presence of **1b** (0.66 mM) in argon saturated MeCN. Red trace: Decay of $^3\text{4CzIPN}^*$ monitored at 820 nm. Blue trace: Formation of $^3\text{1b}^*$ (monitored at 400 nm). C) Kinetic traces after pulsed laser excitation ($\lambda_{\text{ex}}=435$ nm) of **4CzIPN** in the presence of **1f** (0.83 mM) in argon saturated MeCN. Red trace: Decay of $^3\text{4CzIPN}^*$ monitored at 810 nm. Green trace: Formation of $^3\text{1f}^*$ (monitored at 420 nm). D) Determination of the bimolecular triplet quenching rate constant k_q of $^3\text{4CzIPN}^*$ by **1b** (blue) and **1f** (green) using laser flash photolysis with excitation of **4CzIPN** ($\lambda_{\text{ex}}=435$ nm). Right: Electron Paramagnetic Resonance (EPR) investigation upon irradiation of phenyl maleimide **1b** in the presence of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) at 355 nm in MeOH. E) Experimental (blue) and simulated (dotted red) EPR spectra of the trapped species formed upon excitation of maleimides **1b**. F) HPLC/mass spectrometric analysis of the spin trapped species.

ascertained by the decay of the $^3\text{4CzIPN}^*$ absorbance at 820 nm (red decay curve in Figure 3B) and rise in the absorbance centered around 400 nm that corresponded to $^3\text{1b}^*$ (blue raise curve in Figure 3B). Similarly, laser excitation ($\lambda_{\text{ex}}=435$ nm) of **4CzIPN** in the presence of **1f** in argon saturated acetonitrile solution generated the triplet transient $^3\text{1f}^*$ (Figure 3C; $\tau_{\text{1f}}=5$ μs). The generation of $^3\text{1f}^*$ by energy transfer from $^3\text{4CzIPN}^*$ was confirmed by the rise in the absorbance signal corresponding to $^3\text{1f}^*$ (green raise curve in Figure 3C) and the decay of $^3\text{4CzIPN}^*$ absorbance (red decay curve in Figure 3C). This clearly established that a triplet energy transfer mechanism operates under sensitized conditions to generate the triplet excited maleimides rather than an electron transfer mechanism.

Having ascertained triplet energy transfer under sensitized conditions, we then determined the bimolecular quenching rate constants of sensitizer's triplet states ($^3\text{4CzIPN}^*$) by **1b** and **1f** (Figure 3D) by laser flash photolysis. The inverse $^3\text{4CzIPN}^*$ triplet lifetimes determined from triplet absorption decay traces monitored at 820 nm ($^3\text{4CzIPN}^*$ decay) vs varying concentration of **1b** or **1f** in argon saturated MeCN were plotted. The slopes of these plots (Figure 3D) yielded the bimolecular quenching rate constants revealing that triplet excited state of **4CzIPN** are efficiently quenched by both **1b** and **1f**. The rate constant for quenching of $^3\text{4CzIPN}^*$ by **1b** (k_q^{1b}) was $0.72 \pm 0.01 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 3D). On the other hand, the rate constant for quenching of $^3\text{4CzIPN}^*$ by **1f** (k_q^{1f}) was $1.64 \pm 0.05 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 3D). In spite of the higher (2.3 times higher) quenching rate constant for **1f** compared to **1b**, the product yield (Scheme 2) from **1b** was higher (87 % yield of the corresponding photodimer **2b**) compared to product yield from **1f** (47 % yield of the corresponding photodimer **2f**). This showed that the intermediate(s) generated from

the triplet excited maleimide during the course of the [2+4]-photodimerization process played a crucial role in determining the reaction yield.

Based on the experimental data, we propose a mechanism as shown in Scheme 2. As the reaction occurred under both direct (albeit slowly due to inefficient intersystem crossing) as well as triplet sensitized conditions, we propose the involvement of a triplet excited maleimide $^3\text{1}^*$ (based on photophysical investigations; Figure 3). Of particular interest is the stereoselectivity of the photoproducts observed with maleimides **1a–g** and maleimides **1h–i**. In the case of maleimides **1a–g**, the *cis-2* photoproduct is observed as the major isomer in which the succinimide rings are oriented *cis* to each other ($^3J \approx 10$ Hz and ≈ 6 Hz), while for maleimides **1h–i** the *trans-2* isomer was observed as the major photoproduct featuring *trans* orientation of the succinimide rings ($^3J \approx 10$ Hz and ≈ 1 Hz). For example, analysis of the crude reaction mixture of maleimide **1a–g** (under sensitized irradiation by **4CzIPN**) by ^1H NMR spectroscopy showed the *cis-2* photoproduct as the major isomer with ≈ 5 –10 % of the minor *trans-2* photoproduct. Similarly, analysis of the crude reaction mixture of maleimide **1h–i** (under sensitized irradiation by **4CzIPN**) by ^1H NMR spectroscopy showed the *trans-2* photoproduct as the major isomer with minor amounts of *cis-2* photoproduct. These aspects point to the type of intermediate and its stability playing a critical role in determining the stereochemical outcome of the reaction. We conjecture that the reaction trajectory of the triplet excited maleimide $^3\text{1}^*$ with the ground state maleimide can distinctly be labeled in four different ways *viz.*, *syn-HH* approach, *syn-HT* approach, *anti-HH* approach, and *anti-HT* approach. These type of approaches are similar to [2+2]-photodimerization in other systems such as coumarins.^[43–50] In the HH approach, the N-aryl substituents of the maleimides are



Scheme 2. Mechanistic rationale for [2 + 4]-photodimerization of maleimide.

oriented in the same direction, while in the HT approach, the N-aryl substituents of the maleimides are oriented in the opposite direction. In the *syn*-geometry, the C3-aryl functionality on the maleimide is oriented on the same side while in the *anti*-geometry, the C3-aryl functionality on the maleimide is oriented away from each other. [2 + 4]-Photodimerization of the maleimides via *syn*-HH and *anti*-HT approaches lead to the formation of triplet 1,4-diradical tDR-1 that features a bond between the C4 centers in the maleimides and a resonance stabilized tertiary benzylic biradical (Scheme 2-left-yellow inset). We believe that the stability of this triplet diradical tDR-1 coupled with C4–C4 bond rotation dictated by π – π stacking interactions between the N-aryl and phenyl substituents, leads to ring closure between the maleimide radical center and the phenyl ring (featuring a six membered transition state) resulting in intermediate int-1. This int-1 subsequently intersystem crosses and reestablish aromaticity enroute to the formation of an enol-2 product that tautomerizes to the final photoproduct 2. This conjecture of π – π stacking interactions driving the stereochemical outcome of [2 + 4]-photodimerization reaction is bolstered by our observation in maleimides 1h and 1i. In the case of 1h (and 1i), the triplet excited maleimide ³1h* (and ³1i*) reacts with ground state maleimide via *anti*-HH and *syn*-HT approaches (Scheme 2-right-blue inset) instead of *syn*-HH and *anti*-HT approaches leading to the formation of triplet 1,4-diradical tDR-1'. The triplet 1,4-diradical tDR-1' is also highly resonance stabilized

in which radical ring closure occurs between the maleimide radical center and the phenyl ring (featuring a six membered transition state) resulting in intermediate int-2'. This int-2' further intersystem crosses and reestablish aromaticity enroute to the formation of an enol-2' product which tautomerizes to the final photoproduct *trans*-2. The reason this approach (*anti*-HH and *syn*-HT approach) is favored with indole maleimide 1i is due to the hydrogen bonding interactions which dictates the orientation of the reacting maleimides. In addition, comparison of 2-naphthyl maleimide 1g and 1-naphthyl maleimide 1h shows that *cis*-2g and *trans*-2h is favored respectively. This is due to the difference in the π -stacking interactions that has been well established for 1-naphthyl and 2-naphthyl substituted derivatives.^[51]

As we have invoked the formation of a triplet maleimide in our reaction, we investigated this process by electron paramagnetic resonance (EPR) spectroscopy to investigate the involvement of a radical species.^[52] The photogenerated diradical is resonance stabilized, therefore it is anticipated that it may be trapped by a molecule such as a nitron. Irradiation of maleimide 1b (5 mM) and DMPO (20 mM) in methanol at 355 nm Nd-YAG Laser resulted in a strong EPR signal that was simulated using the EasySpin software (Figure 3E). Based on the extracted values of the hyperfine splitting constants (a^N = 13.36 G, a_p^H = 8.84 G and a_v^H = 1.74 G) it was assigned to DMPO spin adducts STA1-3 in which the DMPO was attached to the maleimide 1b either at the C3 position (STA1) or C4 position (STA2) or at the

carbonyl oxygen atom (**STA3**).^[53] These proposed spin adducts are in agreement with those reported in the literature.^{[54][55]} In addition we were also successful in identifying the spin trapped species by mass spectrometry (Figure 3F). Direct trapping of excited triplets featuring a 1,2-diradical character is unusual, but it is also possible to generate the adduct via an electron transfer mechanism.^[31] Because of the numerous resonance structures featured in the 1,2-diradical (stabilized diradical), the spin-trapped adduct (spin adducts **STA1-3**; Figure 3F) can arise by addition of either a C- or O-centred radical, and at present there is no conclusive evidence for either pathway. However, there is a literature precedence for C-radical addition in a similar system.^[56] The mechanistic details of this spin trapping reaction are interesting and are presently under further investigation. However, we can conclude from the spectrum shown that a paramagnetic reactive intermediate is involved in this photochemical reaction, consistent with our interpretation of all other results within the framework of a triplet state precursor.

Conclusion

Our study has uncovered a novel excited state reactivity of maleimides leading to [2+4]-photodimerization instead of the traditional [2+2]-photodimerization. Based on detailed photophysical studies we have established that the process occurs through a triplet hypersurface. Successful trapping experiments investigated by EPR spectroscopy shows that the diradical species generated has enhanced stability (likely due to resonance). Further, the stability of the generated diradical species (due to resonance) likely plays a crucial role in dictating the mode of reactivity. Given the importance of dimerization process in photochemistry, synthetic chemistry and materials chemistry,^[57] we anticipate that this new excited state reactivity will stir interest across disciplines.

Supporting Information

Supporting Information is available free of charge. Single-crystal XRD data (CIF), Experimental procedures, characterization data, analytical conditions, and photophysical studies (PDF). The XRD structures of **2a-c** and **2f** are available in CCDC and the CCDC numbers are 2241290 (**2a**), 2241309 (**2b**), 2241291 (**2c**), and 2241305 (**2f**).

Author Contributions

Manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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