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# Transient absorption spectroscopy detection of sensitized delayed fluorescence in chiral benzophenone/naphthalene systems

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## Abstract

Transient absorption spectroscopy has proven to be a powerful tool to investigate the formation and decay of excited singlet states upon triplet-triplet annihilation, following T-T energy transfer from a selectively excited sensitizer. Thus, upon selective excitation of benzophenone (BZP) by laser flash photolysis (LFP) at  $\lambda = 355$  nm in the presence of naphthalene (NPT), a negative band centred at 340 nm has been detected, with growth and decay in the microsecond timescale. It has been assigned to the P-type NPT delayed-fluorescence. In the case of chiral BZP/NPT systems, stereodifferentiation has been observed in the kinetics of the involved photophysical processes.

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## Introduction

Benzophenone (BZP) and naphthalene (NPT) are classical textbook examples of photoactive chromophores, which can undergo a number of photophysical and photochemical processes.<sup>[1,2]</sup> Transient species generated upon excitation of BZP and NPT are detectable by the usual emission or absorption spectroscopies, and their main features have been described in detail.<sup>[3,-21]</sup>

Specifically, BZP exhibits several remarkable characteristics that make it very useful for photochemical studies. Thus, the presence of an absorption band at  $\lambda > 320$  nm allows selective BZP excitation in the presence of a large number of organic substrates (and therefore its use as photosensitizer); besides, the intersystem crossing quantum yield ( $\phi_{ISC}$ ) is close to the unity, which makes BZP a suitable "triplet source" for T-T energy transfer to substrates with lower triplet energy ( $E_T$ ). On the other hand, both the lowest triplet excited state ( $n\pi^*$ ,  $E_T = 69$  kcal/mol,  $\lambda = 520$ -530 nm) and the benzhydryl radical ( $\lambda = 550$  nm) are observable in the transient absorption spectrum obtained upon laser flash photolysis (LFP) in acetonitrile.<sup>[22]</sup>

Concerning NPT, emission from the first singlet excited state ( $^1NPT^*$ ,  $E_S = 92$  kcal/mol,  $\phi_F = 0.19$ -0.21) is centred at 350 nm, although longer-wavelength fluorescence from NPT excimers has also been reported. Intersystem crossing (ca 0.75) leads to  $^3NPT^*$ , which exhibits a maximum at 410-430 nm in the LFP spectrum.<sup>[22,23]</sup> Under specific experimental conditions, the radical cation ( $NPT^{\cdot+}$ ) can also be detected (685 nm).<sup>[24]</sup> Delayed P-type fluorescence in NPT derivatives may arise from interaction of two molecules in the triplet state ( $^3NPT^* + ^3NPT^*$ , triplet-triplet annihilation) thus producing one NPT molecule in the excited singlet state. The lifetime of this process, which is usually observed by emission measurements upon direct irradiation of NPT, is half the value of that found for the concomitant phosphorescence.<sup>[25]</sup>

Photoprocesses occurring in systems containing both chromophores have attracted considerable attention in the past. Upon long-wavelength excitation of BZP in the presence of NPT, the expected intermolecular T-T energy transfer from  $^3BZP^*$  to NPT does actually take place. In addition, formation of  $^3(BZP/NPT)^*$  triplet exciplexes constitutes an efficient channel for  $^3NPT^*$  deactivation.<sup>[26]</sup> Bichromophoric compounds containing covalently linked BZP and NPT units have also been investigated; similar deactivation pathways have been proposed for these dyads, albeit with kinetics markedly faster than in the intermolecular case.<sup>[27]</sup>

In the present work, we wish to report on the direct LFP observation of the characteristic  $^1NPT^*$  emission in the microsecond time domain, upon selective excitation of the  $n\pi^*$  carbonyl band in BZP/NPT systems, as well as on the stereodifferentiation in the kinetics of the involved photophysical processes. Benzophenone (**1a**) and (*S*)-, (*R*)-ketoprofen (**1b**) have been employed as sensitizers, while naphthalene (**2a**) and (*S*)- or (*R*)-1-(1-naphthyl)ethylamine (**2b**) have been chosen as triplet energy acceptors (Chart 1).

- Insert Chart 1-

## Results and Discussion

**Benzophenone/naphthalene systems.** The UV-Vis absorption spectrum of **1a** in acetonitrile ( $2.6 \times 10^{-3}$  M) did not show any noticeable change at  $\lambda > 330$  nm after addition of increasing amounts of **2a** up to  $4.0 \times 10^{-4}$  M. Thus, upon long-wavelength photolysis of **1a/2a** mixtures, the BZP chromophore is selectively excited. The transient absorption spectrum ( $\lambda_{exc} = 355$  nm) of **1a** under  $N_2$  exhibited the characteristic band centred at 530 nm ( $\tau_T = 1.7$   $\mu$ s) due to  $^3BZP^*$ , whereas in the presence of **2a**, the LFP trace presented additional features.

Under these conditions, the band peaking at 525 nm due to  $^3BZP^*$  was efficiently quenched through T-T energy transfer ( $k_q = 9.6 \times 10^9$   $M^{-1} s^{-1}$ ), leading to  $^3NPT^*$  ( $\lambda_{max} = 420$  nm). Expectedly, the process was faster at higher **2a** concentrations (Figure 1A). The growth and decay of the 420 nm band is clearly visible in Figure 1B for  $[2a] = 2.6 \times 10^{-4}$  M.

- Insert Figure 1 -

Remarkably, the most relevant observation was the presence of a negative band centred at 340 nm, corresponding to an emitting transient species with growth and decay in the microsecond timescale. In order to ascertain the nature of this new transient, the photophysical pathways occurring upon selective BZP excitation in the presence of NPT were considered (Scheme 1).

- Insert Scheme 1 -

Thus, excitation of **1a** to its first singlet excited state (i) is followed by a very efficient intersystem crossing (ii), affording  $^31a^*$  ( $\lambda_{max} = 530$  nm). Triplet-triplet energy transfer from  $^31a^*$  to **2a** affords  $^32a^*$  (iii), observed at 420 nm. Deactivation of  $^32a^*$  can take place through an exciplex with **1a** (iv + v). Collision of two triplets could lead to  $^12a^*$  (vi). The biphotonic nature of the process is in agreement with the variations observed for the 340 nm signal intensity as a function of the laser power or the BZP absorbance at the excitation wavelength (see Supporting Information). Since, according to Scheme 1,  $^12a^*$  would be generated from a long-lived triplet precursor, its radiative decay to the ground state would occur as a P-type delayed fluorescence (vii).

**Ketoprofen/1-(1-naphthyl)ethylamine systems.** Looking for a possible stereodifferentiation in the excited state interactions, the (*R*)-form of ketoprofen (*(R)*-**1b**), was submitted to LFP in the presence of each enantiomer of 1-(1-naphthyl)ethylamine (*(S)*-**2b** or *(R)*-**2b**). The photophysical properties of **1b** and **2b** (absorption, emission and laser flash photolysis) were very similar to those of their parent compounds **1a** and **2a** (see Supporting Information). Interestingly, triplet-triplet energy transfer from  $^31b^*$  to **2b** affording  $^32b^*$  (iii) resulted to be significantly stereoselective, with  $k_q = (8.8 \pm 0.6) \times 10^9$  and  $(10.4 \pm 0.8) \times 10^9$   $M^{-1}s^{-1}$  for *(S)*-**2b** or *(R)*-**2b**, respectively. The Stern-Volmer plots are shown in Figure 2. Consistent results were obtained using *(S)*-**1b** as donor; in this case, the *(S)*/*(S)* combination gave rise to the higher rate constant for quenching of the BZP-like triplet.

- Insert Figure 2-

The corresponding NPT-type triplets exhibited a maximum centered at 430 nm in the transient absorption spectrum; decay of these species occurred with different kinetics (Figure 3A) for each **2b** enantiomer. Stereodifferentiation in the deactivation of  $^3\mathbf{2b}^*$  must be related to exciplex formation (iv + v), <sup>[27]</sup> so chiral discrimination would result from stereochemical recognition by (*R*)-**1b**.

Interestingly, the P-type delayed fluorescence was also observed in **1b/2b** combinations as a negative band peaking at 340 nm. The formation and decay of this transient is shown in Figure 3B. Again, the kinetics recorded for recovery of the baseline was configuration-dependent, being clearly faster in the case of (*R*)-**2b**. Although delayed fluorescence involves collision between two triplets should be intrinsically insensitive to the (*R*)- or (*S*)- nature of the asymmetric carbon of **2b**, the observed stereodifferentiation reflects the decay differences between the corresponding NPT triplet precursors. This is in accordance with the expected lifetime of the process, which can be predicted to be half the value found for the triplet lifetimes.

- Insert Figure 3-

Similar results were obtained when an excess of acetic acid (XX M) was added to the **1b/2b** mixtures, ruling out that the observed stereodifferentiation originates from carboxylate/ammonium ion interactions (see Figure 3C,D or Supporting Information).

### Conclusions

Transient absorption spectroscopy has proven to be a powerful tool to investigate the formation and decay of excited singlet states upon triplet-triplet annihilation, following T-T energy transfer from a selectively excited sensitizer. Delayed emission is observed as a negative band in the microsecond timescale. In the case of chiral benzophenone/naphthalene pairs, stereodifferentiation has been observed in the kinetics of T-T energy transfer,  $^3\text{NPT}^*$  decay through exciplex formation and  $^1\text{NPT}^*$  fluorescence.

### Experimental Section

Chemicals. Benzophenone (**1a**), (*S*)- and (*R*)-ketoprofen ((*S*)-, (*R*)-**1b**), naphthalene (**2a**), (*S*)- and (*R*)-1-(1-naphthyl)ethylamine ((*S*)-, (*R*)-**2b**), were commercially available. Their purity was checked by  $^1\text{H-NMR}$  and HPLC analysis.

Laser flash photolysis measurements were performed by using a Q-switched Nd:YAG laser (Quantel Brilliant, 355 nm, 10 mJ per pulse, 5 ns fwhm) coupled to a mLFP-111 Luzchem miniaturized equipment. All transient spectra were recorded in acetonitrile, employing 10 x 10 mm<sup>2</sup> quartz cells with 4 mL capacity. The samples were bubbled during 30 min with N<sub>2</sub>, prior to acquisition. The absorbance of the BZP chromophore was adjusted to 0.20 at the laser excitation wavelength. All the experiments were carried out at room temperature (22 °C).

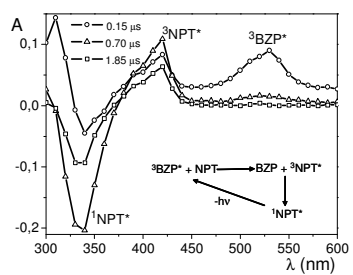
### Acknowledgements

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## Graphical abstract



Benzophenone (BZP) sensitized, delayed naphthalene (NPT) emission is observed in laser flash photolysis as a negative band in the microsecond timescale. In the case of chiral BZP/NPT pairs, stereodifferentiation is observed in the kinetics of all photophysical processes.

## Legends for Charts:

**Chart 1.** Chemical structures of the benzophenones and naphthalenes studied in this work.

## Legends for Schemes:

**Scheme 1.** Main photophysical processes occurring after excitation of BZP in the presence of NPT.

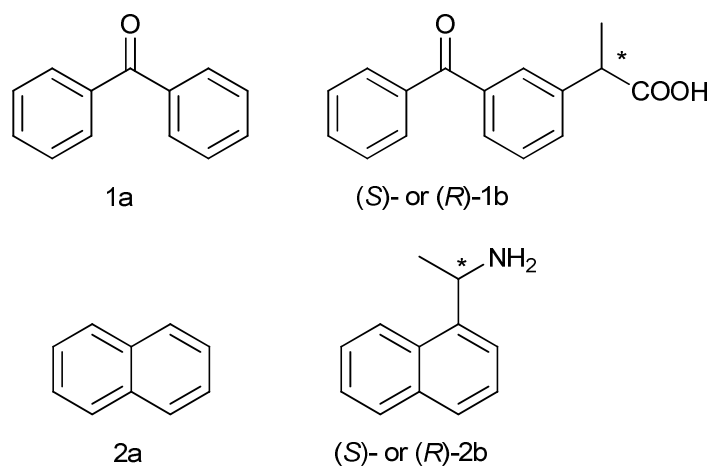
## Legends for Figures:

**Figure 1. A.** Laser flash photolysis of **1a** ( $2.6 \times 10^{-3}$  M) in acetonitrile/N<sub>2</sub> at  $\lambda_{\text{exc}} = 355$  nm. **A:** Spectra recorded in the presence of increasing amounts of **2a**, 0.15  $\mu\text{s}$  after the laser pulse. **B:** Spectra obtained in the presence of **2a** ( $2.6 \times 10^{-4}$  M) at different time windows.

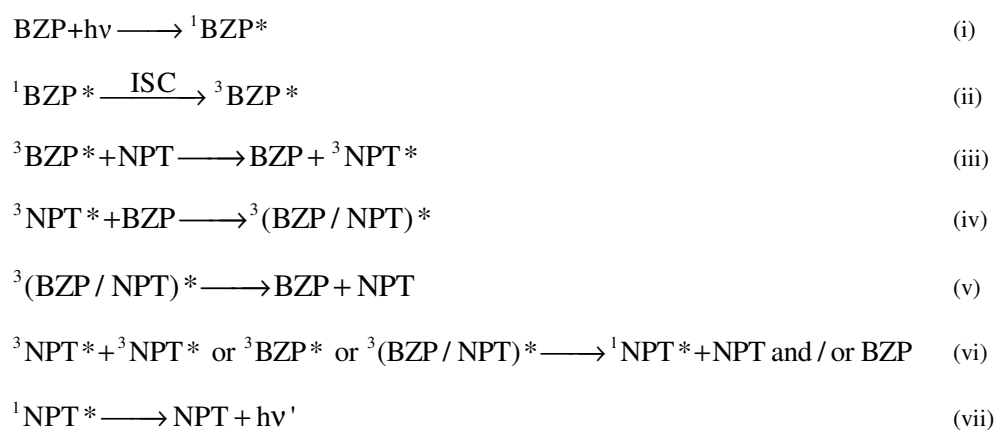
**Figure 2.** Stern-Volmer plots for the quenching of  $^3(R)\text{-1b}^*$  at 600 nm in the presence of increasing amounts of (S)-**2b** or (R)-**2b**.

**Figure 3.** Laser flash photolysis of (R)-**1b** ( $\lambda_{\text{exc}} = 355$  nm, MeCN, N<sub>2</sub>,  $2.6 \times 10^{-3}$  M) in the presence of (R)-**2b** and (S)-**2b** at  $2.0 \times 10^{-4}$  M concentration. Kinetic traces monitored at **A**) 430 nm or **B**) 340 nm.

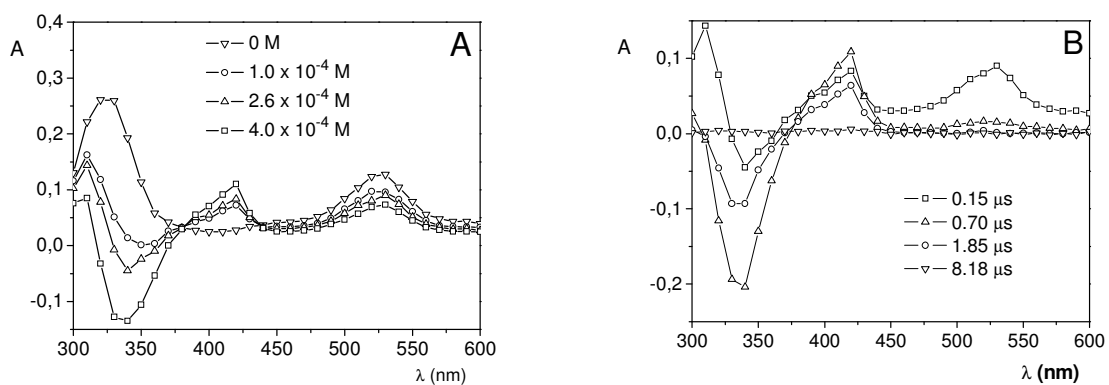




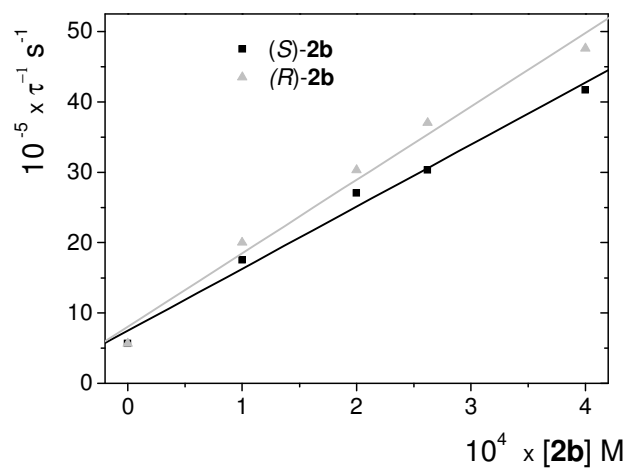
**Chart 1.** Chemical structures of the benzophenones and naphthalenes studied in this work



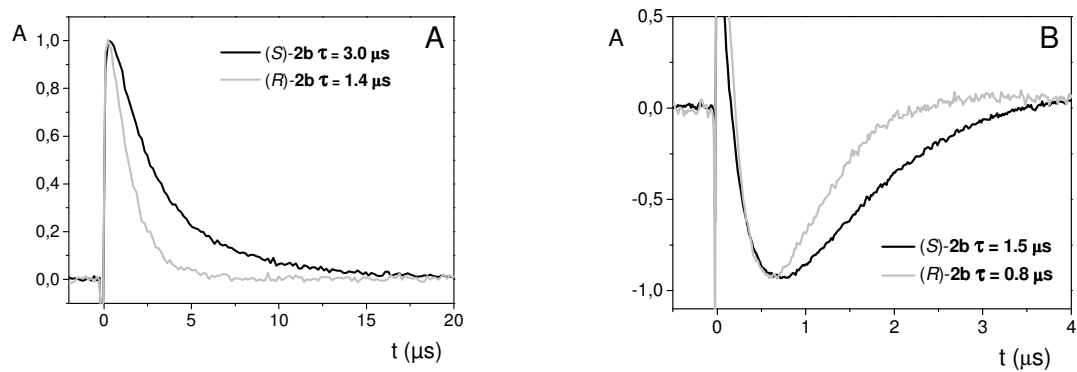
**Scheme 1.** Main photophysical processes occurring after excitation of BZP in the presence of NPT



**Figure 1.** Laser flash photolysis of **1a** ( $2.6 \times 10^{-3}$  M) in acetonitrile/N<sub>2</sub> at  $\lambda_{exc} = 355$  nm. **A:** Spectra recorded in the presence of increasing amounts of **2a**, 0.15  $\mu$ s after the laser pulse. **B:** Spectra obtained in the presence of **2a** ( $2.6 \times 10^{-4}$  M) at different time windows.



**Figure 2.** Stern-Volmer plots for the quenching of  ${}^3(R)\text{-1b}^*$  at 600 nm in the presence of increasing amounts of (S)-2b or (R)-2b.



**Figure 3.** Laser flash photolysis of (*R*)-**1b** ( $\lambda_{\text{exc}} = 355 \text{ nm}$ , MeCN,  $\text{N}_2$ ,  $2.6 \times 10^{-3} \text{ M}$ ) in the presence of (*R*)-**2b** and (*S*)-**2b** at  $2.0 \times 10^{-4} \text{ M}$  concentration. Kinetic traces monitored at **A**) 430 nm or **B**) 340 nm.