

## Supporting Material

### **“Photoreduction of chlorothalonil fungicide on plant leaf models”**

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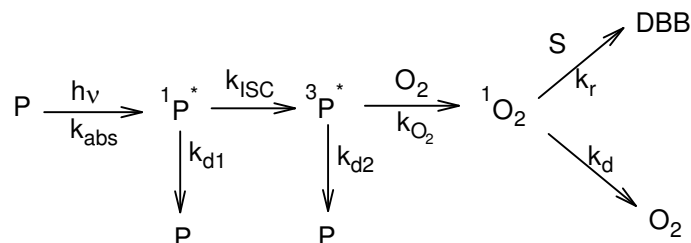
Number of figures: 12

Number of tables: 1

## Supporting Material

### 1. Quantum yield of singlet oxygen production measurement

The quantum yield of singlet oxygen production by chlorothalonil was measured using perinaphtenone as a reference.



**Figure S1: Scheme of photosensitized oxidation of the probe**

Where, P is the photosensitizer (here perinaphtenone or chlorothalonil) and S the probe (1,3-diphenyl isobenzofuran) reacting with  $^1\text{O}_2$ . DBB (o-dibenzoylbenzene) is the transformation product of the probe. The range of concentrations used in our experiments is  $10^{-5}$  to  $10^{-6}$  M for the probe S and  $5 \times 10^{-6}$  M for perinaphtenone or chlorothalonil.

$k_{\text{abs}}$  : rate constant of photon absorption by P ( $\text{s}^{-1}$ )

$k_{\text{d1}}$  : deactivation rate constant of  $^1\text{P}^*$  ( $\text{s}^{-1}$ )

$k_{\text{d2}}$  : deactivation rate constant of  $^3\text{P}^*$  ( $\text{s}^{-1}$ )

$k_{\text{ISC}}$  : rate constant of internal system crossing ( $\text{s}^{-1}$ )

$k_{\text{O}_2}$  : reaction rate constant of  $^3\text{P}^*$  with  $\text{O}_2$  ( $\text{M}^{-1} \text{s}^{-1}$ )

$k_{\text{r}}$  : reaction rate constant of S with  $^1\text{O}_2$  ( $\text{M}^{-1} \text{s}^{-1}$ )

$k_{\text{d}}$  : deactivation rate constant of  $^1\text{O}_2$  ( $\text{s}^{-1}$ )

Using the hypothesis of the steady state for  $^1\text{P}^*$  and  $^3\text{P}^*$ , one gets:

$$\frac{d[{}^1\text{P}^*]}{dt} = 0 = k_{\text{abs}}[P][h\nu] - k_{\text{ISC}}[{}^1\text{P}^*] - k_{\text{d1}}[{}^1\text{P}^*] \quad (1)$$

$$\frac{d[{}^3P^*]}{dt} = 0 = k_{ISC}[{}^1P^*] - k_{O_2}[O_2][{}^3P^*] - k_{d2}[{}^3P^*] \quad (2)$$

The quantum yield of singlet oxygen production is expressed as followed:

$$\phi_{so} = \frac{\text{number of } {}^1O_2 \text{ molecules formed}}{\text{number photons received per unit of surface}}$$

The number of photons received per unit of surface ( $I_a$ ) is equal to  $k_{abs}[P][hv]$ .

$$\text{We therefore have: } \phi_{so} = \frac{[{}^1O_2]}{k_{abs}[P][hv]} = \frac{k_{O_2}[O_2][{}^3P^*]}{I_a} \quad (3)$$

$$\text{Using equation (3) and (2)} \quad \phi_{so} = \frac{k_{O_2} \cdot [O_2]}{I_a} \cdot \frac{k_{ISC}[{}^1P^*]}{k_{O_2}[O_2] + k_{d2}}$$

$$\text{then using equation (1)} \quad \phi_{so} = \frac{k_{O_2}[O_2]k_1}{I_a(k_{O_2}[O_2] + k_{d2})} \cdot \frac{k_{abs}[P][hv]}{k_{ISC} + k_{d1}}$$

$$\phi_{so} = \frac{k_{O_2}[O_2] \cdot k_{ISC}}{k_{abs}[P][hv] \cdot (k_{O_2}[O_2] + k_{d2})} \cdot \frac{k_{abs}[P][hv]}{k_{ISC} + k_{d1}} = \boxed{\frac{k_{ISC}}{k_{ISC} + k_{d1}} \cdot \frac{k_{O_2}[O_2]}{(k_{O_2}[O_2] \cdot k_{d2})}} \quad (4)$$

We make the hypothesis of the steady state for  $[{}^1O_2]$ .

$$\frac{d[{}^1O_2]}{dt} = 0 = k_{O_2}[O_2][{}^3P^*] - k_d[{}^1O_2] - k_r[S][{}^1O_2] \quad (5)$$

$$\frac{d[S]}{dt} = k_r[S][{}^1O_2]$$

$$\text{Using equation (5) we have } \frac{d[S]}{dt} = k_r[S] \cdot \frac{k_{O_2}[O_2][{}^3P^*]}{k_d + k_r[S]}$$

Using equations (2), (1) and (4)

$$\frac{d[S]}{dt} = k_r[S] \cdot \frac{k_{O_2}[O_2]}{k_d + k_r[S]} \cdot \frac{k_{ISC}[{}^1P^*]}{k_{O_2}[O_2] + k_{d2}}$$

$$\frac{d[S]}{dt} = k_r[S] \cdot \frac{k_{O_2}[O_2]}{k_d + k_r[S]} \cdot \frac{k_{ISC}}{k_{O_2}[O_2] + k_{d2}} \cdot \frac{k_{abs}[P][hv]}{k_{ISC} + k_{d1}}$$

$$\frac{d[S]}{dt} = \frac{k_r[S]}{k_d + k_r[S]} \cdot \phi_{SO} \cdot k_{abs}[P][hv]$$

The quantum yield of the probe (S) is expressed as followed:

$$\phi_s = \frac{\text{number of } S \text{ molecules converted to DBB}}{\text{number photons received per unit of surface}}$$

$$\text{We therefore have } \phi_s = \frac{\frac{d[S]}{dt}}{k_{abs}[P][hv]}$$

$$\text{Thus, we can express } \phi_s \text{ as: } \phi_s = \phi_{SO} \cdot \frac{k_r[S]}{k_d + k_r[S]}$$

As [S] is small,  $k_r[S]$  can be neglected behind  $k_d$ , and the quantum yield of S disappearance is linked to the quantum yield of singlet oxygen production according to:

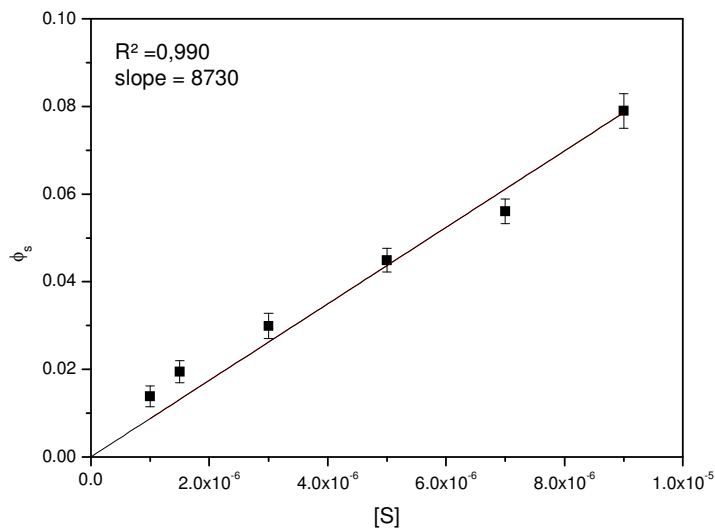
$$\phi_s = \phi_{SO} \cdot \frac{k_r}{k_d} \cdot [S]$$

Some values of rate constants  $k_r$  and  $k_d$  were obtained from literature (table S1). Since rate constants depend strongly on the solvent and no values are available in n-heptane, we performed experiments to estimate the ratio  $k_r/k_d$  using perinaphtenone as a sensitizer (figure S2).

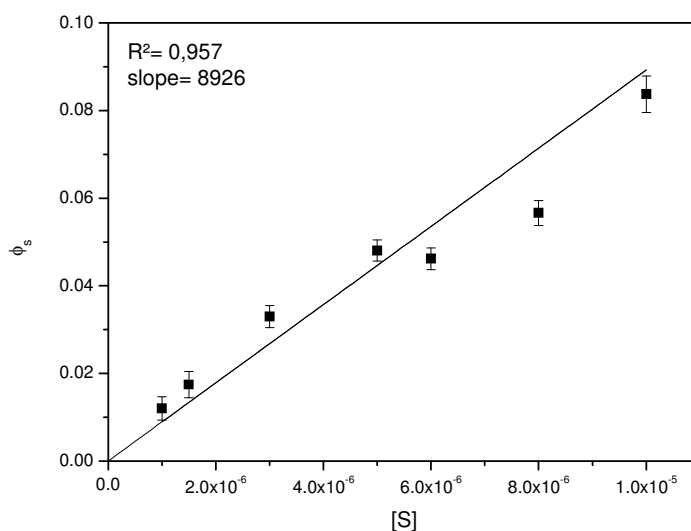
**Table S1 : Reaction rate constants  $k_r$  and  $k_d$  obtained from literature data for perinaphtenone**

solvent	$k_r$ ( $M^{-1} s^{-1}$ )	$k_d$ ( $s^{-1}$ )	$k_r / k_d$	reference
benzene	$6.6 \times 10^8$	$(4.2 \pm 0.9) \times 10^4$	15714	1,2
cyclohexanol	$2.1 \times 10^8$	$(6.3 \pm 0.9) \times 10^4$	3333	2,3
cyclohexane		$(5.9 \pm 0.2) \times 10^4$		4
n-hexane	$3.9 \times 10^9$	$(5.9 \pm 0.2) \times 10^4$	66667	5

In Figure S2, we have plotted  $\phi_s$  against  $[S]$ . As expected from equation given below, the plot is linear. The slope is equal to  $8730 \text{ M}^{-1}$ . Taking the value  ${}^P\phi_{SO}=0.97$  in n-heptane<sup>6</sup>, we estimate  $k_r/k_d = 9000 \text{ M}^{-1}$  in n-heptane.



**Figure S2:  $\phi_s = f([S])$  using perinaphtenone as the sensitizer**

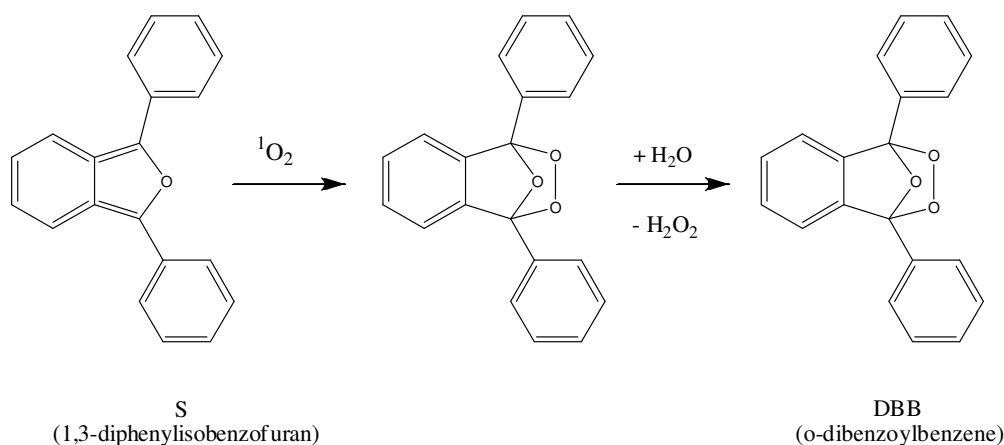


**Figure S3 :  $\phi_s = f([S])$  using chlorothalonil as the sensitizer**

The linear regression of Figure S3 gives a slope of 8926. Taking the previous value for  $k_r/k_d = 9000 \text{ M}^{-1}$ , we obtain  ${}^{CT}\phi_{SO} = 0.99$

## 2. Use of DPBF as the probe

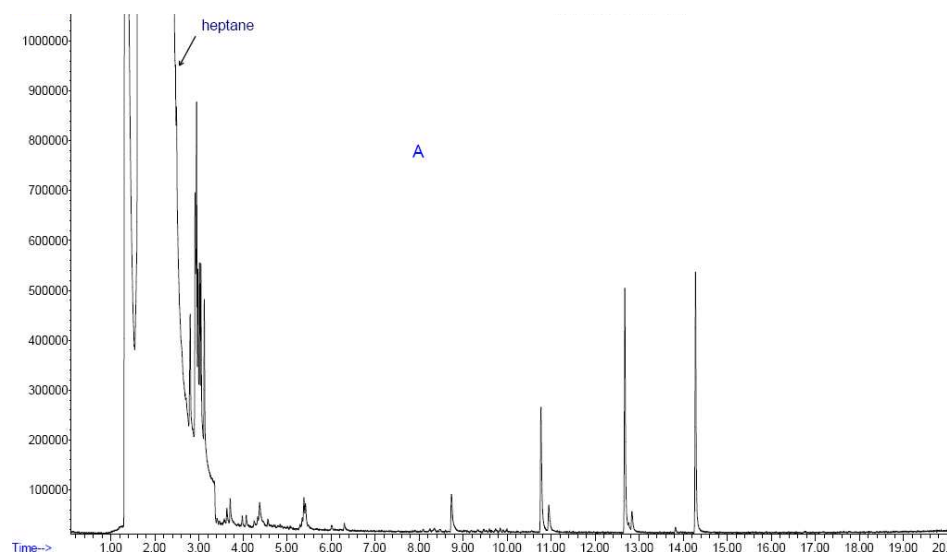
The reaction of the probe, diphenylisobenzofuran, with oxygen singlet leads first to an intermediate which is then converted to o-dibenzoylbenzene. The reaction is described in figure S4<sup>7</sup>. DPBF concentration was followed by fluorescence,  $\lambda_{\text{ex}} = 410 \text{ nm}$  and  $\lambda_{\text{em}} = 454 \text{ nm}$  using the method described previously<sup>8</sup>. DBB is not fluorescent and thus does not interfere with DPBF fluorescence signal.



**Figure S4: reaction of the probe with singlet oxygen**

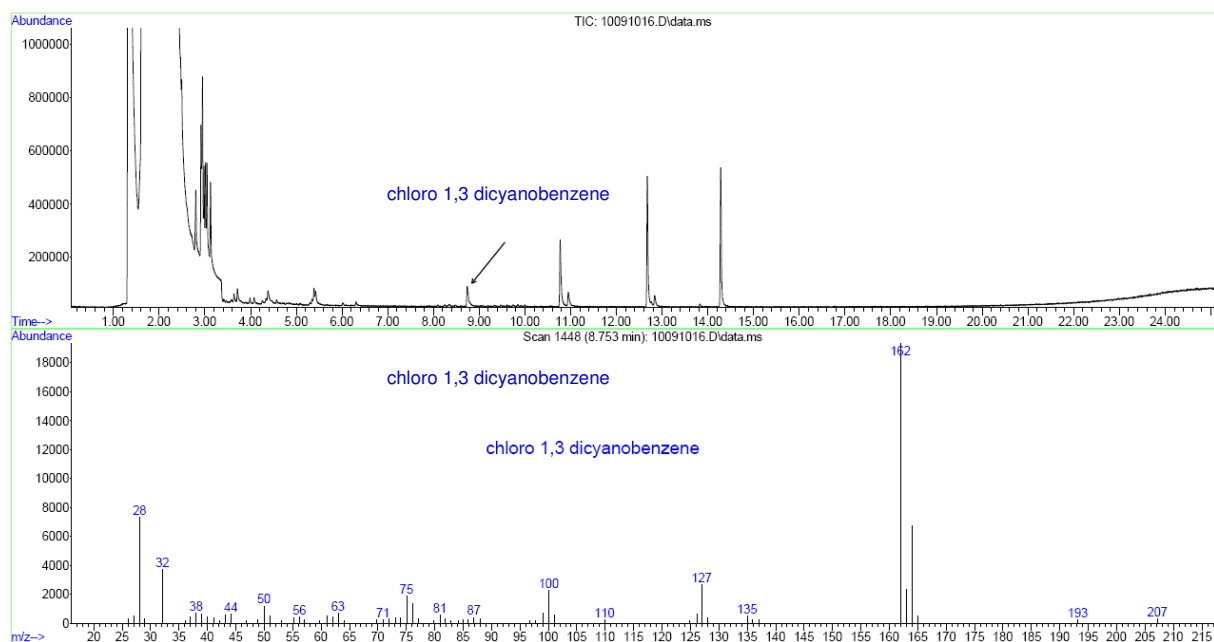
## 3. GC-MS data:

The GC-MS analyses of irradiated solutions of chlorothalonil in air-saturated n-heptane show the formation of 3 major photoproducts (figure S5).



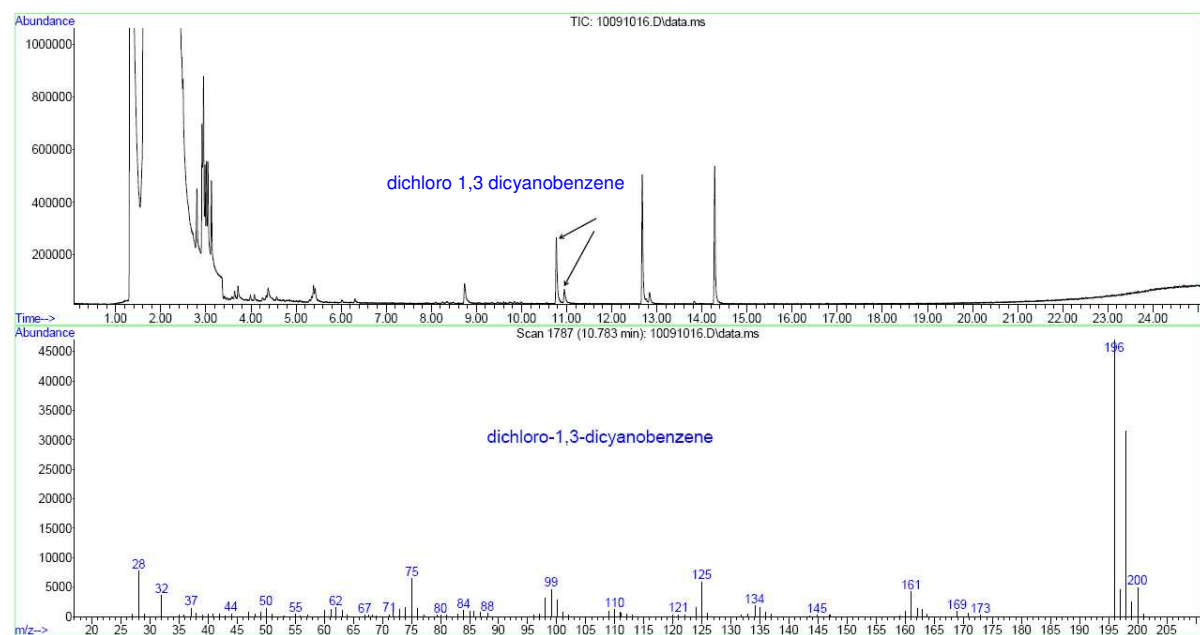
**Figure S5: Chromatogram of an irradiated solution of chlorothalonil in n-heptane**

The first photoproduct with a retention time of 8.7 min is the chloro-1,3-dicyanobenzene (figure S6).



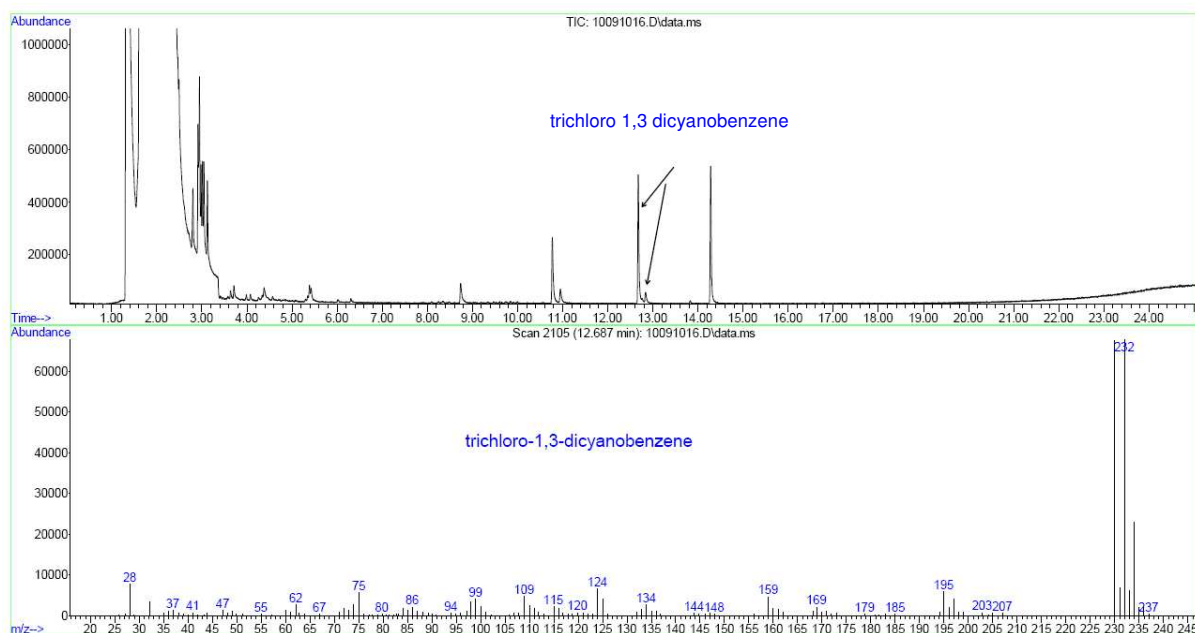
**Figure S6 : Mass spectra of chloro-1,3-dicyanobenzene**

The second identified photoproducts are the congeners dichloro-1,3-dicyanobenzenes (figure S7).



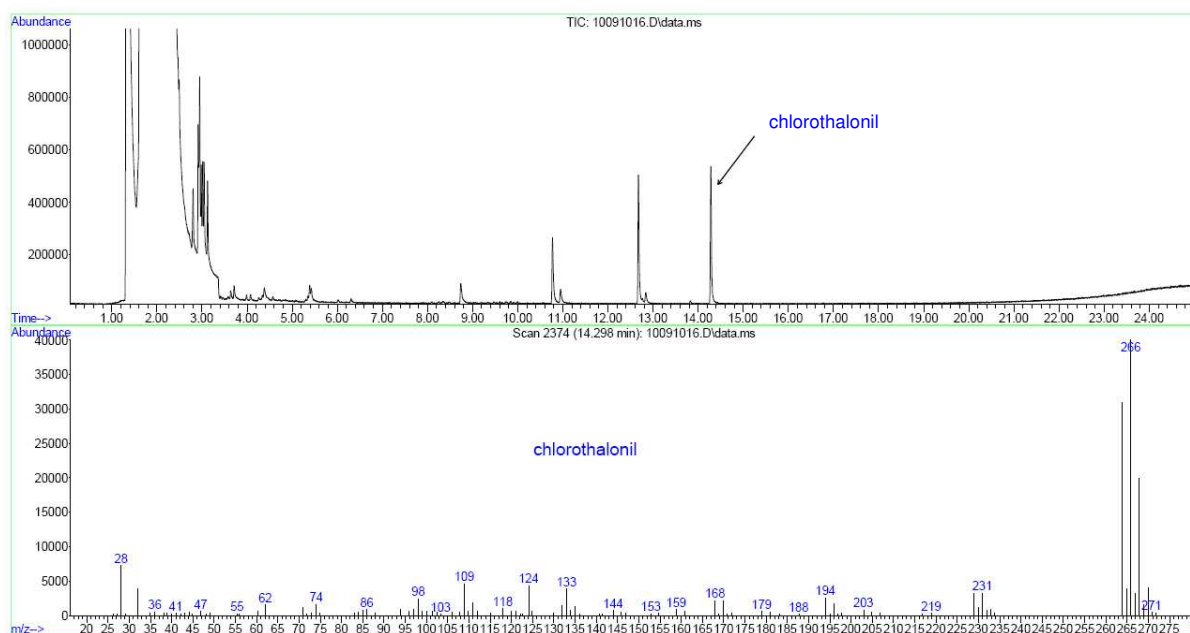
**Figure S7: Mass spectra of the dichloro-1,3-dicyanobenzene congeners**

The mono dechlorinated chlorothalonil isomers have retention time around 12 minutes, their mass spectra is given in figure S8.



**Figure S8: Mass spectra of trichloro-1,3-dicyanobenzene**

In figure S9 is reported the mass spectra of the parent compound.



**Figure S9: Mass spectra of chlorothalonil**

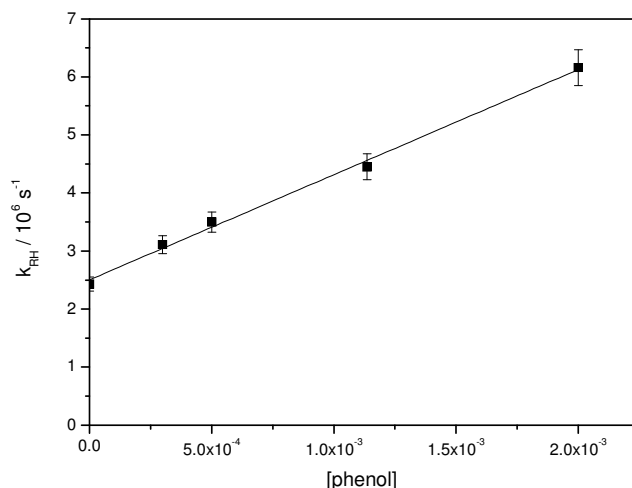
The chromatograms show two isomers of dichloro-1,3-dicyanobenzene and two isomers of tri-1,3-dicyanobenzene.



#### 4. Quenching of CT triplet by phenol

The quenching of CT triplet by phenol was monitored in air-saturated n-heptane. Thus, in the plot  $k_{\text{obs}}$  against [phenol] (Figure S10), the intercept is the sum of the first order rate constant of triplet deactivation and triplet quenching by oxygen. The slope is  $k_{\text{RH}}$ , the bimolecular rate constant of triplet scavenging by phenol.

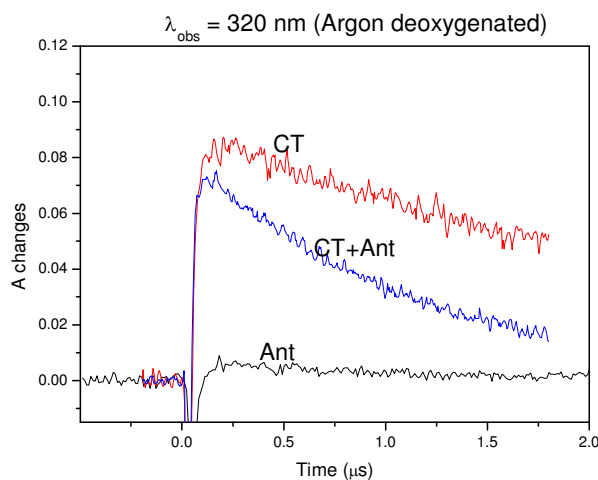
We obtained  $k_{\text{RH}} = (1.83 \pm 0.14) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  with  $R^2 = 0.994$



**Figure S10: Quenching of the CT triplet excited state by phenol**

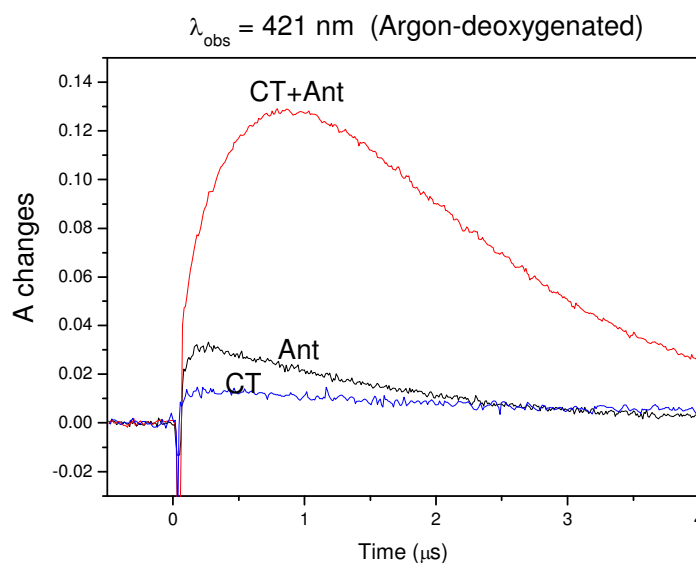
#### 5. Energy transfer from CT triplet to anthracene:

To confirm that the transient species observed is the triplet and to measure the quantum yield of inter-system crossing, we used anthracene as an energy acceptor. The figure S11 shows the 320-nm absorbance variation with time upon laser excitation of CT ( $10^{-4} \text{ M}$ ), anthracene ( $4 \times 10^{-4} \text{ M}$ ) and CT+ anthracene solutions. The lifetime of triplet CT is faster in the presence of anthracene than in the absence of anthracene showing that anthracene has reacted with the CT triplet.



**Figure S11: Absorbance decay from CT alone, anthracene alone and mixture CT + anthracene at 320-nm**

This second graph (figure S10) shows that the formation of the triplet of anthracene at 421 nm. The absorbance is drastically more important in the system CT+ anthracene than in the solution of anthracene alone. This evidences the energy transfer between triplet CT and ground state anthracene.



**Figure S12: Anthracene triplet formation monitoring**

To measure the quantum of inter system crossing of CT, we made as follows. We measured the product  $\epsilon_T \times \phi_{\text{ISC}}$  for anthracene alone using peroxodisulfate as actinometer ( $\epsilon_T \times \phi_{\text{ISC}} = 1880 \text{ M}^{-1} \text{ cm}^{-1}$  at 450 nm). We found  $33600 \text{ M}^{-1} \text{ cm}^{-1}$  at 421 nm at 0.2 microsecond. Then one measured the  $\epsilon_T \times \phi_{\text{ISC}}$  of anthracene in the mixture CT+anthracene from absorbances monitored at 1 microsecond. We found  $31100 \text{ M}^{-1} \text{ cm}^{-1}$  at 421 nm. Using that  $\phi_{\text{ISC}}$  for anthracene is equal to 0.71 (9) and using the relative absorbances of anthracene and CT in the mixture, one finally got that  $\phi_{\text{ISC}}$  for CT is around 0.7.

1. Merkel, P. B. and Kearns, D. R. Remarkable solvent effects on the lifetime of  $^1\Delta_g$  oxygen. *J. Am. Chem. Soc.* **1972**, 94 (3), 1029-1030.
2. Stevens, B., Ors, J. A., Pinsky, M. L. The photo-peroxidation of unsaturated organic molecules.  $\text{O}_2$   $^1\Delta_g$  acceptor re-encounter probabilities. *Chem. Phys. Lett.* **1974**, 27 (2), 157-160.
3. Young, R. H. and Brewer, D. R. *Singlet Oxygen, reactions with organic compounds and polymers*, Ranby, B.; Rabek, J. F. Eds.; John Wiley & sons: 1976.
4. Merkel, P. B. and Kearns, D. R. Radiationless decay of singlet molecular oxygen in solution. An experimental and theoretical study of electronic-to-vibrational energy transfer. *J. Am. Chem. Soc.* **1972**, 94 (21), 7244-7253.
5. Olmsted, J. and Karal, G. Iodine-sensitized phototransformation of singlet oxygen. *J. Am. Chem. Soc.* **1972**, 94 (10), 3305-3313.
6. Oliveros, E., Bossmann, S. H., Nonell, S., Mart, C., Heit, G., Tröscher, G., Neuner, A., Martinez, C., Braun, A. M. Photochemistry of the singlet oxygen [ $\text{O}_2$ ] sensitizer perinaphthenone (phenalenone) in N,N'-dimethylacetamide and 1,4-dioxane. *New J. Chem.* **1999**, 85-93.

7. Howard, J. A. and Mendenhall, G. D. Autoxidation and Photooxidation of 1,3-diphenylisobenzofuran : A Kinetic and Product Study. *Can. J. Chem.* **1975**, 53 2199-2201.
8. Wozniak, M., Tanfani, F., Bertoli, E., Zolese, G., Apreaa, C., Antosiewicz, J. A new fluorescence method to detect singlet oxygen inside phospholipid model membranes. *Biochim. Biophys. Acta* **1991**, 1082 94-100.
9. Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, CRC Press: NY. 1993.