

**New route to toxic nitro and nitroso products upon irradiation of micropollutants mixtures containing imidacloprid: role of NO<sub>x</sub> and effet of natural organic matter**

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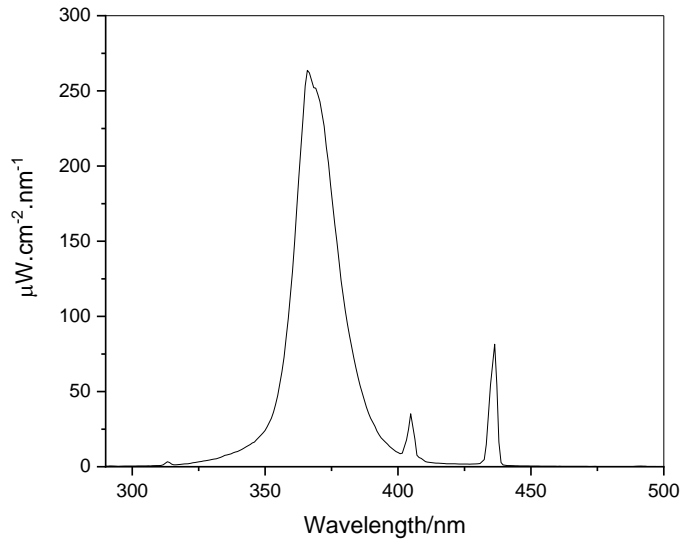
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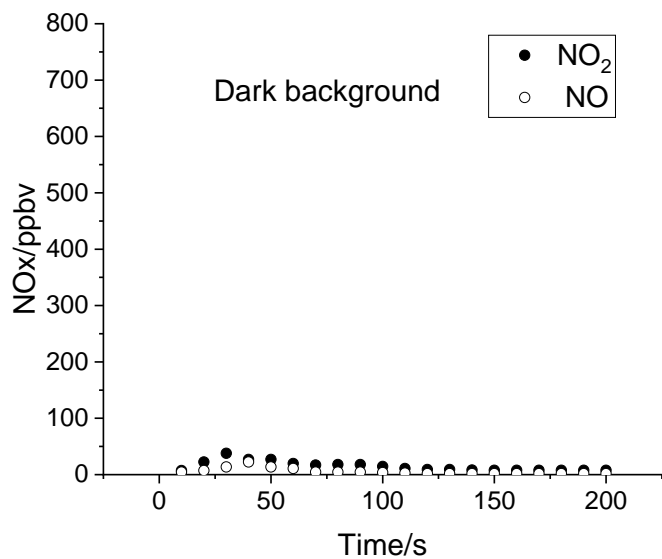
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**Figure SI-1 .** Irradiance of the fluorescent tubes Sylvania F15W/BL 368S used in devices 1 and 2.

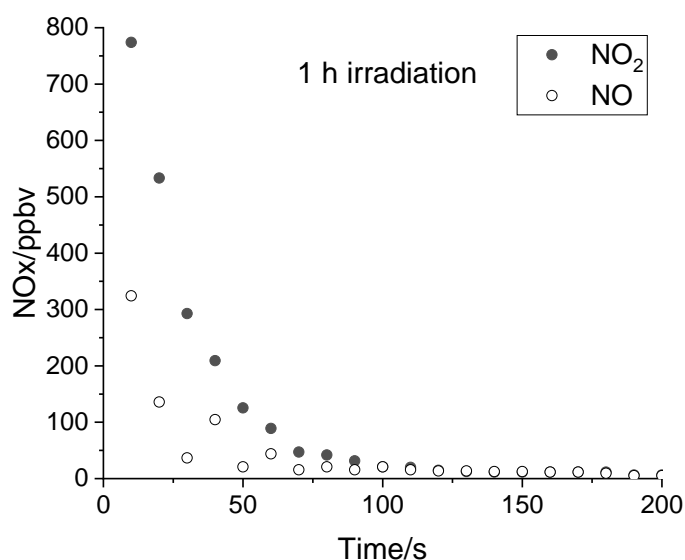


**Figure SI-2 .** Background level of NO<sub>x</sub> formation (A) and NO<sub>x</sub> formation upon irradiation of IMD ( $10^{-4}$  M) for 1 h in device 1 (B). After selected irradiation times, the light was turned off and the outlet of the reactor connected to the NO<sub>x</sub> analyzer. NO<sub>x</sub> were measured every 10 seconds for a period of 1-2 min at a flow rate of  $0.7 \text{ L min}^{-1}$ . The time profile of NO<sub>x</sub> concentrations corresponds to the decay of NO<sub>x</sub> level in the reactor due to the dilution with clean air.

A)



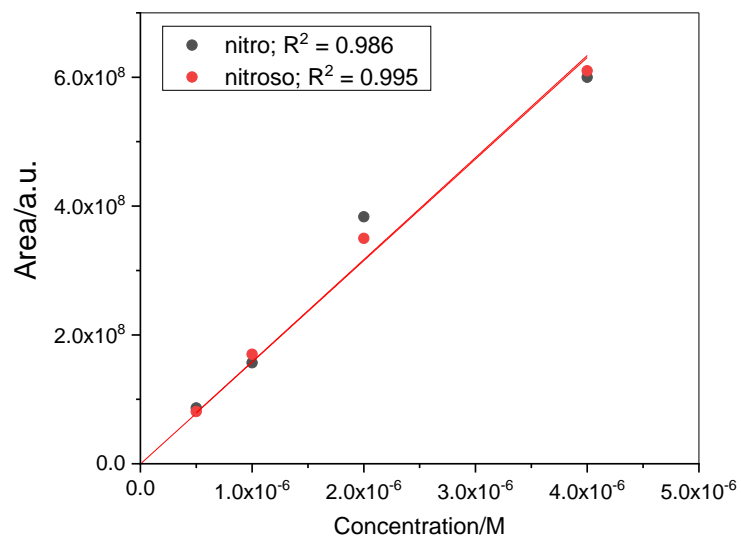
B)



**Table SI-2.** HPLC conditions used for separation and analysis of the different compounds.

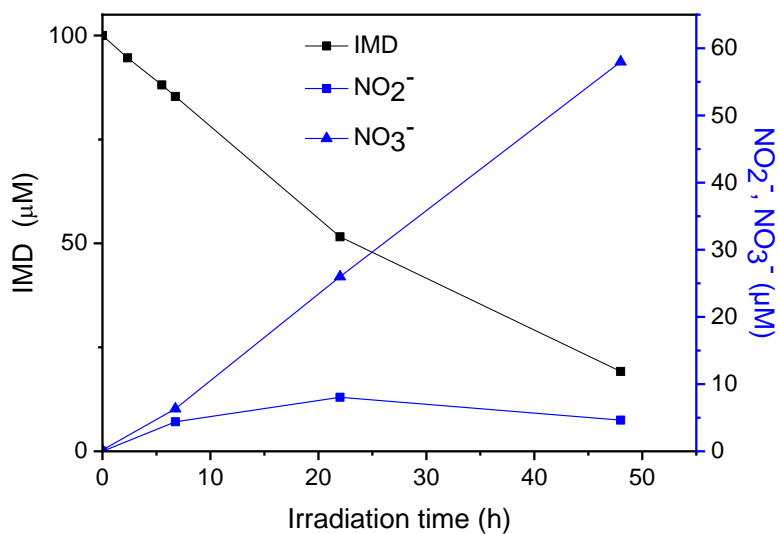
<b>Compound</b>	<b>H<sub>2</sub>O (%)</b>	<b>ACN</b>	<b>Detection wavelength/nm</b>
IMD	60	40	270
Phenol	60	40	270
L-tryptophan	85	15	280
Resorcinol	70	30	274
NO <sub>2</sub> <sup>-</sup> (derivatized)	60	40	307

**Figure SI-3 .** Calibration curve for nitroso-phenol (open circles) and for nitro-phenol (black circles). Area were obtained by UPLC-HR-MS analyses in electrospray negative mode. For nitrosophenol  $m/z= 122.0237$  (5 ppm) and for nitrophenol  $m/z=138.0186$  (5 ppm).

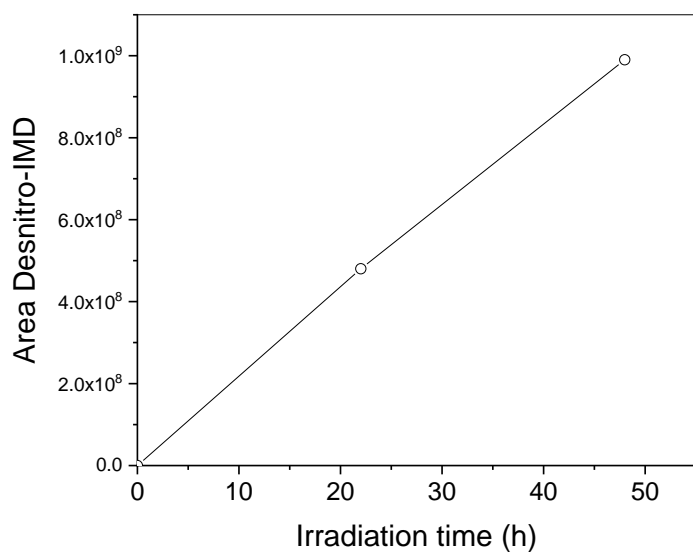


**Figure SI-4.** Consumption profile of aqueous IMD ( $10^{-4}$  M) irradiated in device 1, formation of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  (A) and area UPLC-HRMS of desnitro-IMD (B). IMD was analyzed by HPLC-UV,  $\text{NO}_3^-$  by ionic chromatography,  $\text{NO}_2^-$  by HPLC-UV after derivatization by DNPH. Desnitro-IMD was identified by UPLC-HRMS ( $m/z = 22.0740/213.0709$ ,  $\Delta = 2.2$  ppm)

A)



B)

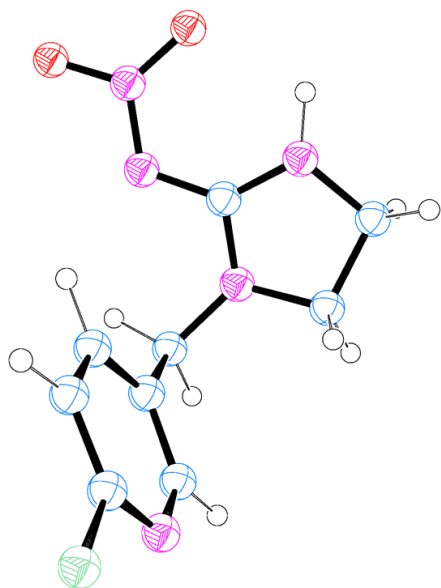


**Table SI-2 : UPLC-HMRS of IMD and photoproducts**

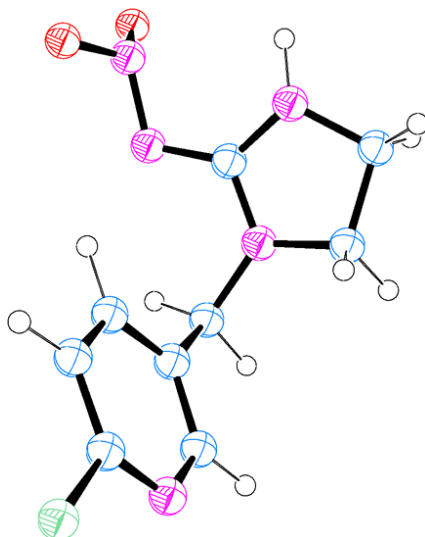
Name	m/z exp. in ES <sup>+</sup>	m/z theor. in ES <sup>+</sup>	Δppm	Formula of the neutral molecule
IMD	256.0603/ 258.0571	256.0596/ 258.0566	2.82	C <sub>9</sub> H <sub>10</sub> ClN <sub>5</sub> O <sub>2</sub>
IMD+O	272.0549/ 274.0517	272.0545/ 274.0515	1.38	C <sub>9</sub> H <sub>10</sub> ClN <sub>5</sub> O <sub>3</sub>
IMD-O	240.0650/ 242.0620	240.0647/ 242.0617	1.52	C <sub>9</sub> H <sub>10</sub> ClN <sub>5</sub> O
Desnitro-IMD	211.0746/ 213.0717	211.0745/ 213.0716	0.33	C <sub>9</sub> H <sub>11</sub> ClN <sub>4</sub>
Desnitro-IMD+2O	243.0650/ 245.0619	243.0643/ 245.0614	2.84	C <sub>9</sub> H <sub>11</sub> ClN <sub>4</sub> O <sub>2</sub>



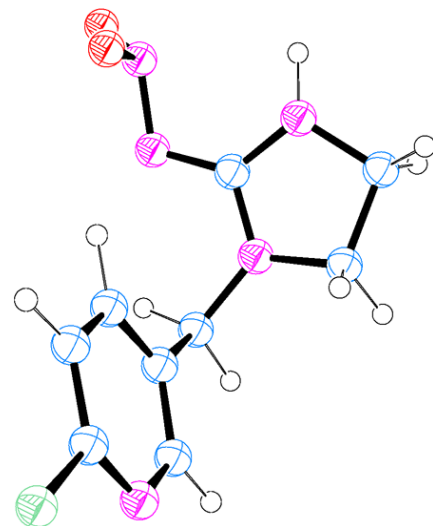
**Figure SI-5.** Structures (a)-(k) of the minimum energy structures and TSs at the MN12SX/6-311++G(d,p),PCM/MN12SX/6-31+G(d,p),PCM level. Energies are given relatively to the global minimum (see Figure 4). Specific bond distances (Å) are also indicated.



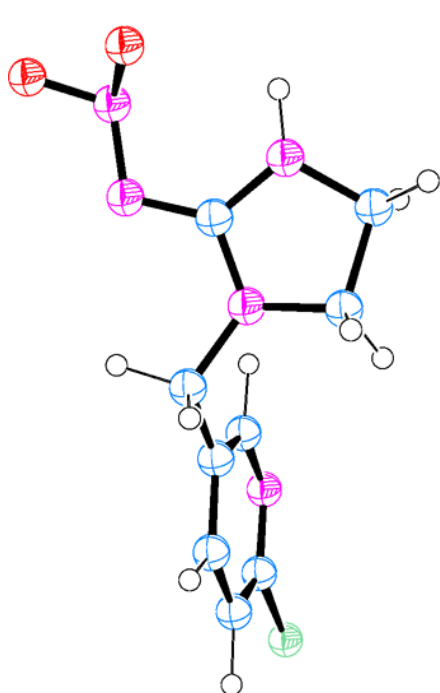
Global min in  $S_0$ ,  ${}^1\text{RNNNO}_2$  (a)  
0.0 kcal mol $^{-1}$



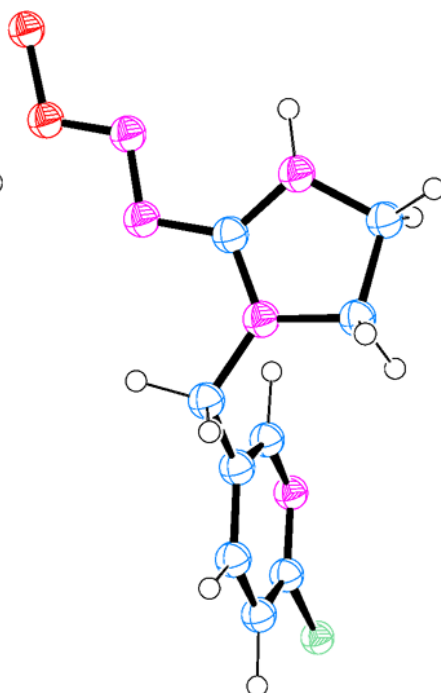
Min in  $S_1$  (b)  
79.3 kcal mol $^{-1}$



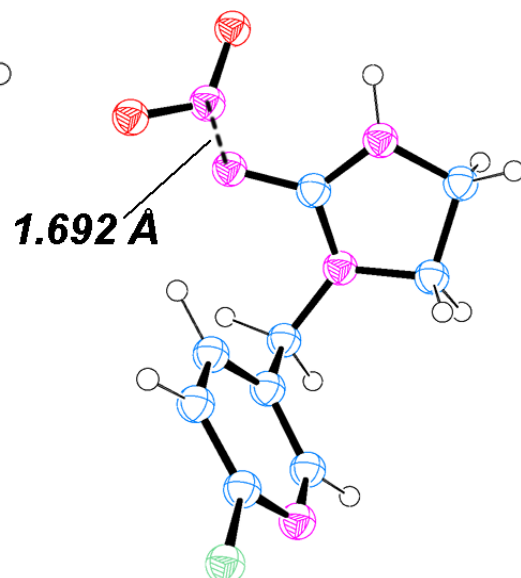
Min in  $T_1$ ,  ${}^3\text{RNNNO}_2$  (c)  
67.3 kcal mol $^{-1}$



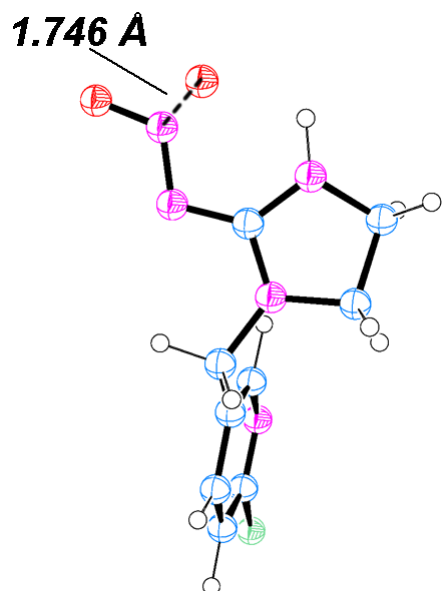
TS in  $S_0$  (d)  
106.1 kcal mol $^{-1}$



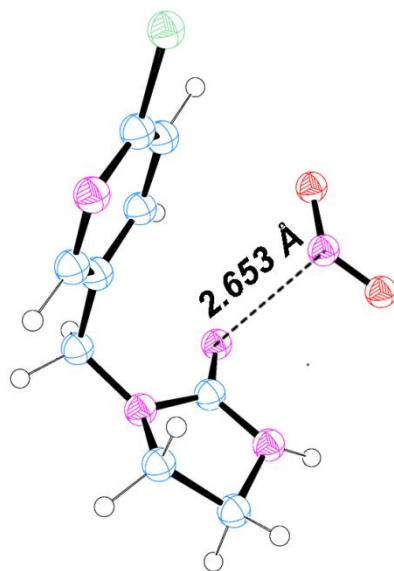
${}^1\text{RNNNO-O}$  (e)  
56.4 kcal mol $^{-1}$



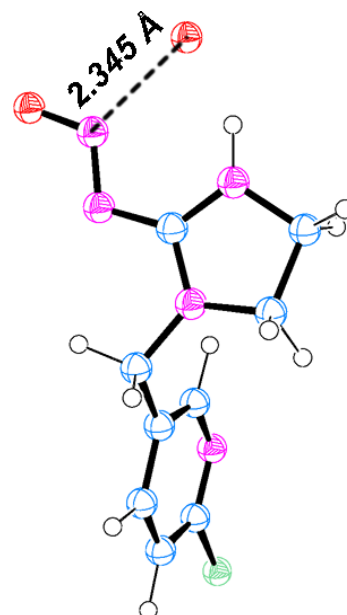
TS $_1$  in  $T_1$  (f)  
73.4 kcal mol $^{-1}$



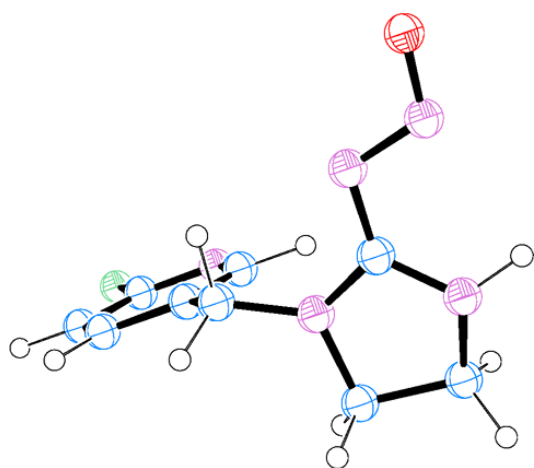
**TS<sub>2</sub> in T<sub>1</sub> (g)**  
78.7 kcal mol<sup>-1</sup>



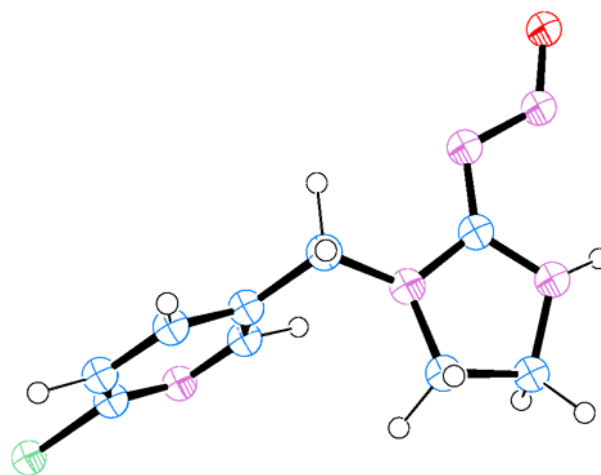
**<sup>3</sup>RN---NO<sub>2</sub> (h)**  
59.8 kcal mol<sup>-1</sup>



**<sup>3</sup>RNNO-O in T<sub>1</sub> (i)**  
76.1 kcal mol<sup>-1</sup>



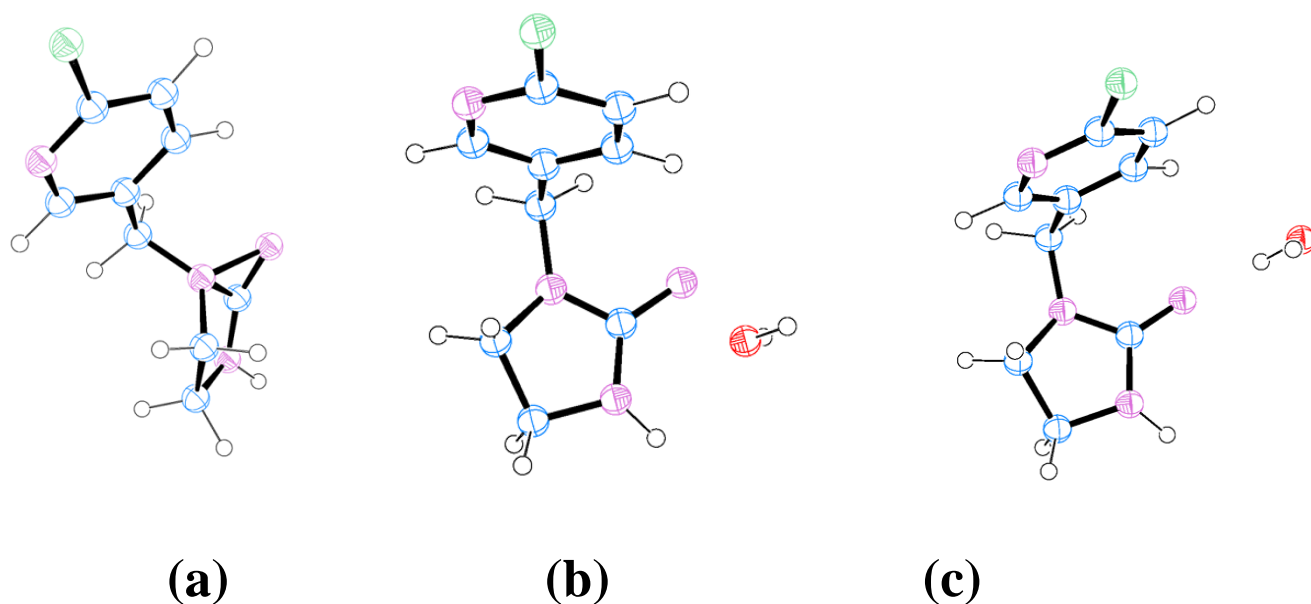
**<sup>1</sup>RNNO (j)**  
80.4 kcal/mol



**<sup>3</sup>RNNO (k)**  
121.4 kcal/mol



**Figure SI-6.** Structures of  $\text{RN}^+$  (a),  $\text{RN}^+\cdot\text{H}_2\text{O}$  (b) and  $\text{RN}\cdot\text{H}_2\text{O}$  (c) obtained at the MN12SX/6-31+G(d,p),PCM level and calculation of  $\text{RN}^+$  energy:



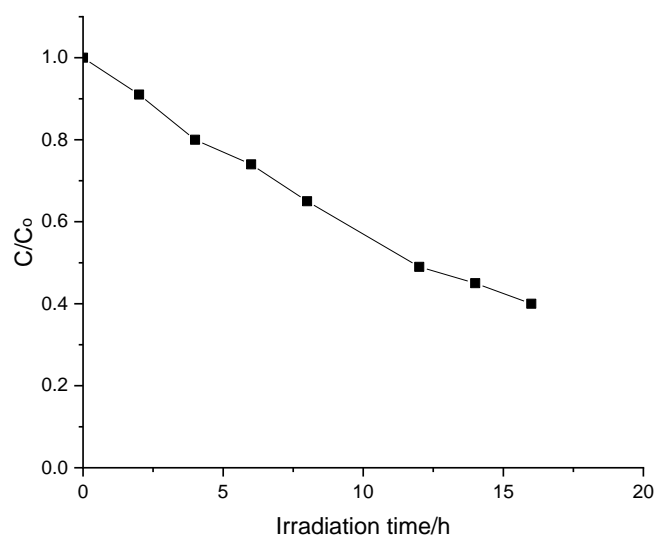
#### Calculation of $\text{RN}^+$ energy:

Optimization of  $\text{RN}^+$  at the MN12SX/6-31+G(d,p),PCM level gave rise to the high energy cyclized species in Fig SI-6a. This structure is similar to that found in the gas phase (MN12SX/6-31+G(d,p)) and it became clear that the PCM model was not sufficient to account for solvent effects here. It was thus decided to optimize  $\text{RN}^+$  at the MN12SX/6-31+G(d,p),PCM level in the presence of one water molecule (implicit + explicit solvation model). The obtained geometry is shown below in Figure SI-6b (no spurious cyclization). Thus, the more accurate energy of  $\text{RN}^+$  ( $\text{RN}^+/\text{NO}_2^-$  at 69.0 kcal/mol in Figure 4) was that of  $\text{RN}^+$  obtained at the MN12SX/6-31+G(d,p),PCM level and corrected with the energy difference below, i.e:

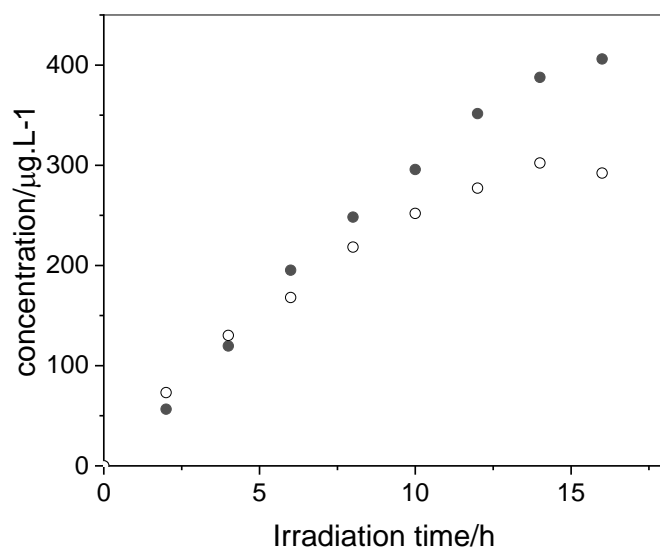
$$E_{\text{text}}(\text{RN}^+) = E(\text{RN}^+) + \underbrace{[\text{E}(\text{RN}^+, \text{H}_2\text{O}) - \text{E}(\text{RN}, \text{H}_2\text{O})] - [\text{E}(\text{RN}^+) - \text{E}(\text{RN})]}_{\substack{\text{These species computed at the} \\ \text{MN12SX/6-311++G(d,p),PCM // MN12SX/6-31+G(d,p),PCM} \\ \text{level}}}$$

i.e: 
$$E_{\text{text}}(\text{RN}^+) = E(\text{RN}) + [\text{E}(\text{RN}^+, \text{H}_2\text{O}) - \text{E}(\text{RN}, \text{H}_2\text{O})]$$

**Figure SI-7 .** Consumption profile of IMD ( $10^{-4}$  M) upon irradiation in device 2. The concentrations of IMD were determined by HPLC-UV.



**Figure SI-8 :** Formation of nitroso-resorcinol (open circles) and nitro-resorcinol (full circles) upon irradiation in device 2 of IMD ( $10^{-4}$  M) and resorcinol ( $10^{-4}$  M). The concentrations of nitroso and nitro-resorcinols were estimated using calibration curves of Figure SI-3.



**Table SI-4 :** Photonitration and photonitrosation of the probes after 16 h of irradiation in device 2 in presence of IMD ( $10^{-5}$  or  $10^{-4}$  M) or a mixture of  $\text{NO}_3^-$  ( $2 \times 10^{-5}$  M) and  $\text{NO}_2^-$  ( $5 \times 10^{-6}$  M). The concentrations of IMD and of the probes were obtained by HPLC-UV while the amounts of nitro and nitro-derivatives by UPLC-HRMS.

Conditions	% of converted IMD	% of converted probe	Nitroso derivative formed ( $\mu\text{g.L}^{-1}$ )	Nitro derivative formed ( $\mu\text{g.L}^{-1}$ )	Sum ( $\mu\text{g.L}^{-1}$ )
Phenol ( $10^{-4}$ M)	-	< 0.5	-	-	-
Phenol ( $10^{-4}$ M)+ IMD ( $10^{-4}$ M)	56±3	14±1	34±2	202±10	236±12
Phenol ( $10^{-4}$ M)+ $\text{NO}_2^-/\text{NO}_3^-$	-	3.4±0.1	0.28±0.02	34±2	34±2
Resorcinol ( $10^{-4}$ M)	-	< 0.5	-	-	-
Resorcinol ( $10^{-4}$ M)+IMD ( $10^{-4}$ M)	58±3	29±1	406±40	292±29	498±69
Resorcinol ( $10^{-4}$ M)+IMD ( $10^{-5}$ M)	61±3	46±5	43±4	16±2	59±6
Resorcinol ( $10^{-5}$ M)+IMD ( $10^{-4}$ M)	62±3	58±5	3.6±0.8	100±20	104±21
Resorcinol ( $10^{-4}$ M)+ $\text{NO}_2^-/\text{NO}_3^-$	-	6.2±0.3	99±9	70.8±7	170±16
Tryptophan ( $10^{-4}$ M)	-	91±5	-	-	-
Tryptophan ( $10^{-4}$ M)+IMD ( $10^{-4}$ M)	60±3	95±5	19±2	9.4±0.9	28±3
Tryptophan ( $10^{-4}$ M)+ $\text{NO}_2^-/\text{NO}_3^-$	-	96±5	7.4±0.7	6.2±0.6	14±2