

## Supporting Information

# Rapid and Facile Chemical Actinometric Protocol for Photo-microfluidic Systems using Azobenzene and NMR Spectroscopy

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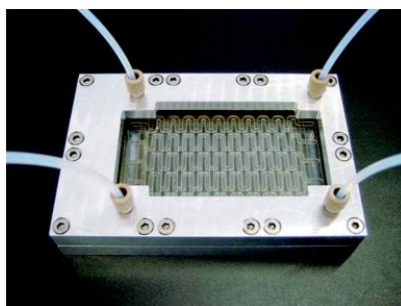
**Table S5.** The % of (*Z*)-azobenzene in response to the irradiation of  $6.4 \times 10^{-4}$  M (*E*)-azobenzene in isooctane and irradiated by LEDs A in flow

## 1. Materials

(*E*)-Azobenzene and all of the solvents were purchased from Sigma-Aldrich (St. Louis, MO, USA). All of the reagents were used as received.

### Flow System

Mikroglas Dwell Device® microreactor (Invenios Europe, Langen, Germany) made of Foturan® glass of dimensions (1.15 m × 2000 μm × 500 μm). The 1.15 m long channel of this dwell device offers extended reaction time. Moreover, the reactor includes a channel for the flow of heat exchange fluid thus providing temperature control. The Foturan® glass is resistant to aggressive liquids (strong acids, bases) allowing the usage of a wide range of solvents in addition to its transparency up to 300 nm making it favorable for UV/Vis photochemical reactions (Figure S1).



**Figure S1.** Mikroglas Dwell Device®.

### Syringe pump

The different flow rates of the reactions performed were regulated using a Harvard Apparatus (Holliston, MA, USA) PHD ULTRA CP syringe pump fitted with 8 mL stainless steel syringes.

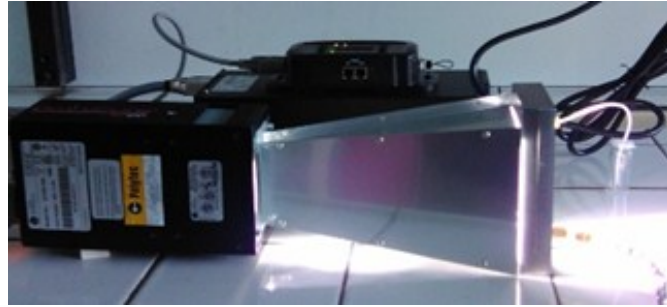
### LED Systems

- 1- A lab assembled UV LEDs composed of 18 identical LEDs from Roithner Lasertechnik (Vienna, Austria),  $365 \pm 15$  nm ), placed at equal distances to provide homogeneous illumination (LEDs A). The wavelength of the emitted irradiation is 365 nm. The average emitted photon flux of this UV LEDs assembly is around  $90 \text{ mW} \cdot \text{cm}^{-2}$  (Figure S2).



**Figure S2.** Mikroglas Dwell device irradiated by LEDs A.

- 2- UV LEDs (365 nm, irradiance up to  $250 \text{ mW}\cdot\text{cm}^{-2}$ ) Omnicure® AC475 model from Lumen Dynamics (Excelitas Technologies, Waltham, MA, USA) (LEDs B). The power of these UV LEDs can be changed, thus 30 % power (irradiance  $70 \text{ mW}\cdot\text{cm}^{-2}$ ) and 100 % power (irradiance  $230 \text{ mW}\cdot\text{cm}^{-2}$ ) were assessed (Figure S3). Note that in all of the cases the irradiance was measured at the surface of the reactor using a radiometer.



**Figure S3.** Mikroglass Dwell device irradiated by LEDs B.

## **Radiometer**

The X9<sub>2</sub> meter in combination RCH-008-4 light detector (Gigahertz-Optiks, Türkenfeld, Germany) was used to measure the irradiance of the light that reaches to the surface of the used microfluidic device (Figure S4).



**Figure S4.** The X9<sub>2</sub> radiometer used for measuring  $Q_{emitted}$ .

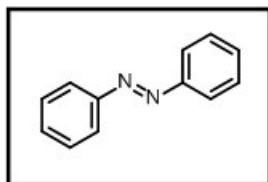
## UV/Vis Spectrometer

A PerkinElmer LAMBDA 35, purchased from PerkinElmer Life & Analytical Sciences (Zaventem, Belgium), was used to measure the UV/Vis absorbance utilized in this study. Note that the quartz cell used had a width of 1 cm. The data was collected using WinLab software.

## NMR measurements

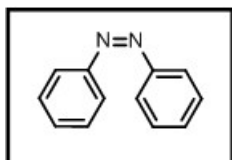
Proton and carbon magnetic resonance spectra ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) were recorded on a Bruker AVANCE 300 spectrometer ( $^1\text{H}$  300 MHz and  $^{13}\text{C}$  75 MHz) using tetramethylsilane (TMS) as the internal standard. Chemical shifts,  $\delta$ , are given in ppm and coupling constants,  $J$ , in Hz.  $^1\text{H}$  NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, m = multiplet, brs = broad singlet), coupling constants and integration.

Azobenzene (*E*)



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93-7.87 (multiplet, 4H),  $\delta$  7.54-7.42 ppm (multiplet, 6H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.25, 130.96, 129.02, 122.86 ppm.

Azobenzene (*Z*)



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.22-7.17 (multiplet, 4H),  $\delta$  7.14-7.07 (multiplet, 2H),  $\delta$  6.82-6.78 ppm (multiplet, 4H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.99, 129.36, 127.78, 120.32 ppm.

## 2. Kinetics

### Thermal isomerization

As indicated by Zimmerman *et al.*,<sup>1</sup> the thermal isomerization follows a typical first order kinetics (Equation S1).  $Z_0$  is the fraction of (Z)-azobenzene right after irradiation,  $Z_t$  is the fraction of Z isomer after leaving the sample in dark for interval of time “ $t$ ” and  $k'$  is the thermal rate constant.

$$\ln \frac{Z_t}{Z_0} = -k' t \quad \text{Equation S1}$$

Thus plotting  $\ln Z_t$  vs time will give a linear curve whose slope is  $k'$ .  $Z_t$  can be expressed as in Equation S2

$$Z_t = Z_0 e^{-k' t} \quad \text{Equation S2}$$

### Photoisomerization

The irradiation of a sample of (E)-azobenzene will not go to completion but rather to (PSS) that depends on the quantum yields of both photoisomerizations. In order to calculate the irradiance of a light source using azobenzene, the following differential equation is derived.

Given that  $Z$  is the fraction of (Z)-azobenzene,  $(1-Z)$  is the fraction of (E)-azobenzene,  $\Delta A$  is the absorbance of the irradiated solution,  $\epsilon_x$  is the extinction coefficient ( $\text{mole}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ ) of the isomer  $x$ ,  $C_0$  is the initial concentration ( $\text{mol} \cdot \text{L}^{-1}$ ) and  $I_0$  ( $\text{ein} \cdot \text{s}^{-1}$ ) and  $I$  ( $\text{ein} \cdot \text{s}^{-1}$ ) are the intensities of light emitted by the source and that transmitted by the irradiated solution respectively.

**Beer lambert's law** (Equation S3, Equation S4 and Equation S5):

$$\Delta A = \epsilon C l \quad \text{Equation S3}$$

$$\Delta A = \log \frac{I_0}{I} \quad \text{Equation S4}$$

$$\Delta I = I_0(1 - 10^{-\Delta A}) \quad \text{Equation S5}$$

So in this case, the absorbance of the fractions of both (E)-azobenzene and (Z)-azobenzene fractions can be expressed as in Equation S6 and Equation S7 respectively:

$$\Delta A_E = \epsilon_E (1 - z) C_0 l \quad \text{Equation S6}$$

$$\Delta A_Z = \epsilon_Z z C_0 l \quad \text{Equation S7}$$

Using the approximation provided by Taylor's series, Equation S5 can be written in the following logarithmic form (Equation S8):

$$\Delta I = I_0(1 - 10^{-\Delta A}) = I_0 \ln 10 \Delta A \quad \text{Equation S8}$$

The overall rate of formation of the Z isomer is affected by three processes: the rate of photoisomerization (E) to (Z), the reverse photoisomerizations and the thermal isomerization that is neglected.

For photoisomerization reactions, the rate depends on the quantum yield of the photoisomerization ( $\phi_x$ ) and the intensity of light per unit volume ( $I^*$ ). This is known as the photokinetic factor that is represented in Equation S9.<sup>2</sup>

$$\frac{d_{[photoisomer]}}{dt} = \phi I^* \text{ where } I^* = \frac{\Delta I}{V} \quad \text{Equation S9}$$

So the rate of formation of the (Z)-azobenzene ( $d[Z]/dt$ ), excluding the thermal isomerization effect, can be written as in Equation S10:

$$\frac{d[Z]}{dt} = \frac{\phi_E I_0 \ln 10 \varepsilon_E (1-Z) C_0 l}{V} - \frac{\phi_Z I_0 \ln 10 \varepsilon_Z Z C_0 l}{V} \quad \text{Equation S10}$$

The term  $\frac{I_0 l}{V}$  can be replaced by  $I_{photon}$  (ein.s.m<sup>-2</sup>) and  $C_0$  can be simplified from both sides of Equation S10 giving Equation S11:

$$\frac{dZ}{dt} = I_{photon} \ln 10 [\phi_E \varepsilon_E (1-Z) - \phi_Z \varepsilon_Z Z] \quad \text{Equation S11}$$

At PSS,  $\frac{dZ_{PSS}}{dt} = 0$  thus giving Equation S12 from Equation S11:

$$I_{photon} \log 10 [\phi_E \varepsilon_E (1 - Z_{PSS}) - \phi_Z \varepsilon_Z Z_{PSS}] = 0 \quad \text{Equation S12}$$

By rearrangement,  $\phi_Z$  can be expressed as in Equation S13:

$$\phi_Z = \frac{\phi_E \varepsilon_E (1 - Z_{PSS})}{\varepsilon_Z Z_{PSS}} \quad \text{Equation S13}$$

Substituting Equation S13 in Equation S12 will give Equation S14:

$$\frac{dZ}{dt} = I_{photon} \ln 10 \left[ \phi_E \varepsilon_E (1-Z) - \frac{\phi_E \varepsilon_E (1 - Z_{PSS})}{\varepsilon_Z Z_{PSS}} \varepsilon_Z Z \right] \quad \text{Equation S14}$$

$$\frac{dZ}{dt} = I_{photon} \ln 10 \frac{\phi_E \varepsilon_E}{Z_{PSS}} [Z_{PSS}(1-Z) - (1 - Z_{PSS})Z] \quad \text{Equation S14}$$

$$\frac{dZ}{dt} = \frac{I_{photon} \ln 10 \phi_E \varepsilon_E}{Z_{PSS}} [Z_{PSS} - Z] \quad \text{Equation S14}$$

Or Equation S15 where  $w = \frac{I_{photon} \ln 10 \phi_E \varepsilon_E}{Z_{PSS}}$  :

$$\frac{dZ}{dt} = w [Z_{PSS} - Z] \quad \text{Equation S15}$$

Consider  $y = Z_{PSS} - Z$ , so Equation S15 can be written in the form of Equation S16:

$$\frac{dy}{dt} = -w y \quad \text{Equation S16}$$

Integrating Equation S16, will finally give Equation S17:

$$\ln y = -wt + \text{constant} \quad \text{Equation S17}$$

So plotting the graph of  $\ln y$  vs  $t$  will exhibit a linear relationship whose slope will be used to determine the value of  $I_0$ .

Rearrangement of Equation S13 will give Equation S18. In this case, by knowing the  $Z_{PSS}$ ,  $\varphi_E$  and  $\varepsilon_E$  one can use them to find the product of  $\varphi_Z \times \varepsilon_Z$  without the need to know the exact values of these two constants that cannot be easily determined as (E)-azobenzene is the stable and the commercially available form:

$$\varphi_Z \varepsilon_Z = \frac{\varphi_E \varepsilon_E (1 - Z_{PSS})}{Z_{PSS}} \quad \text{Equation S18.}$$

***Rate law of the reversible isomerization of azobenzene***

To determine the equilibrium constant  $K_{PSS}$ , the rate constant of the (E) to (Z) photoisomerization  $k_1$  and the rate constant of (Z) to (E) photoisomerization  $k_{-1}$ , a kinetic model that is used for reversible reactions is applied. The relation between  $K_{PSS}$ ,  $k_1$ ,  $k_{-1}$  is represented in Equation S19:

$$K_{PSS} = \frac{[Z]_{PSS}}{[E]_{PSS}} = \frac{k_1}{k_{-1}} \quad \text{Equation S19}$$

The rate of formation of the Z isomer can be expressed as in Equation S20:

$$\frac{d[Z]_t}{dt} = k_1[E]_t - k_{-1}[Z]_t \quad \text{Equation S20}$$

Where  $[E]_t$  and  $[Z]_t$  are the concentrations of the (E) and (Z) isomers at instant t. However,  $[E]_t$  can be written as in Equation S21 where  $[E]_0$  is the initial concentration of the (E) isomer:

$$[E]_t = [E]_0 - [Z]_t \quad \text{Equation S21}$$

The substitution of this value of  $[E]_t$  in Equation S20 will give Equation S22:

$$\frac{d[Z]_t}{dt} = -(k_1 + k_{-1})[Z]_t + k_1[E]_0 \quad \text{Equation S22}$$

At equilibrium  $[Z]_t$  will be represented by  $[Z]_{PSS}$ , so Equation S21 can be modified to Equation S23 and the equilibrium constant  $K_{PSS}$  can be expressed by Equation S24:

$$[Z]_{PSS} = [E]_0 - [E]_{PSS} \quad \text{Equation S23}$$

$$K_{PSS} = \frac{[Z]_{PSS}}{[E]_0 - [Z]_{PSS}} = \frac{k_1}{k_{-1}} \quad \text{Equation S24}$$

Rearrangement of Equation S24 will give Equation S25:

$$[E]_0 = \frac{k_{-1} + k_1}{k_1} [Z]_{PSS} \quad \text{Equation S25}$$

Substituting the value of  $[E]_0$  of Equation S25 in Equation S22 will give Equation S26:

$$\frac{d[Z]_t}{dt} = -(k_1 + k_{-1})([Z]_{PSS} - [Z]_t) \quad \text{Equation S26}$$

$$\frac{d[Z]_t}{[Z]_{PSS} - [Z]_t} = -(k_1 + k_{-1}) dt \quad \text{Equation S26}$$

Note that this equation is the same as that of Equation S15 so that  $w = k_1 + k_{-1}$ .

The integration of Equation S26 will give a relation between  $[Z]_t$  and t in the linear, form Equation S27.



$$\ln \frac{[Z]_{PSS} - [Z]_t}{[Z]_{PSS} - [Z]_0} = -(k_1 + k_{-1}) t \quad \text{Equation S27}$$

Using Equations S23 and S22, numerical expressions between  $K_{PSS}$  and  $[Z]_{PSS}$ , Equation S28, and  $K_{PSS}$  with  $[E]_{PSS}$ , Equation S29, are established.

$$[Z]_{PSS} = \frac{K_{PSS}[E]_0}{K_{PSS} + 1} \quad \text{Equation S28}$$

$$[E]_{PSS} = \frac{[E]_0}{K_{PSS} + 1} \quad \text{Equation S29}$$

The nonlinear forms of the variation of  $[Z]_t$  and  $[E]_t$  that will be used to determine the overall rate law of the reversible photoisomerization of azobenzene are expressed in Equation S30 and Equation S31 respectively:

$$[Z]_t = \frac{K_{PSS}[E]_0}{K_{PSS} + 1} (1 - e^{-(k_1 + k_{-1})t}) = [Z]_{PSS} (1 - e^{-(k_1 + k_{-1})t}) \quad \text{Equation S30}$$

$$[E]_t = \frac{[E]_0}{K_{PSS} + 1} (1 + K_{PSS} e^{-(k_1 + k_{-1})t}) = [E]_{PSS} (1 + K_{PSS} e^{-(k_1 + k_{-1})t}) \quad \text{Equation S31.}$$

### ***Fresnel's law***

#### ***Effect of refraction on the photon flux emitted by the light source***

Consider that the light emitted has a photon flux  $Q_{emitted}$ . When propagating through the reactor, this beam of light will be subjected to two refractions: air – glass and glass – solvent. Assuming that the light beam is orthogonal to the surface of the reactor thus  $i = r = 0$  and by applying Fresnel's Law the reflectance of light R is determined using the following Equation S32:

$$R = \left[ \frac{n_1 \cos i - n_2 \cos r}{n_1 \cos i + n_2 \cos r} \right]^2 \text{ or } R = \left[ \frac{n_1 - n_2}{n_1 + n_2} \right]^2 \quad \text{Equation S32}$$

Due to the law of conservation of energy, the transmittance T, which is the ratio of the light delivered to the system, is calculated using Equation S33:<sup>3</sup>

$$T = 1 - R \quad \text{Equation S33}$$

So the photon flux determined by chemical actinometry,  $Q_{inside}$  is not the actual one delivered by the light source but rather the one received by the system. Additional calculation, indicated in Equation S34, should be done to get that emitted by the light source:<sup>4</sup>

$$Q_{emitted} = \frac{Q_{inside}}{T} \quad \text{Equation S34}$$

### **Physical and chemical constants**

The physical constants  $\varphi_z$  and  $\varepsilon_z$  that are needed to calculate the photon flux (Equation S14), and the refractive index of each medium covered in this study needed to convert  $Q_{inside}$  to  $Q_{outside}$  are

### *Actinometric Protocol in Photomicrofluidic Systems using Azobenzene*

summarized in Table S1. Note that the refractive indices and the quantum yield values are taken from literature whereas the extinction coefficient values are determined experimentally.

**Table S1. Physical and chemical constants used for calculations**

Substance	Refractive index n	$\epsilon_E$ (L.mol <sup>-1</sup> cm <sup>-1</sup> )	$\varphi_E$	$\varphi_Z$
Air	1.000	--	--	--
Foturan glass ® <sup>5</sup>	1.515	--	--	--
Methanol	1.3284	312	0.15	0.35
Acetonitrile	1.3441	277	0.15	--
Isooctane	1.3914	95	0.12	0.48

***Total transmittance***

By referring to Fresnel's law (Equation S32):

$$R_{air-Foturan} = \left[ \frac{1 - 1.515}{1 + 1.515} \right]^2 = 0.042$$

Thus  $T_{air-Foturan} = 1 - R_{air-Foturan} = 0.958$ .

Similarly,  $R_{Foturan-isooctane} = 0.0018$  and  $T_{Foturan-isooctane} = 0.998$ .

The total transmittance  $T_{total} = T_{air-Foturan} \times T_{Foturan-isooctane} = 0.956$

Table 1 includes the total transmittance of light when working with the three solvents isooctane, acetonitrile and methanol.

***Determination of the Absorption Coefficient  $\epsilon$  of (E)-azobenzene***

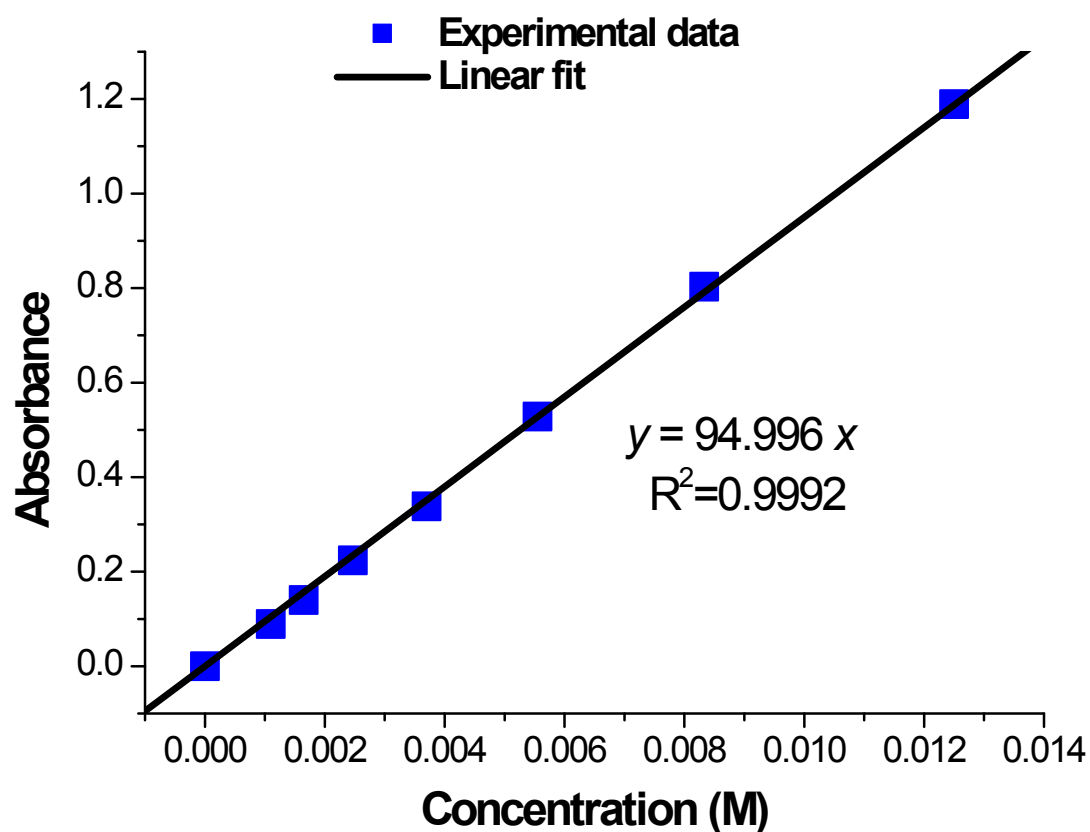
The  $\epsilon$  values of the *E* isomer in isooctane, acetonitrile and methanol were determined by classical calibration curves having the absorbance vs concentration. Using Beer-Lambert's law, the slope of each of the plotted straight lines corresponds to the absorption coefficient of azobenzene in the corresponding solvent.

*In isooctane:*

Table S2 and Figure S5 correspond to the variation of the absorbance  $A$  as function of the concentration of azobenzene in isooctane. The linear plot with  $R^2$  of 0.999 has a slope of  $95 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  is then the absorption coefficient  $\epsilon$  ( $E$ )-azobenzene in isooctane.

**Table S2. Variation of Absorbance of ( $E$ )-azobenzene in Isooctane as Function of Concentration**

[ $E$ ] mol.L <sup>-1</sup>	Absorbance
0.00E+00	0
1.10E-03	0.089
1.65E-03	0.14
2.47E-03	0.224
3.70E-03	0.338
5.55E-03	0.528
8.33E-03	0.803
1.25E-02	1.189



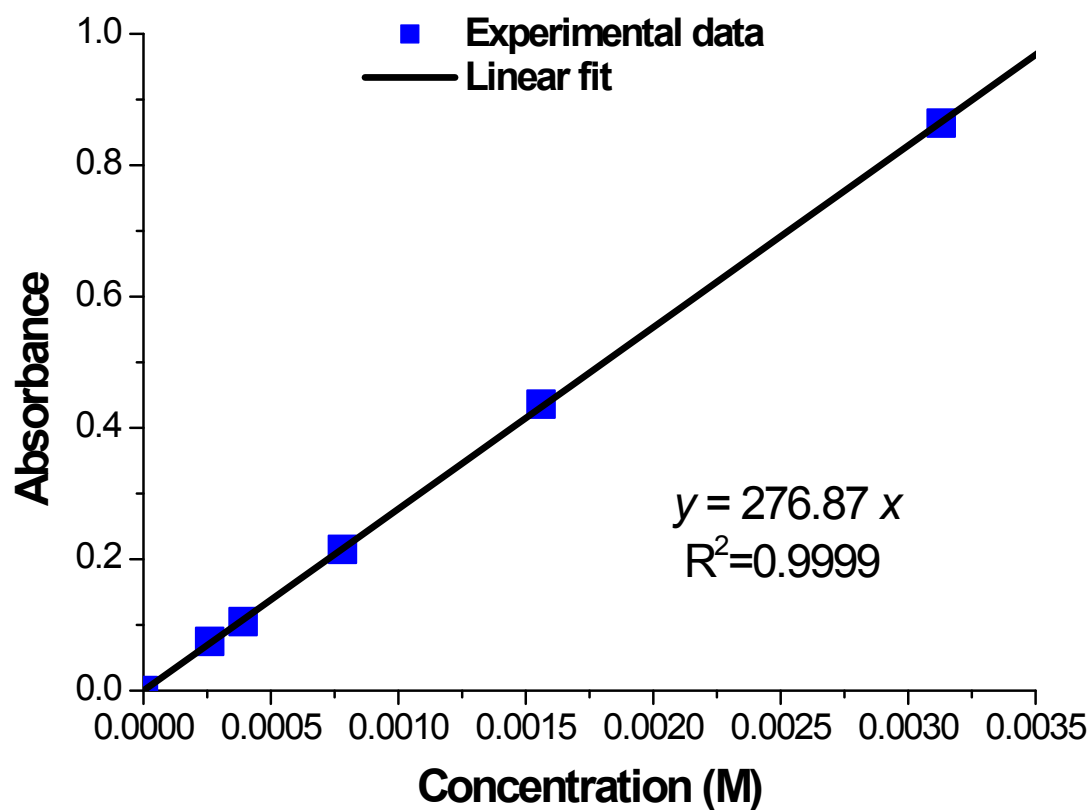
**Figure S5.** Plot of Absorbance vs Concentration of ( $E$ )-azobenzene in Isooctane.

*In acetonitrile:*

Similarly, by observing Table S3 and Figure S6, the absorption coefficient of (*E*)-azobenzene in acetonitrile is 276.9 L.mol<sup>-1</sup>cm<sup>-1</sup>.

**Table S3. Variation of Absorbance of (*E*)-azobenzene in Acetonitrile as Function of Concentration**

[ <i>E</i> ] mol.L <sup>-1</sup>	Absorbance
0.00E+00	0
2.60E-04	0.075
3.91E-04	0.105
7.81E-04	0.215
1.56E-03	0.436
3.13E-03	0.864



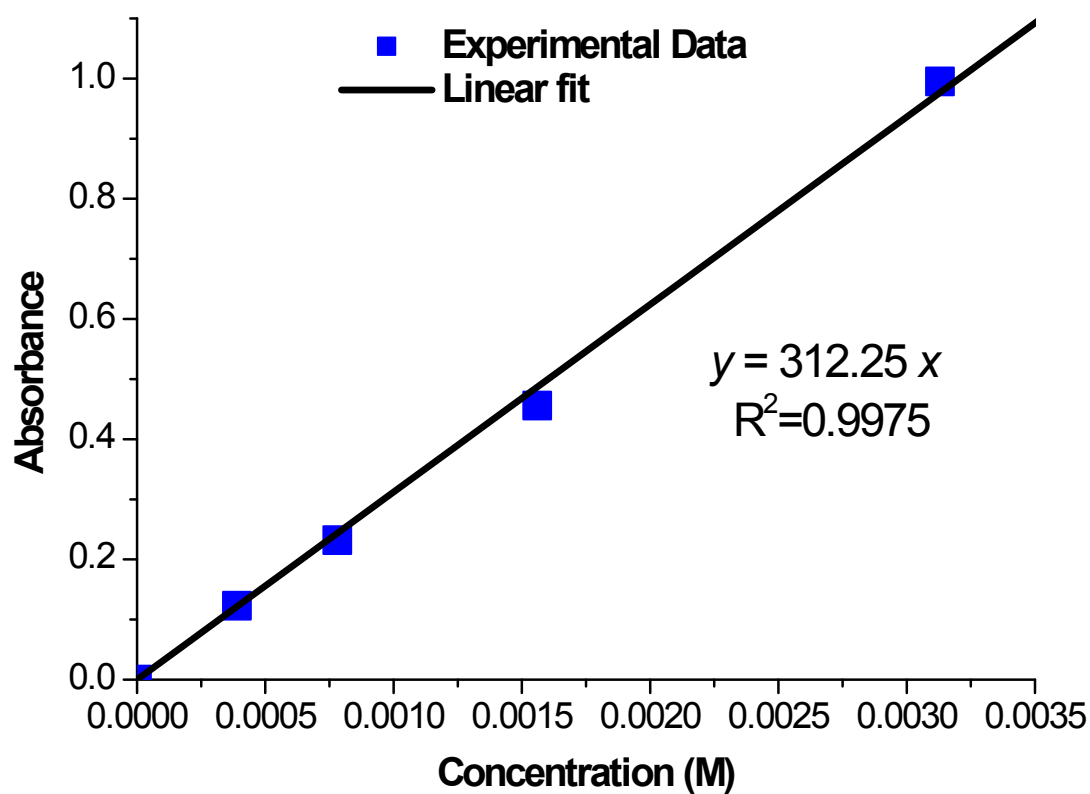
**Figure S6.** Plot of Absorbance vs Concentration of (*E*)-azobenzene in Acetonitrile.

*In methanol:*

The absorption coefficient of (*E*)-azobenzene in methanol is 312 L.mol<sup>-1</sup>cm<sup>-1</sup> in reference to the results of Table S4 and Figure S7.

**Table S4. Variation of Absorbance of (*E*)-azobenzene in Methanol as Function of Concentration**

[E] mol.L <sup>-1</sup>	Absorbance
0.00E+00	0.000
3.90E-04	0.123
7.81E-04	0.232
1.56E-03	0.456
3.13E-03	0.995



**Figure S7.** Plot of Absorbance vs. Concentration of (*E*)-azobenzene in methanol

### 3. Photoisomerization of Azobenzene

#### General procedure of photoisomerization of Azobenzene

A solution of (*E*)-azobenzene of concentration  $6.4 \times 10^{-4}$  M in isooctane was injected into the Mikroglas Dwell Device, irradiated by UV LEDs A ( $90 \text{ mW.cm}^{-2}$ ), at various flow rates. The flow rates were chosen depending on the desired irradiation times ranging between 9 s and 140 s. The Dwell device was kept at a constant temperature of  $20^\circ\text{C}$  using a cryostat. The solvent of irradiated samples was evaporated and the residue was then dissolved in  $500 \mu\text{l}$  of  $\text{CDCl}_3$  to be injected in the NMR spectrometer. The degree of conversion was calculated using the  $^1\text{H}$  spectrum by integrating the peaks that correspond to the (*Z*) and (*E*) isomers of azobenzene. The results obtained were then used to determine the photon flux inside the microreactor. A more concentrated solution (0.01 M) in isooctane, acetonitrile and methanol were also assessed. The chemical actinometry of azobenzene in isooctane (0.01 M) was then performed using UV LEDs B at 30 % ( $70 \text{ mW.cm}^{-2}$ ) and 100 % ( $230 \text{ mW.cm}^{-2}$ ) power.

The composition at the PSS was determined by the irradiation of a sample for an extended time (around 2 h). As for the thermal isomerization, one PSS sample was placed in dark at room temperature and the variation in its composition was then monitored by  $^1\text{H}$  NMR during the following 48 h. This experiment was done to determine the value of  $k_{\text{thermal}}$  to verify the exclusion of this factor in the calculations mentioned in the kinetics section. Note that all of the experiments were repeated for 3 times and the mean values of the results are displayed.

#### Calculation of the Degree of Conversion

The fraction of the formed *Z* isomer was determined using Equation S33 where  $I_z$  and  $I_E$  are the integrals of the peaks that correspond to the *Z* and *E* isomers respectively. Figure S8 is the  $^1\text{H}$  NMR of (*E*)-azobenzene whereas Figure S9 is the Spectrum of an irradiated sample of (*E*)-azobenzene having both isomers that can be easily distinguished from each other.

$$\% Z = \frac{\sum I_z}{\sum I_z + \sum I_E} \quad \text{Equation S33}$$

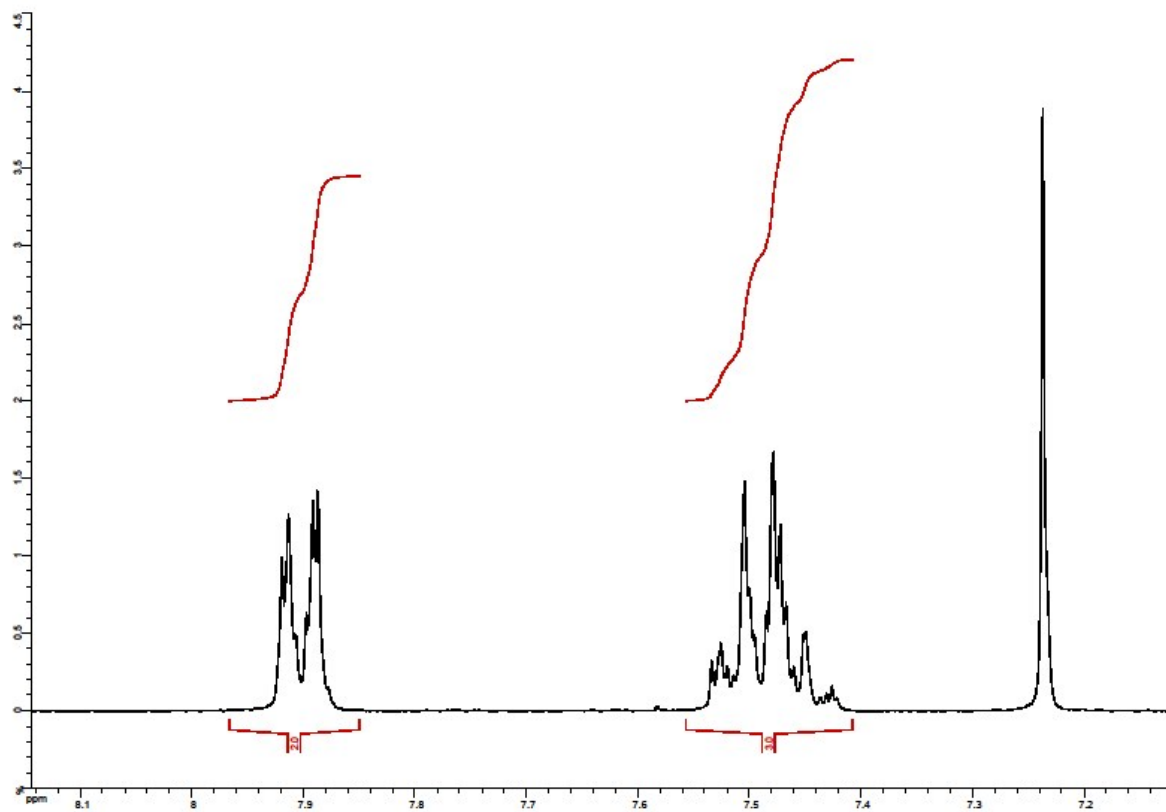


Figure S8.  $^1\text{H}$  NMR Spectrum of (*E*)-Azobenzene

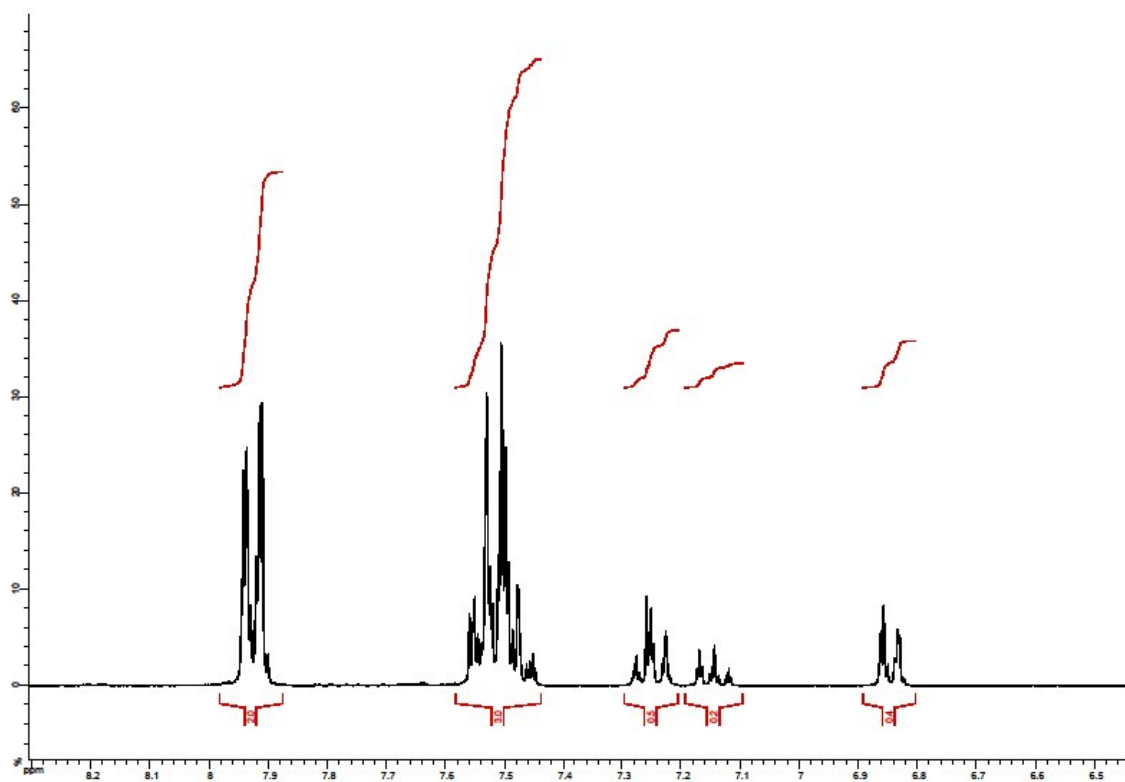


Figure S9.  $^1\text{H}$  NMR Spectrum of a mixture of (*E*) and (*Z*)-azobenzene after 23 min of irradiation



## Results

### **$6.4 \times 10^{-4}$ M (*E*)-azobenzene in isooctane and irradiated by LEDs A**

Table S5 includes the variation of the photoisomerization of azobenzene in response to the variation in the flowrate (irradiation time).

**Table S5. The % of (*Z*)-azobenzene in response to the irradiation of  $6.4 \times 10^{-4}$  M (*E*)-azobenzene in isooctane and irradiated by LEDs A in flow**

Flow rate (ml/min)	Irradiation time (s)	% ( <i>Z</i> )-azobenzene
4.0	17	4.4
3.0	23	8.0
2.0	35	11.6
1.0	69	18.0
0.5	138	20.5

### **$1.0 \times 10^{-2}$ M (*E*)-azobenzene in isooctane and irradiated by LEDs A**

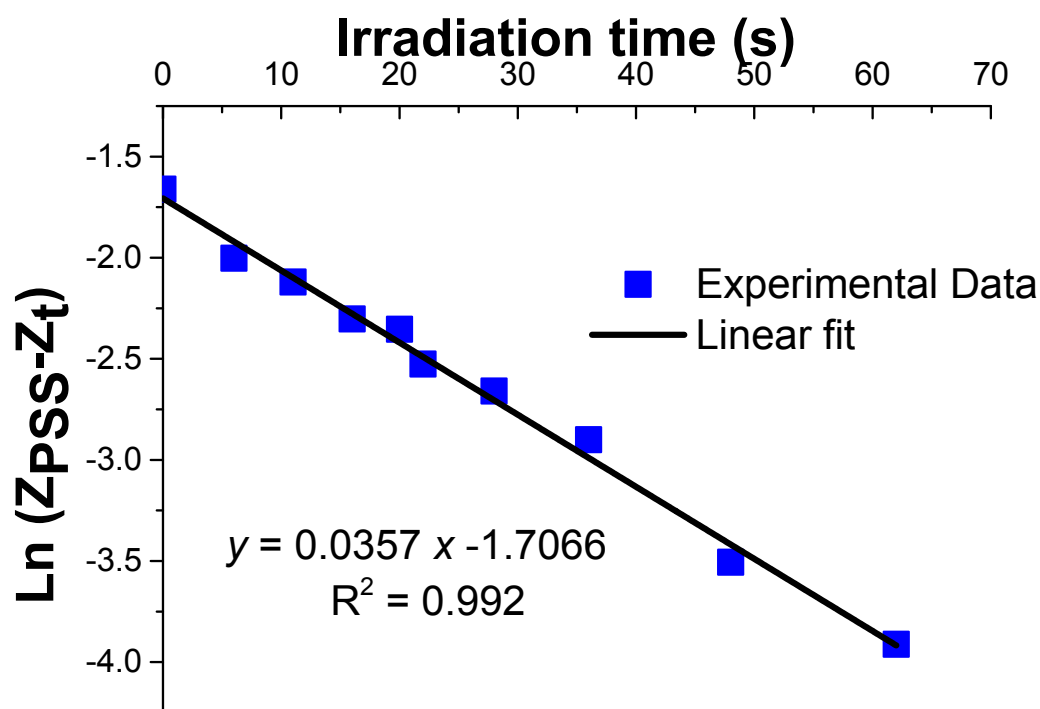
Table S6 includes the variation of the photoisomerization of azobenzene in response to the variation in the flowrate (irradiation time).

**Table S6. The % of (*Z*)-azobenzene in response to the irradiation of  $1.0 \times 10^{-2}$  M (*E*)-azobenzene in isooctane and irradiated by LEDs A in flow**

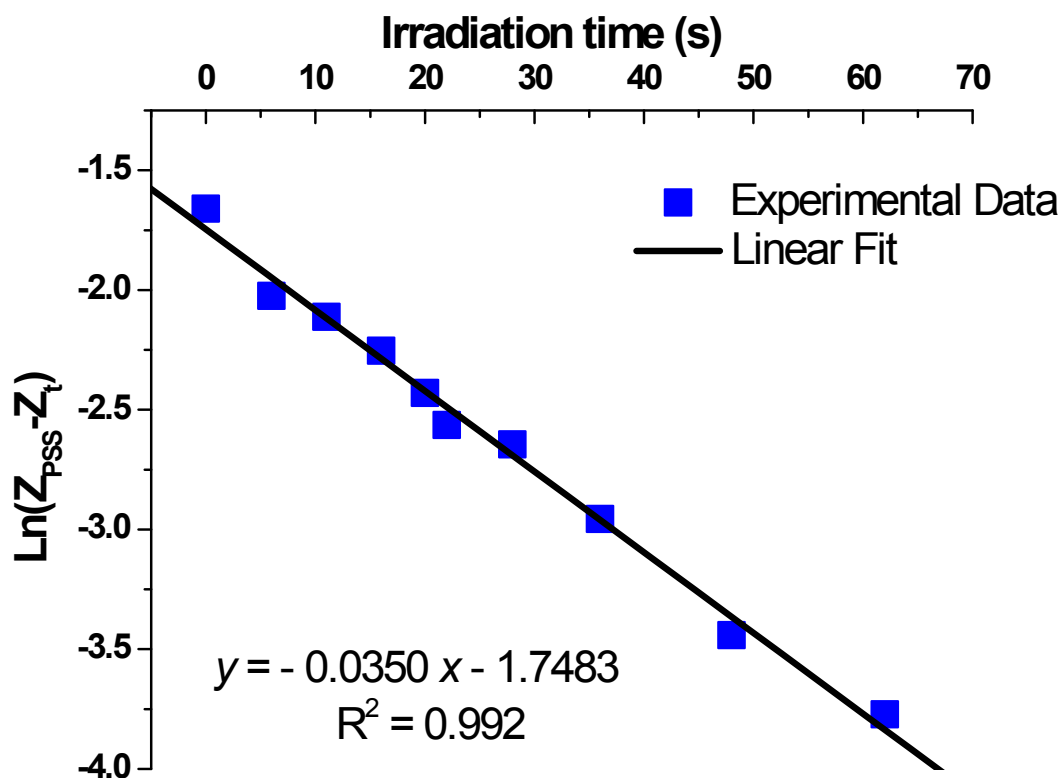
Flow rate (ml/min)	Irradiation time (s)	% ( <i>Z</i> )-azobenzene (experiment a)	% ( <i>Z</i> )-azobenzene (experiment b)	% ( <i>Z</i> )-azobenzene (experiment c)
11.5	6	5.5	5.8	4.9
6.3	11	7.0	6.9	7.5
4.3	16	9.0	8.5	9.3
3.5	20	9.5	10.2	9.5
3.0	22	11.0	11.3	10.6
2.5	28	12.0	11.9	12
2.0	36	13.5	13.8	13.6
1.5	48	16.0	15.8	15.6
1.0	62	17.0	16.7	17.2

**0.01 M (*E*)-azobenzene in isooctane and irradiated by LEDs A**

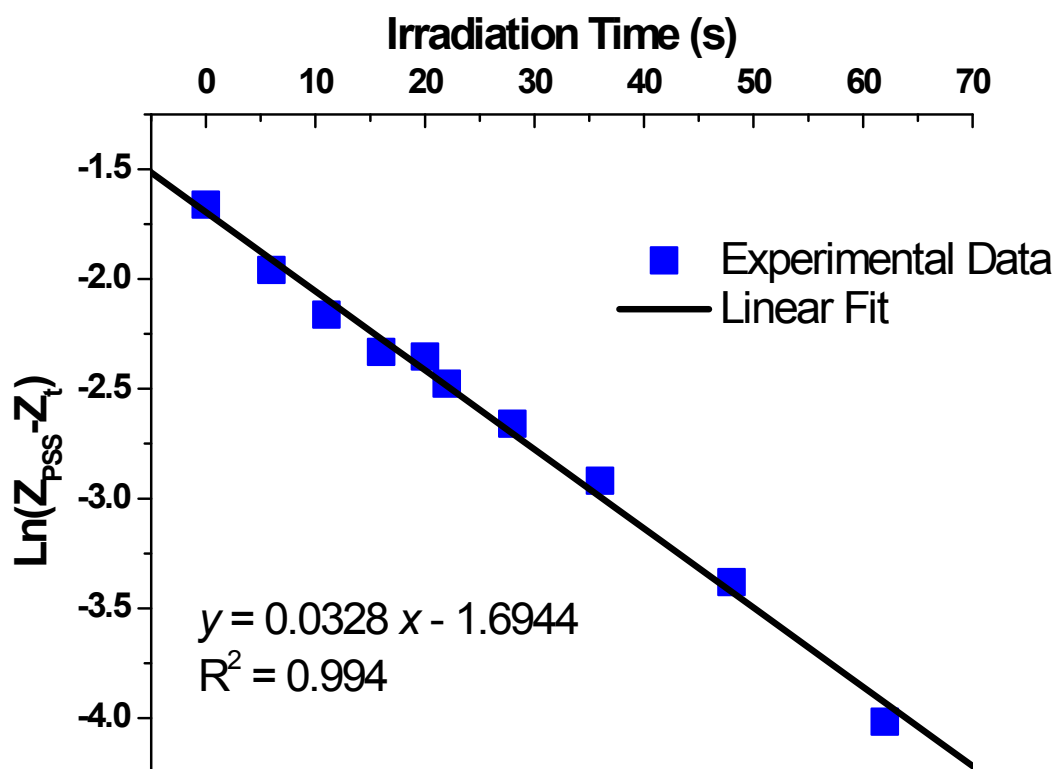
Figure S10 includes graph of  $\ln(Z_{PSS}-Z_t)$  vs. time whose slope was used to ( $I_{photon}$ ) inside the microreactor when using 0.01 M of (*E*)-azobenzene in isooctane (Table 4, entry 2) for 3 independent experiments (Fig. S10a, b, c) with  $Z_{PSS}$  fitted values (expressed as  $Z_{PSS} / (E_{PSS} + Z_{PSS})$  percent:  $Z_{PSS} (exp 1) = 19.2\%$ ;  $Z_{PSS} (exp 2) = 18.8\%$ ;  $Z_{PSS} (exp 3) = 19.5\%$ ). Figure S10d shows the 3 experiments on the same graph.



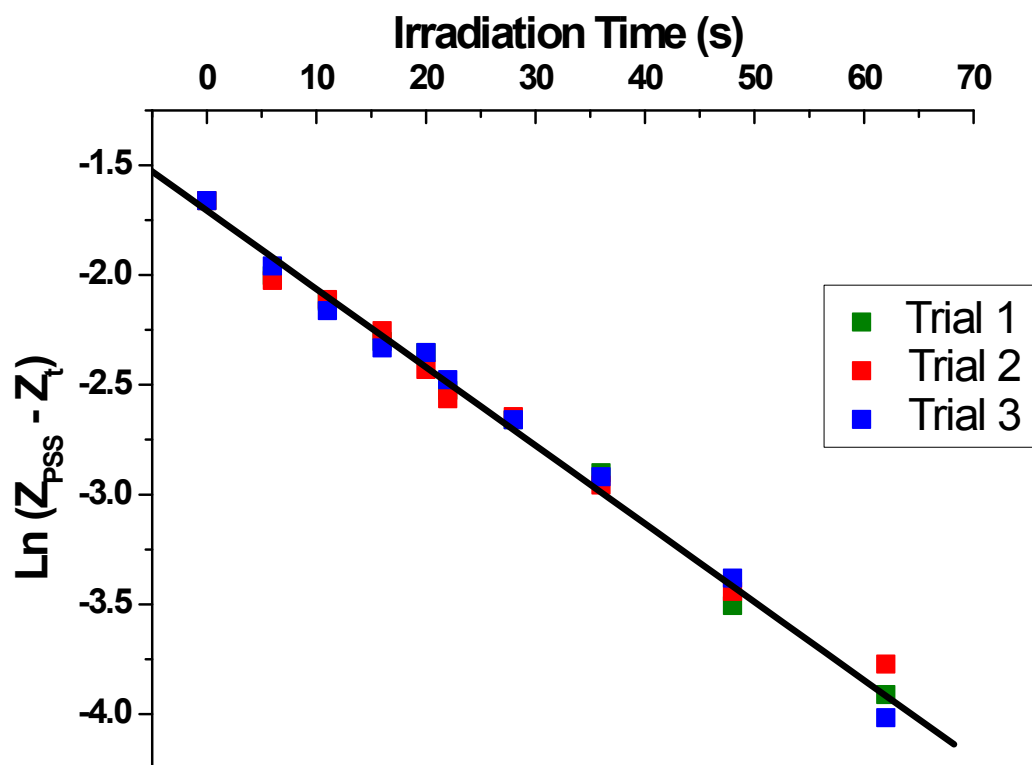
**Figure S10a.** Graph of  $\ln(Z_{PSS} - Z_t)$  vs time (s) following the irradiation of 0.01 M (*E*)-azobenzene in isooctane and irradiated by LEDs A in flow for experiment a.



**Figure S10b.** Graph of  $\ln(Z_{PSS} - Z_t)$  vs time (s) following the irradiation of 0.01 M (*E*)-azobenzene in isooctane and irradiated by LEDs A in flow for experiment b.



**Figure S10c.** Graph of  $\ln(Z_{PSS} - Z_t)$  vs time (s) following the irradiation of 0.01 M (*E*)-azobenzene in isoctane and irradiated by LEDs A in flow for experiment c.



**Figure S10d.** Graph of  $\ln(Z_{PSS} - Z_t)$  vs time (s) following the irradiation of 0.01 M (*E*)-azobenzene in isooctane and irradiated by LEDs A in flow for experiments a,b,c altogether.

0.01 M (*E*)-azobenzene in acetonitrile and irradiated by LEDs A

Figure S11 includes graph of  $\ln(Z_{PSS}-Z_t)$  vs. time whose slope was used to ( $I_{\text{photon}}$ ) inside the microreactor when using 0.01 M of (*E*)-azobenzene in acetonitrile (Table 2, entry 3).

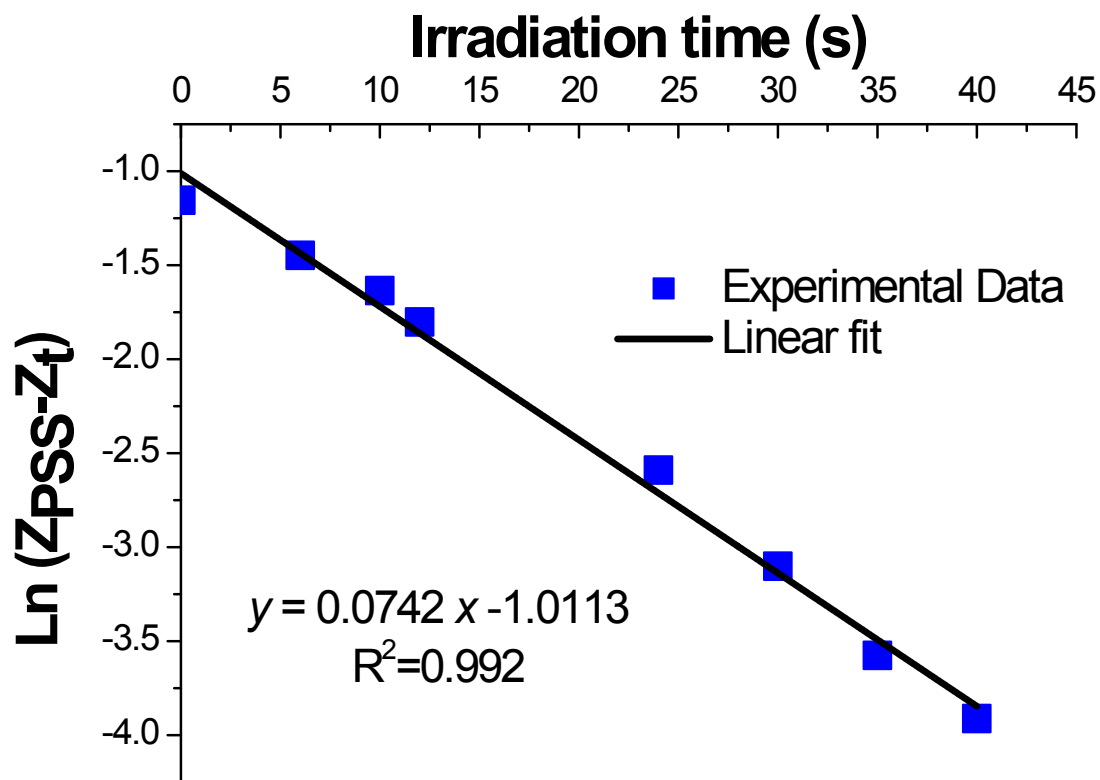
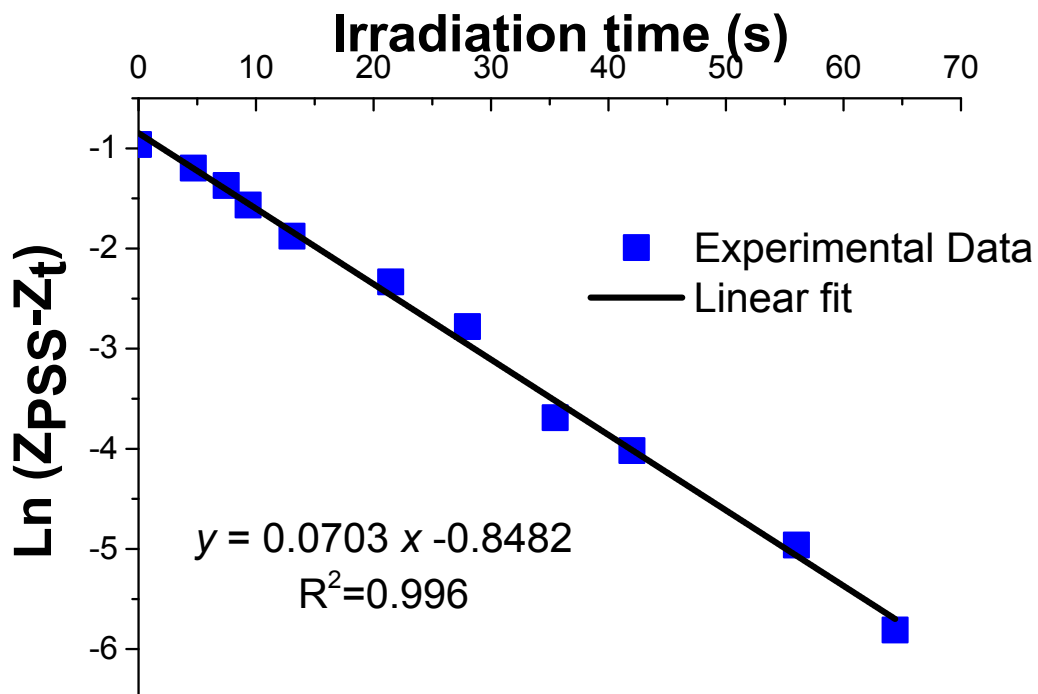


Figure S11. Graph of  $\ln(Z_{PSS} - Z_t)$  vs time (s) following the irradiation of 0.01 M (*E*)-azobenzene in acetonitrile and irradiated by LEDs A in flow.

**0.01 M (*E*)-azobenzene in methanol and irradiated by LEDs A**

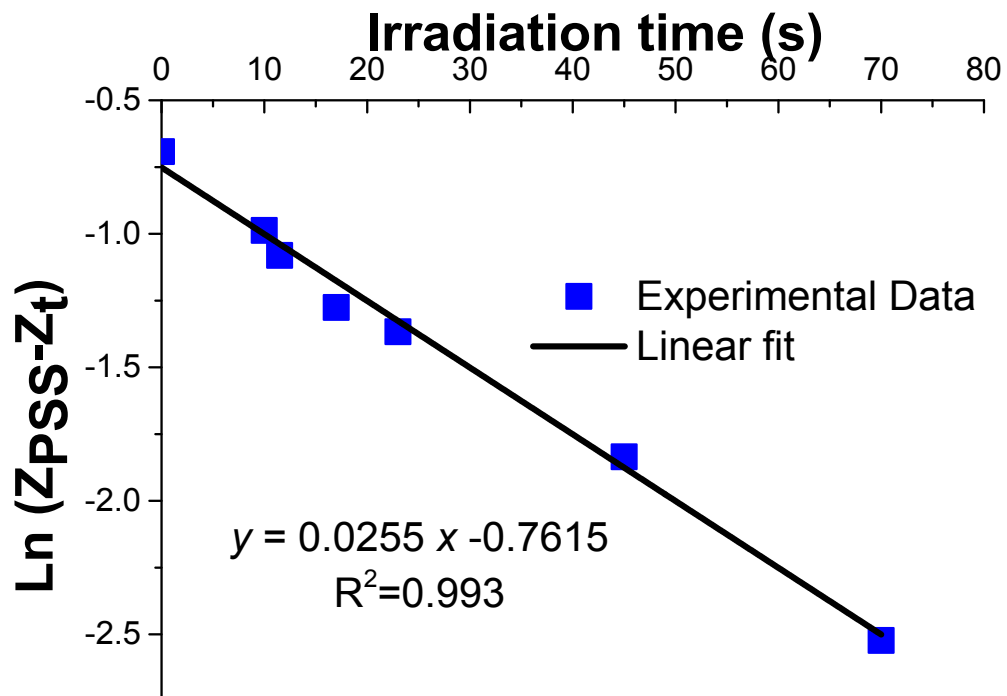
Figure S12 includes graph of  $\ln(Z_{PSS}-Z_t)$  vs. time whose slope was used to ( $I_{photon}$ ) inside the microreactor when using 0.01 M of (*E*)-azobenzene in methanol (Table 2, entry 4).



**Figure S12.** Graph of  $\ln(Z_{PSS} - Z_t)$  vs time (s) following the irradiation of 0.01 M (*E*)-azobenzene in methanol and irradiated by LEDs A in flow

**0.01 M (*E*)-azobenzene in isooctane and irradiated by LEDs B (30% power)**

Figure S13 includes graph of  $\ln(Z_{PSS}-Z_t)$  vs. time whose slope was used to ( $I_{photon}$ ) inside the microreactor when using 0.01 M of (*E*)-azobenzene in isooctane irradiated by LEDs ( $70 \text{ mW}\cdot\text{cm}^{-2}$ ) (Table 2, entry 5).

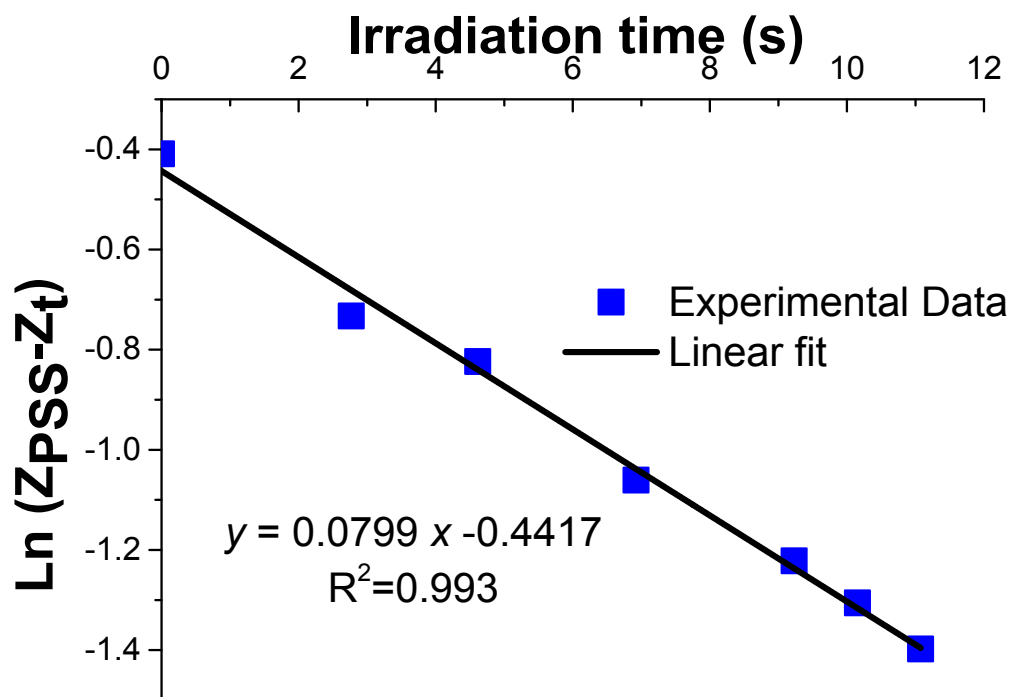


**Figure S13.** Graph of  $\ln(Z_{PSS} - Z_t)$  vs time (s) following the irradiation of 0.01 M (*E*)-azobenzene in isooctane and irradiated by LEDs B (30 % power) in flow.



**0.01 M (*E*)-azobenzene in isooctane and irradiated by LEDs B (100% power)**

Figure S14 includes graph of  $\ln(Z_{PSS} - Z_t)$  vs. time whose slope was used to ( $I_{photon}$ ) inside the microreactor when using 0.01 M of (*E*)-AB in isooctane irradiated by LEDs (70 mW.cm<sup>-2</sup>) (Table 2, entry 5).



**Figure S14.** Graph of  $\ln(Z_{PSS} - Z_t)$  vs time (s) following the irradiation of 0.01 M (*E*)-azobenzene in isooctane and irradiated by LEDs B (100 % power) in flow.

## References:

- (1) Zimmerman, G.; Chow, L.-Y.; Paik, U.-J., *J. Am. Chem. Soc.* **1958**, *80*, 3528-3531.
- (2) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T., *Handbook of Photochemistry*, , 3<sup>rd</sup> Ed. CRC press: Boca Raton, 2006.
- (3) Berns, R. S., Measuring color. In *Billmeyer and Saltzman principles of color technology*, 3<sup>rd</sup> Ed., Wiley, J., Ed. New York, 2000; pp 75-105.
- (4) Kuhn, H.; Braslavsky, S.; Schmidt, R., *Pure Appl. Chem.* **2004**, *76*, 2105-2146.
- (5) <http://invenios.com/products/glass-materials/photo-structurable-glass/>