Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Supporting information for

Construction of a photochemical reactor combining a CCD spectrophotometer and a LED radiation source

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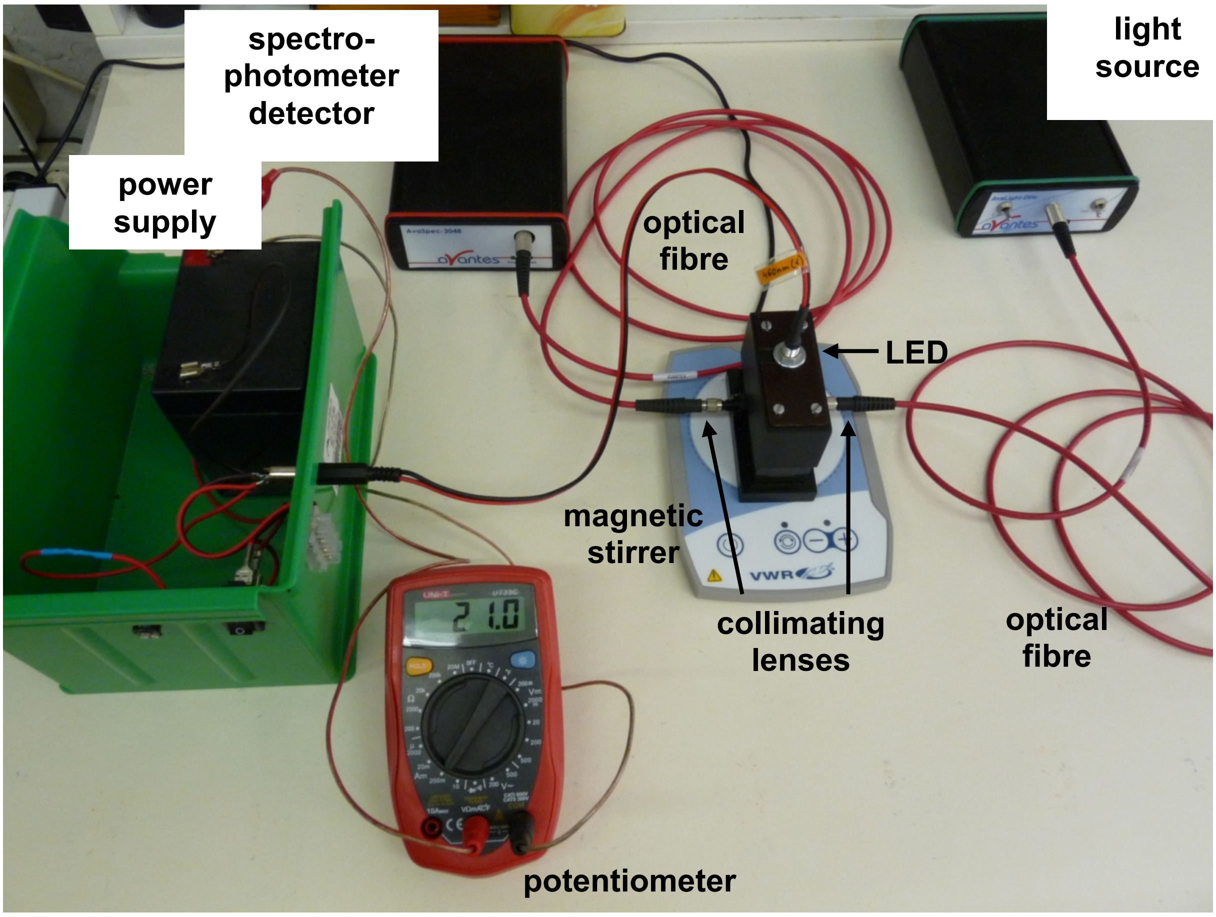


Figure S1 Measurement setup for the analogue photoreactor arrangement

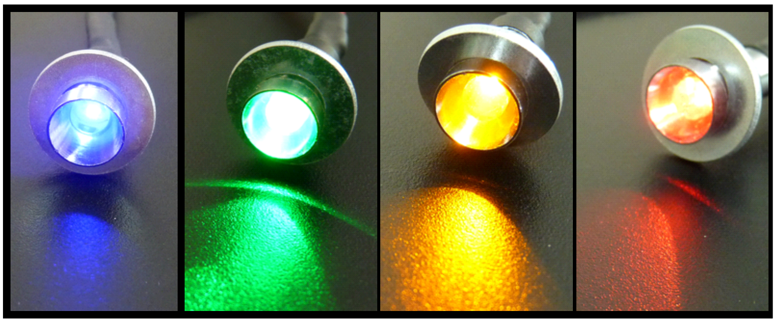


Figure S2 Different color monochromatic LED light sources: LED_{460}, LED_{522}, LED_{595} and LED_{635}

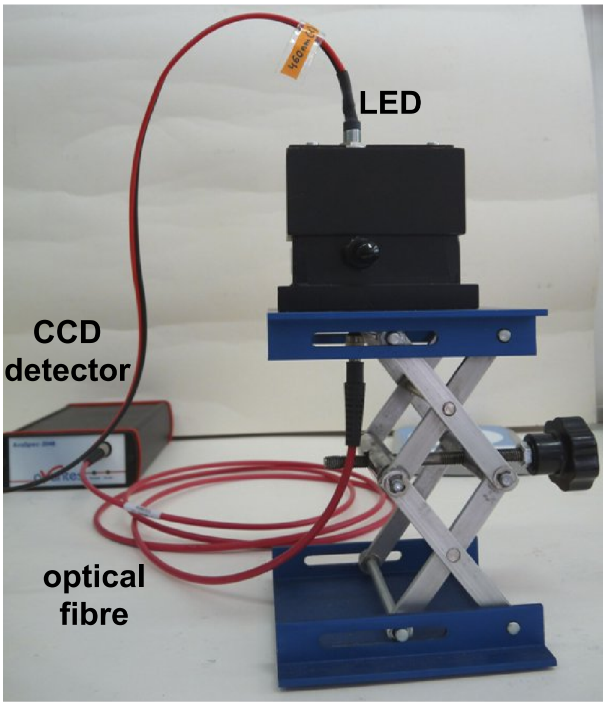


Figure S3 Measurement setup to investigate the spectral properties of the LED light sources

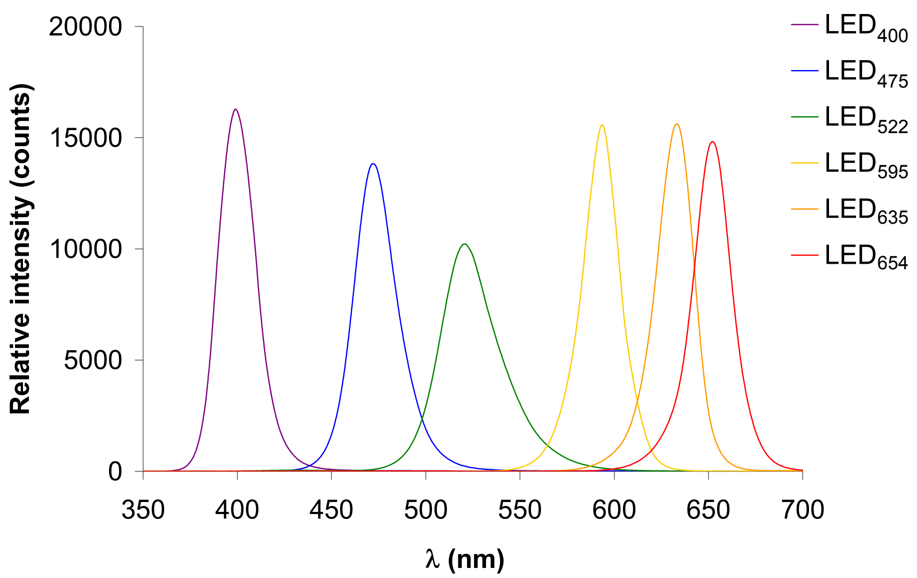


Figure S4 Spectra of monochromatic LED light sources

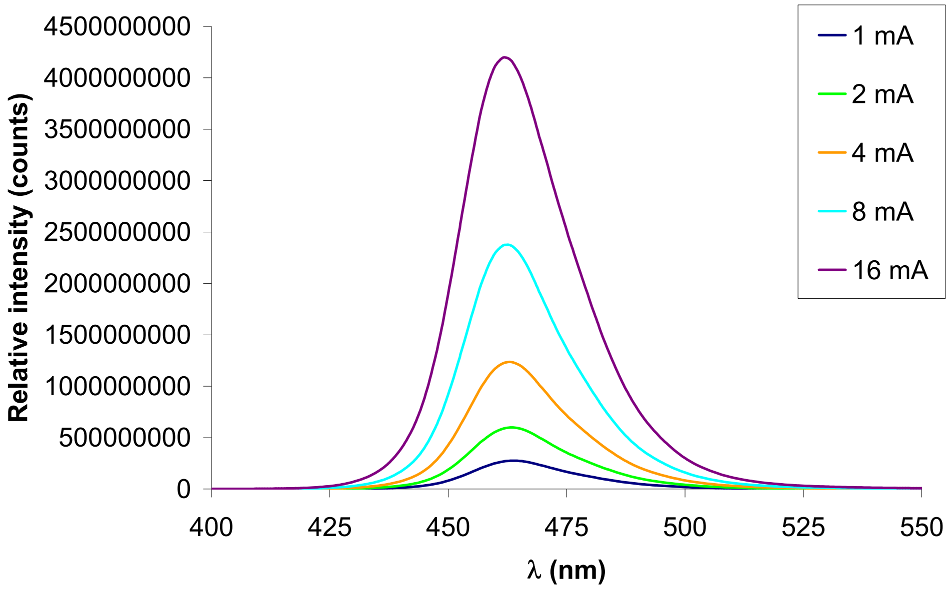


Figure S5 Spectra of LED_{475} at different current strength values

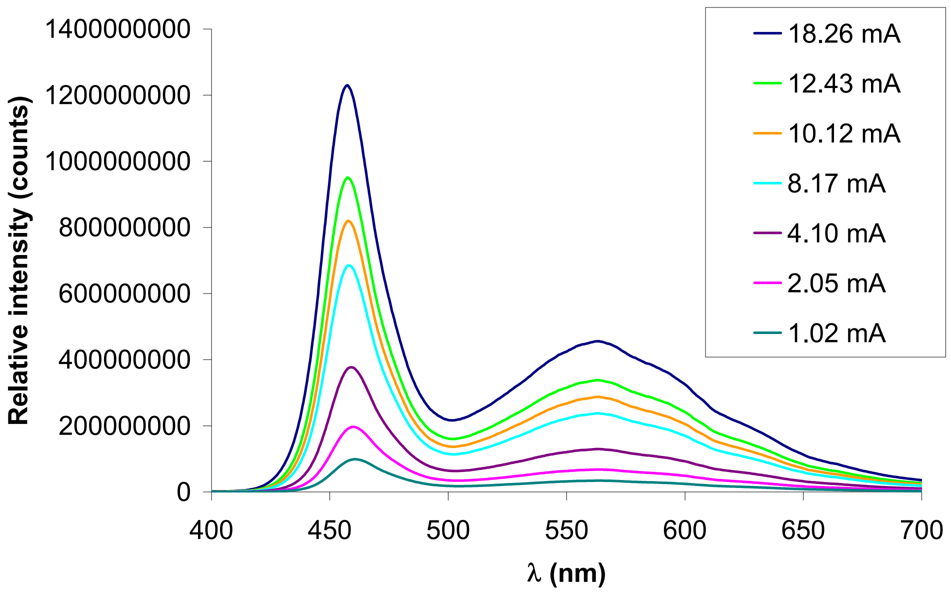


Figure S6 Spectra of white LED at different current strength values

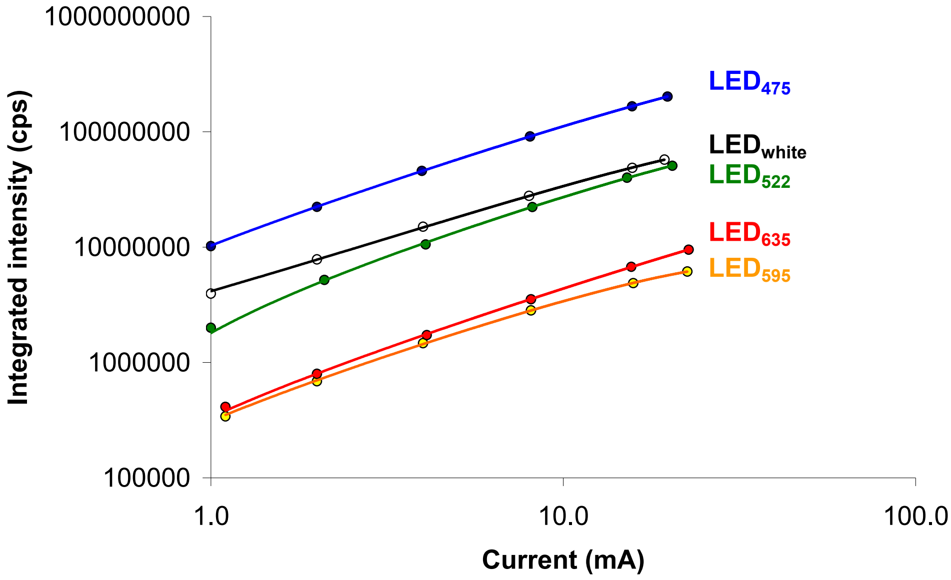
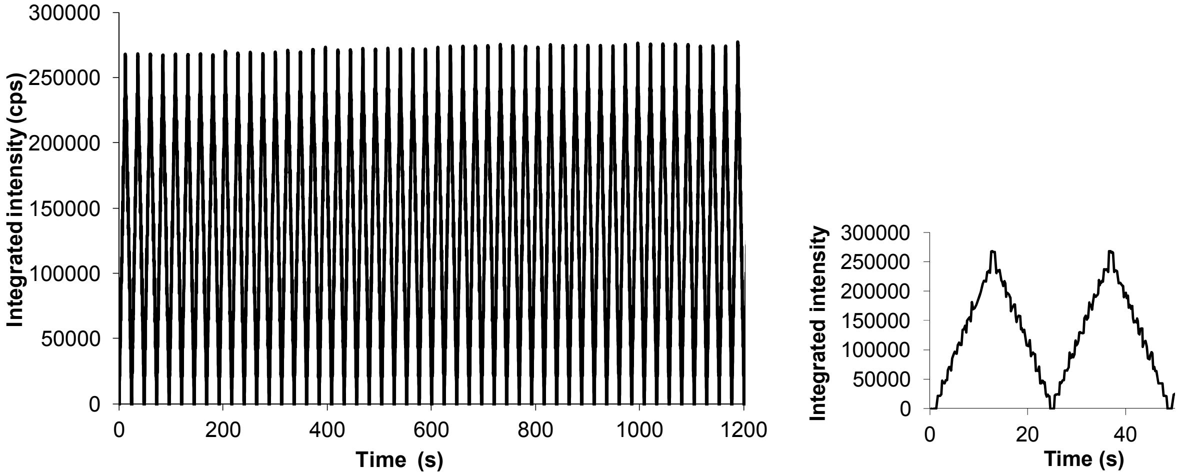


Figure S7 Dependence of integrated intensity on current strength

(a)



(b)

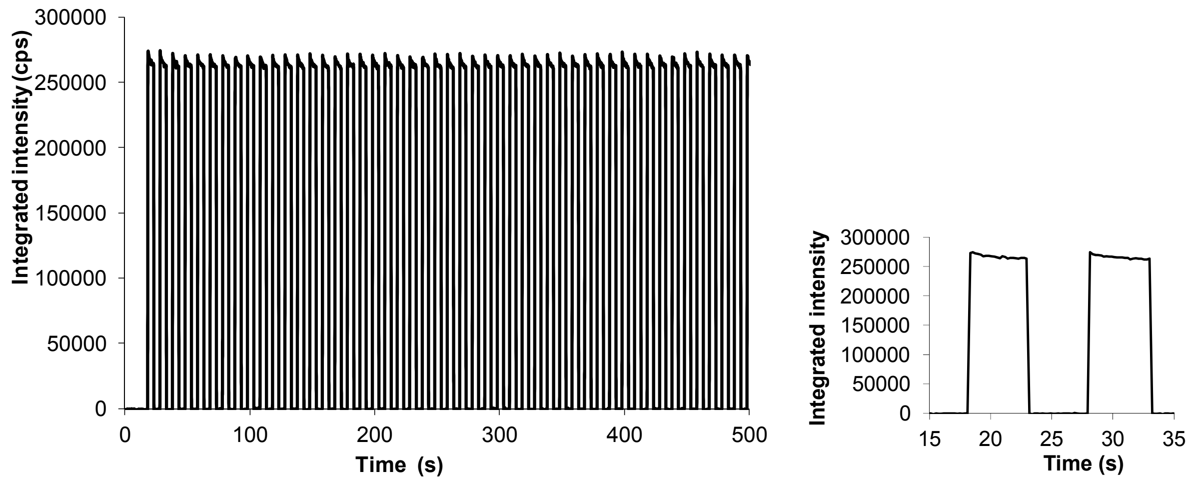


Figure S8 Some of the possible illumination schemes for the photoreactor using LED_{400}: saw-tooth (a) and interrupted illumination (b)

Derivation of equations 1 and 2:

The photon flow of the lamp is $q_{n,\mathrm{p}}$, the detected initial absorbance of the solution at the wavelength of illumination is A_{Φ}^{ini}. The optical path length of illumination is larger bay a factor of β than the optical path length for illumination, therefore the absorbed part of the photon flow is:

$$q_{n,\mathrm{p}}\left(1-10^{-\beta A_{\Phi}^{ini}}\right) \tag{S1}$$

If the quantum yield of the process is Φ, then the initial rate of the photochemical process is (keeping in mind that the rate is given as an intensive quantity in terms of concentrations):

$$v_{ini} = \frac{\Phi q_{n,\mathrm{p}}}{V}\left(1-10^{-\beta A_{\Phi}^{ini}}\right) \tag{S2}$$

The stoichiometry of the studied process does not change over time, so the absorbance change reflects the progress of the reaction in a linear fashion. This means that the initial rate of the reaction can be directly determined from the initial rate of absorbance change at the wavelength of monitoring:

$$v_{ini} = \frac{dA_{\lambda}}{dt}\frac{c_0}{(A_{\lambda}^{fin} - A_{\lambda}^{ini})} \tag{S3}$$

Equation S4 follows from a combination and re-arrangement of equations S2 and S3:

$$\Phi = \frac{dA_{\lambda}}{dt}\frac{c_0 V}{(A_{\lambda}^{fin} - A_{\lambda}^{ini})q_{n,\mathrm{p}}}\left(1-10^{-\beta A_{\Phi}^{ini}}\right)^{-1} \tag{S4}$$

Equation 2 simply follows from the fact that the absorbance changes with the concentration of the absorbing species in a directly proportional manner and that the stoichiometry of the studied process does not change over time.

$$A_{\lambda} = (1-\xi)A_{\lambda}^{ini} + \xi A_{\lambda}^{fin} \tag{2}$$

In effect, this equation states that the reaction coordinate can be calculated from the absorbance values in a linear fashion. The absorbance at the wavelength of illumination can be calculated in a very similar manner:

$$A_{\Phi} = (1-\xi)A_{\Phi}^{ini} + \xi A_{\Phi}^{fin} \tag{S5}$$

The part of the photon flow absorbed by the reactant is at the wavelength of illumination is given as:

$$q_{n,\mathrm{p}}\left(1-10^{-(1-\xi)\beta A_{\Phi}^{ini}-\xi\beta A_{\Phi}^{fin}}\right)\frac{(1-\xi)A_{\Phi}^{ini}}{(1-\xi)A_{\Phi}^{ini}+\xi A_{\Phi}^{fin}} \tag{S6}$$

Therefore, the rate of reactant loss at any time instant is:

$$v = \frac{q_{n,\mathrm{p}}\Phi}{V}\left(1-10^{-(1-\xi)\beta A_{\Phi}^{ini}-\xi\beta A_{\Phi}^{fin}}\right)\frac{(1-\xi)A_{\Phi}^{ini}}{(1-\xi)A_{\Phi}^{ini}+\xi A_{\Phi}^{fin}} \tag{S7}$$

The definition of the reaction coordinate ensures that the rate of reactant loss is connected to the first derivate of the reaction coordinate through the following equation:

$$v = c_0\frac{d\xi}{dt} \tag{S8}$$

A comparison of equations S7 and S8 yields equation 1 in the main text.