Supporting Information

Photo-ionic cells: Two solutions to store solar energy and generate electricity on demand

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1 Validation of the finite element method

The finite element method was validated by reproducing the calculations by W. John Albery for a thin layer photogalvanic concentration cell.[1] In the system the photoexited dye A will react with the electron donor R, as described in Eq. S1.

$$\mathrm{A} + \mathrm{R} \xrightarrow{h\nu} \mathrm{B} + \mathrm{O} \tag{S1}$$

Now the reduced dye can be oxidized by O in the recombination reaction:

$$\mathrm{B} + \mathrm{O} \rightarrow \mathrm{A} + \mathrm{R} \tag{S2}$$

The absorption of light is described by

$$\partial I / \partial x = -\varepsilon c_{\mathrm{A}} I \tag{S3}$$

where I is the light intensity, ε the extinction coefficient of A and c_{A} is the concentration of A. The light at the intensity of I_0 is shining through the light electrode at $x = 0$. In the steady state the transport and kinetics of A is:

$$D_{\mathrm{A}} \frac{\partial^2 c_{\mathrm{A}}}{\partial x^2} - \phi \varepsilon c_{\mathrm{A}} I + k_{rec} c_B c_O = 0 \tag{S4}$$

where ϕ is the quantum efficiency for the generation of B and k_{rec} is the recombination rate constant. Correspondingly for other species

$$D_{\mathrm{R}} \frac{\partial^2 c_{\mathrm{R}}}{\partial x^2} - \phi \varepsilon c_{\mathrm{A}} I + k_{rec} c_B c_O = 0 \tag{S5}$$

$$D_B \frac{\partial^2 c_{\mathrm{B}}}{\partial x^2} + \phi \varepsilon c_{\mathrm{A}} I - k_{rec} c_B c_O = 0 \tag{S6}$$

$$D_{\mathrm{O}} \frac{\partial^2 c_{\mathrm{O}}}{\partial x^2} + \phi \varepsilon c_{\mathrm{A}} I - k_{rec} c_B c_O = 0 \tag{S7}$$

In the simulated case the O/R –couple does not react at the electrode, so insulating boundary condition is used. The electrode processes are the reduction of A to B at the dark electrode at $x = l$ and oxidation of B to A at the illuminated electrode at $x = 0$. The boundary conditions are therefore

$$D_{\mathrm{A}}\left(\frac{\partial c_{\mathrm{A}}}{\partial x}\right)_{x=l} = -D_{\mathrm{B}}\left(\frac{\partial c_{\mathrm{B}}}{\partial x}\right)_{x=l} = -i/FA \tag{S8}$$

$$D_{\mathrm{A}}\left(\frac{\partial c_{\mathrm{A}}}{\partial x}\right)_{x=0} = -D_{\mathrm{B}}\left(\frac{\partial c_{\mathrm{B}}}{\partial x}\right)_{x=0} = i/FA \tag{S9}$$

The initial values were $c_{\mathrm{A}} = c_{\mathrm{A},0}$, $c_{\mathrm{B}} = 0$, $c_{\mathrm{O}} = 0$ and $c_{\mathrm{R}} = c_{\mathrm{R},0}$. The diffusion coefficients for the all the species were set as D.

The analytical model for the dimensionless form was presented,[1] where

$$\chi = x/l \tag{S10}$$

$$u = c_{\mathrm{B}}/c_{\mathrm{A}}^{0} \tag{S11}$$

$$p = I/I_0 \tag{S12}$$

$$\beta = l\varepsilon c_{\mathrm{A}} \tag{S13}$$

$$\gamma = l\sqrt{\phi\varepsilon I_0/D_{\mathrm{A}}} \tag{S14}$$

$$\kappa = l\sqrt{k_{\mathrm{rec}}c_{\mathrm{O}}/D_{\mathrm{B}}} \tag{S15}$$

The three parameters β, γ and κ compare a characteristic length with the cell length l. The parameter β, compares the cell length to the optical length, that is the length over which the dye absorbs the light. When $\beta > 1$, all the light is absorbed very efficiently. The parameter γ compares the cell length to the generation length. In the light intensity of I_0 the dye A can diffuse on average a distance of $\sqrt{D_{\mathrm{A}}/\phi\varepsilon I_0}$ before being converted to B. The last parameter κ compares the cell length to the reaction length, so the distance over which B can diffuse before being converted to A in the recombination reaction.

To validate the model we used, calculations presented in ref. 1 were repeated using the finite element model. The concentration profile of the reduced dye obtained form the analytical solutions in the closed circuit conditions, as well as the light intensity profile for three different parameter values for β, γ and κ are shown in Figure S1, and the corresponding results obtained with the finite element method are shown in Figure S2.

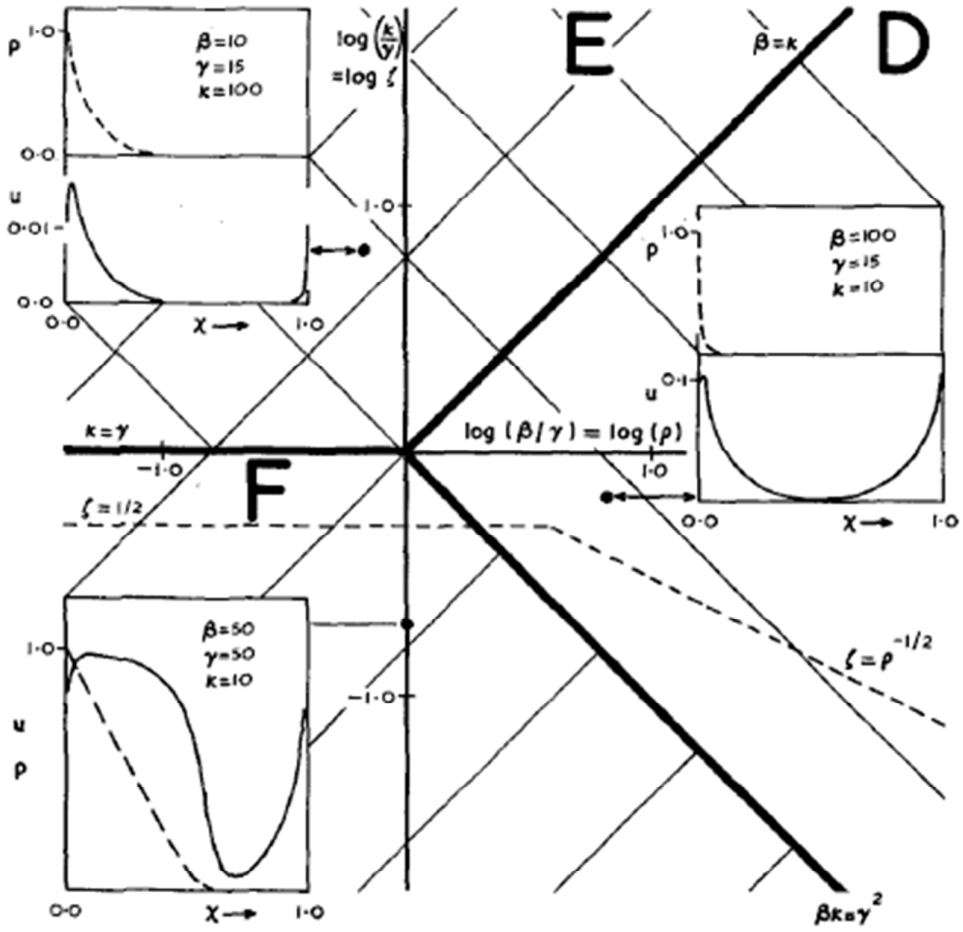


Figure S1. The light intensity profiles and the concentration profiles of the photoproduct B across the cell for three different values of three different parameter values for β, γ and κ.[1] Reprinted with permission from Elsevier.

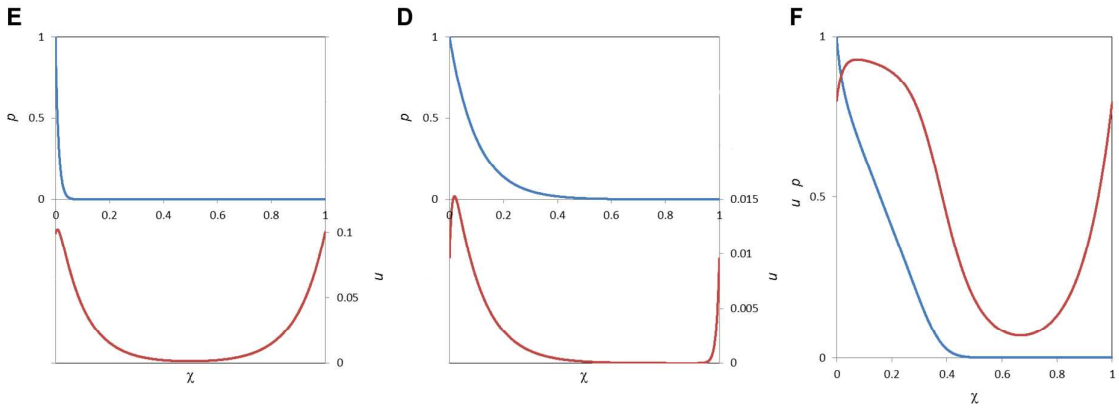


Figure S2. The light intensity profiles of the cases E, D and F calculated with the finite element method.

Comparison of Figures S1 and S2 clearly show that both analytical expressions and finite element method give very similar results. The derivation of the analytical expressions required some assumptions. For finite element method, no assumptions was necessary, and hence the results from the finite element simulations are more accurate, as long as the meshing is refined enough.

2 Model for the light absorption, photoreaction and extraction

The mechanism described in the previous chapter was modified to include the formation of the photoexited state A*, where the average life-time of the photoexited state is τ. Now the reactions are photoexitation of A, followed by reaction with electron donor R producing B and O, or relaxation of the exited state A* back to A.

$$A \xrightarrow{h\nu} A^* \tag{S16}$$

$$A^* + R \xrightarrow{k_{photo}} B + O \tag{S17}$$

As previously, the reduced dye can be oxidized by O in the recombination reaction:

$$B + O \xrightarrow{k_{rec}} A + R \tag{S18}$$

or B can be extracted into the oil phase.

The absorption of light is described as previously (Eq. S3) In the steady state the transport and kinetics of A is:

$$D_{\mathrm{A}}\nabla c_{\mathrm{A}} - \mathbf{u}\cdot\nabla c_{\mathrm{A}} - \varphi\varepsilon c_{\mathrm{A}} I + k_{rec} c_B c_O + \frac{c_{\mathrm{A}*}}{\tau} = 0 \qquad \text{(S19)}$$

where ϕ is the quantum efficiency for the generation of B, k_{rec} is the recombination rate constant and τ is the lifetime of the exited state. $\mathbf{u}$ is the velocity field. Correspondingly for other species

$$D_{\mathrm{A}*}\nabla c_{\mathrm{A}*} - \mathbf{u}\cdot\nabla c_{\mathrm{A}*} + \varphi\varepsilon c_{\mathrm{A}} I - k_{photo} c_{\mathrm{A}*} c_R - \frac{c_{\mathrm{A}*}}{\tau} = 0 \qquad \text{(S20)}$$

$$D_{\mathrm{R}}\nabla c_{\mathrm{R}} - \mathbf{u}\cdot\nabla c_{\mathrm{R}} - k_{photo} c_{\mathrm{A}*} c_R + k_{rec} c_B c_O = 0 \qquad \text{(S21)}$$

$$D_B\nabla c_{\mathrm{B}} - \mathbf{u}\cdot\nabla c_{\mathrm{B}} + k_{photo} c_{\mathrm{A}*} c_R - k_{rec} c_B c_O = 0 \qquad \text{(S22)}$$

$$D_{\mathrm{O}}\nabla c_{\mathrm{O}} - \mathbf{u}\cdot\nabla c_{\mathrm{O}} + k_{photo} c_{\mathrm{A}*} c_R - k_{rec} c_B c_O = 0 \qquad \text{(S23)}$$

The reduced dye B can partition into the oil phase, with the partition coefficient defined as:

$$K = \frac{c_{\mathrm{B}}^{\mathrm{oil}}}{c_{\mathrm{B}}^{\mathrm{aq}}} = \frac{k_f}{k_b} \qquad \text{(S24)}$$

Where k_f and k_b are rate constants for the transfer of B from aqueous phase to DCE phase. This was implemented into the flux boundary condition as described below:

$$D_{\mathrm{B,DCE}}\left(\frac{\partial c_{\mathrm{B,DCE}}}{\partial x}\right)_{x=0} = -D_{\mathrm{B,aq}}\left(\frac{\partial c_{\mathrm{B,aq}}}{\partial x}\right)_{x=0} = k_f c_{\mathrm{B,aq}} - k_b c_{\mathrm{B,DCE}} \qquad \text{(S25)}$$

This set of equations was used to estimate the phase separation in the steady state conditions in 1D. Also, to estimate the photoconversion efficiency of the system

where the two-phase flow in a thin layer is illuminated through the organic phase, 2D simulations with the flow described by the Navier-Stokes equation for the incompressible Newtonian fluids:

$$\rho(\mathbf{u}\cdot\nabla\mathbf{u}) = -\nabla p + \mu\nabla^2\mathbf{u} \tag{S26}$$

Where ρ is the density of the material, p is pressure, and μ is dynamic viscosity of the fluid. The inlet boundary condition for the flow was set as laminar inflow velocity, meaning that for simulation purposes the flow at constant velocity through the inlet 1 m before the cell to allow the fully developed parabolic flow profile at the inlet of the cell. The outlet pressure was set to 0 Pa. The values of water at room temperature were used for both density and viscosity.

For all the species, the boundary conditions at the inflows was constant concentration, and outflow at the outlets (c = 0). The cell walls were set as insulating (no flux through the boundary).

3 Calculation of the Galvani potential difference across the liquid-liquid interface

In a system where ionic species of the two immiscible liquid phases are in equilibrium, the potential difference across the interface can be calculated with the Nernst-Donnan equation[2].

$$\Delta_{\mathrm{o}}^{\mathrm{w}}\phi = \Delta_{\mathrm{o}}^{\mathrm{w}}\phi_{\mathrm{i}}^{0} + \frac{RT}{zF}\ln\frac{c_i^{\mathrm{o}}}{c_i^{\mathrm{w}}} \tag{S27}$$

The mass balance for the species *i* is

$$n_{i,\,\mathrm{total}} = n_i^{\mathrm{o}} + n_i^{\mathrm{w}} \tag{S28}$$

$$V_{\mathrm{o}}c_{i,\,\mathrm{initial}}^{\mathrm{o}} + V_{\mathrm{w}}c_{i,\mathrm{initial}}^{\mathrm{w}} = V_{\mathrm{o}}c_i^{\mathrm{o}} + V_{\mathrm{w}}c_i^{\mathrm{w}} \tag{S29}$$

Additionally, electroneutrality condition of the both phases must be fulfilled:

$$\sum_i z_i c_i^{\mathrm{w}} = \sum_i z_i c_i^{\mathrm{o}} = 0 \qquad \text{(S30)}$$

In a case where $V_o = V_w$ combination of the equations (S27-30) gives

$$\sum_i z_i \frac{c_{i,\,\mathrm{total}}}{1 + \exp\left[\frac{zF}{RT}(\Delta_o^w \phi - \Delta_o^w \phi_i^0)\right]} = 0 \qquad \text{(S31)}$$

Solution of the equation (S31) by iteration gives the Galvani potential difference of the system in equilibrium, and Nernst equation and mass balance equations can be used to calculate the compositions of both phases, as shown in Table 4 of the main text. The values for the standard potentials of ion transfer for different ions were taken from the Gibbs energy database of our group.[3] The value for PF_6^- was estimated from the measured value for dichlorobetzene as –0.070 V, as described in the Supporting Information of ref. 4.

4 Preliminary determination of quantum yield

Preliminary experiments carried out in a 1 cm path length quartz cuvette are presented in Figure S3. The spectra before and after 15 minutes of irradiation are presented in Figure. Estimation of the efficiency with which photons are converted into extracted dye in the organic phase (2 x moles of photons absorbed/moles of HTh extracted into DCE) gives only 0.34 % efficiency. This value is obtained assuming that there is 100% absorption, which is actually not the case as significant amount of light was scattered from the cell. Additionally, since the solution bleaches gradually, more light passes through the cell without being absorbed. In summary, the actual quantum yield is being largely underestimated under these specific experimental conditions. More accurate measurements of the quantum yield are being currently pursued in our lab using a single aqueous droplet and shorter time scales.

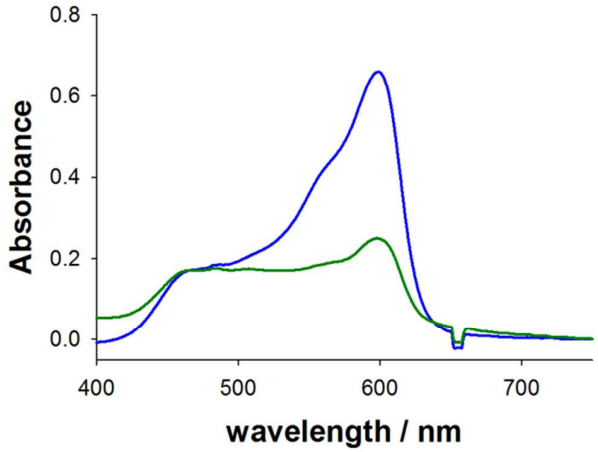


Figure S3. Determining the efficiency of the reaction with respect to the number of photons converted to extracted neutral dye (HTh). The separation efficiency of the photo-product (HTh) was determined after irradiating the biphasic cell initially containing aqueous solubilized Th^{+} and $[Co(II)EDTA]^{2-}$ at 543.5 nm for 15 minutes. The electrochemical cell configuration for the biphasic system before illumination is illustrated in Scheme 1B, main text, (x = 0, y = 0, z = 0.051). UV-visible spectra of five-fold diluted aqueous phase were obtained before (green) and after (violet) irradiation. .

References

(1) Albery, W. J.; Archer, M. D. *J. Electroanal. Chem.* **1978**, *86*, 1.

(2) Peljo, P.; Girault, H. H. Liquid/Liquid Interfaces, Electrochemistry at. In *Encyclopedia of Analytical Chemistry*; John Wiley & Sons, Ltd, 2012.

(3) ElectroChemical database. Gibbs energies of transfer. Available from. Lausanne: Laboratoire d'Electrochimie Physique et Analytique, École Polytechnique Fédérale de Lausanne,; http://sbsrv7.epfl.ch/instituts/isic/lepa/cgi/DB/InterrDB.pl, 2014.

(4) Peljo, P.; Rauhala, T.; Murtomäki, L.; Kallio, T.; Kontturi, K. *Int. J. Hydrogen Energy* **2011**, *36*, 10033.

COMSOL MULTIPHYSICS

Simple Thionine CoEDTA Model

1.1 Definitions

1.1.1 Variables

Variables 1

Selection

Geometric entity level	Entire model

Name	Expression	Description
eps1	6.5e4[L/mol/cm]	extinction coefficient
I0	1.57e-3[mol/m^2/s]	Light intensity
S0	3.5e-5 [mol/L]	Dye concentration
N0	1e-9[mmol/L]	Reduced dye concentration
R0	75[mmol/L]	Concentration of reduced species
O0	1e-9[mmol/L]	Concentration of oxidized species
tau	16e-6 [s]	Lifetime of the exited state of the dye
Abs	-log(I/I0)	Absorbance
K	14.6	Partition of the dye
kf	kb*K	Rate of transfer to oil
kb	1[m/s]	Rate of transfer to water
krec	3e4[L/mol/s]	Recombination rate 3e5 [L/mol/s] should be 9e4
k	1e7[L/mol/s]	Quenching rate original 6.7e9[L/mol/s] should be 6.1e7
Kphoto	k/krec	Photoreaction equilibrium
D_Co	5.35e-6 [cm^2/s]	Diffusion coefficient of Co(II)EDTA in pH 7
D_Th	5.73e-7 [cm^2/s]	Diffusion coefficient of thionine

1.2 Transport of Diluted Species 2 (Aq)

Selection

Geometric entity level	Domain
Selection	Domain 2

Equations

$$\nabla \cdot \left(-D_i \nabla c_i\right) + \mathbf{u} \cdot \nabla c_i = R_i$$

$$\mathbf{N}_i = -D_i \nabla c_i + \mathbf{u} c_i$$

Settings

Description	Value
Concentration	Linear
Compute boundary fluxes	1
Apply smoothing to boundary fluxes	1
Value type when using splitting of complex variables	Real
Equation form	Study controlled
Migration in electric field	0
Convection	1
Convective term	Non - conservative form
Equation residual	Approximate residual
Streamline diffusion	1
Crosswind diffusion	1
Crosswind diffusion type	Do Carmo and Galeão
	0
Isotropic diffusion	0
Enable space-dependent physics interfaces	0
Synchronize with COMSOL Multiphysics	
	{0, 0, 0, 0, 0}
	{1, 1, 1, 1, 1}
Show equation assuming	std1/stat

Used products

COMSOL Multiphysics
Chemical Reaction Engineering Module

1.2.1 Convection and Diffusion 1

Selection

Geometric entity level	Domain
Selection	Domain 2

Equations

$$\underbrace{\nabla \cdot \left(-D_i \nabla c_i\right) + \mathbf{u} \cdot \nabla c_i}_{\mathbf{N}_i = -D_i \nabla c_i + \mathbf{u} c_i} = R_i$$

Settings

Settings

Description	Value
Velocity field	User defined
Velocity field	{0, 0, 0}
Electric potential	User defined
Electric potential	0
Diffusion coefficient	User defined
Diffusion coefficient	{{D_Th, 0, 0}, {0, D_Th, 0}, {0, 0, D_Th}}
Diffusion coefficient	User defined
Diffusion coefficient	{{D_Th, 0, 0}, {0, D_Th, 0}, {0, 0, D_Th}}
Diffusion coefficient	User defined
Diffusion coefficient	{{D_Th, 0, 0}, {0, D_Th, 0}, {0, 0, D_Th}}
Diffusion coefficient	User defined
Diffusion coefficient	{{D_Co, 0, 0}, {0, D_Co, 0}, {0, 0, D_Co}}
Diffusion coefficient	User defined
Diffusion coefficient	{{D_Co, 0, 0}, {0, D_Co, 0}, {0, 0, D_Co}}
Bulk material	None

Used products

COMSOL Multiphysics

1.2.2 No Flux 1

Selection

Geometric entity level	Boundary
Selection	Boundary 3

Equations

$$-\mathbf{n} \cdot \mathbf{N}_i = 0$$

Settings

Settings

Description	Value
Apply for all species	Apply for all species

Used products

COMSOL Multiphysics

1.2.3 Initial Values 1

Selection

Geometric entity level	Domain

Selection	Domain 2

Settings

Settings

Description	Value
Concentration	S0
Concentration	0
Concentration	N0
Concentration	R0
Concentration	O0

Used products

COMSOL Multiphysics

1.2.4 Reactions 1

Selection

Geometric entity level	Domain
Selection	Domain 2

Equations

$$\nabla \cdot \left(-D_i \nabla c_i\right) + \mathbf{u} \cdot \nabla c_i = R_i$$

Settings

Settings

Description	Value
Total rate expression	{krec*Naq*O - I*eps1*S + Sst/tau, I*eps1*S - Sst/tau - k*Sst*R, k*Sst*R - krec*Naq*O, -k*Sst*R + krec*Naq*O, k*Sst*R - krec*Naq*O}

Used products

COMSOL Multiphysics

1.2.5 Flux 1

Selection

Geometric entity level	Boundary
Selection	Boundary 2

Equations

$$-\mathbf{n} \cdot \mathbf{N}_i = N_{0,i}$$

Settings

Settings

Description	Value
Species S	0
Species Sst	0
Species Naq	1
Species R	0
Species O	0
Inward flux	{0, 0, kb*No - kf*Naq, 0, 0}
Flux type	General inward flux
Bulk concentration	0
Mass transfer coefficient	0

Used products

COMSOL Multiphysics

1.3 Transport of Diluted Species (Oil)

Selection

Geometric entity level	Domain
Selection	Domain 1

Equations

$$\nabla \cdot \left(-D_i \nabla c_i\right) = R_i$$

$$\mathbf{N}_i = -D_i \nabla c_i$$

Settings

Description	Value
Concentration	Linear
Compute boundary fluxes	1
Apply smoothing to boundary fluxes	1
Value type when using splitting of complex variables	Real
Equation form	Stationary
Migration in electric field	0
Convection	0
Convective term	Non - conservative form
Equation residual	Approximate residual
Streamline diffusion	1
Crosswind diffusion	1
Crosswind diffusion type	Do Carmo and Galeão
	0

Description	Value
Enable space-dependent physics interfaces	0
Synchronize with COMSOL Multiphysics	
	0
	1
Show equation assuming	std1/stat

Used products

COMSOL Multiphysics

1.3.1 Diffusion

Selection

Geometric entity level	Domain
Selection	Domain 1

Equations

$$\nabla \cdot (-D_i \nabla c_i) = R_i$$

$$\mathbf{N}_i = -D_i \nabla c_i$$

Settings

Settings

Description	Value
Velocity field	User defined
Velocity field	{0, 0, 0}
Electric potential	User defined
Electric potential	0
Diffusion coefficient	User defined
Diffusion coefficient	{{D_Th/.8346, 0, 0}, {0, D_Th/.8346, 0}, {0, 0, D_Th/.8346}}
Bulk material	None

1.3.2 No Flux 1

Selection

Geometric entity level	Boundary
Selection	Boundary 1

Equations

$$-\mathbf{n} \cdot \mathbf{N}_i = 0$$

Settings

Settings

Description	Value
Apply for all species	Apply for all species

1.3.3 Initial Values 1

Selection

Geometric entity level	Domain
Selection	Domain 1

Settings

Settings

Description	Value
Concentration	0

1.3.4 Flux 1

Selection

Geometric entity level	Boundary
Selection	Boundary 2

Equations

$$-\mathbf{n} \cdot \mathbf{N}_i = N_{0,i}$$

Settings

Settings

Description	Value
Species No	1
Inward flux	-kb*No + kf*Naq
Flux type	General inward flux

1.4 General Form PDE (g)

General Form PDE

Selection

Geometric entity level	Domain
Selection	Domain 2

Settings

Description	Value
Shape function type	Lagrange
Element order	Quadratic
Compute boundary fluxes	1
Apply smoothing to boundary fluxes	1

Description	Value
Value type when using splitting of complex variables	Complex
Equation form	Study controlled
Dependent variable quantity	Molar flux (mol/(m^2*s))
Source term quantity	None
Unit	mol/m^3/s
Show equation assuming	0

Used products

COMSOL Multiphysics

1.4.1 General Form PDE 1

General Form PDE 1

Selection

Geometric entity level	Domain
Selection	Domain 2

Equations

$$e_a\frac{\partial^2 I}{\partial t^2}+d_a\frac{\partial I}{\partial t}+\nabla\cdot\Gamma=f$$

$$\nabla=\frac{\partial}{\partial x}$$

Settings

Settings

Description	Value
Source term	-eps1*S*I
Conservative flux	I
Damping or mass coefficient	0
Mass coefficient	0

1.4.2 Zero Flux 1

Selection

Geometric entity level	Boundary
Selection	No boundaries

Equations

$$-\mathbf{n}\cdot\Gamma=0$$

1.4.3 Initial Values 1

Initial Values 1

Selection

Geometric entity level	Domain
Selection	Domain 2

Settings

Settings

Description	Value
Initial value for I	0
Initial time derivative of I	0

1.4.4 Dirichlet Boundary Condition 1

Dirichlet Boundary Condition 1

Selection

Geometric entity level	Boundary
Selection	Boundary 2

Equations

$$I = r$$
$$g_{reaction} = -\mu$$

Settings

Settings

Description	Value
Value on boundary	I0
Prescribed value of I	1
Apply reaction terms on	Individual dependent variables
Use weak constraints	0

1.4.5 Dirichlet Boundary Condition 2

Selection

Geometric entity level	Boundary
Selection	No boundaries

Equations

$$I = r$$
$$g_{reaction} = -\mu$$

Settings

Settings

Description	Value

Description	Value
Value on boundary	0
Prescribed value of I	1
Apply reaction terms on	Individual dependent variables
Use weak constraints	0

1.4.6 Flux/Source 1

Flux/Source 1

Selection

Geometric entity level	Boundary
Selection	Boundary 3

Equations

$$-\mathbf{n} \cdot \Gamma = g - qI$$

Settings

Settings

Description	Value
Boundary flux/source	0
Boundary absorption/impedance term	1

1.5 Mesh 1

Mesh statistics

Property	Value
Minimum element quality	1.0
Average element quality	1.0
Edge elements	10000
Vertex elements	3

Mesh 1

1.5.1 Size (size)

Settings

Name	Value
Maximum element size	2.0E-7
Minimum element size	4.0E-8
Resolution of curvature	0.2
Resolution of narrow regions	1000
Maximum element growth rate	1.5

Name	Value
Predefined size	Extremely fine
Custom element size	Custom

1.5.2 Distribution 1 (dis1)

Selection

Geometric entity level	Domain
Selection	Domain 1

Distribution 1

Settings

Name	Value
Distribution properties	Predefined distribution type
Number of elements	5000
Element ratio	10000
Distribution method	Geometric sequence
Reverse direction	On

1.5.3 Distribution 2 (dis2)

Selection

Geometric entity level	Domain
Selection	Domain 2

Distribution 2

Settings

Name	Value
Distribution properties	Predefined distribution type
Number of elements	5000
Element ratio	10000
Distribution method	Geometric sequence

1.5.4 Edge 2 (edg2)

Selection

Geometric entity level	Remaining

2 Study 2

2.1 Time Dependent

Study settings

Property	Value
Include geometric nonlinearity	Off

Times: .01, .1, 1, 100, 1000, 10000, 100000

Mesh selection

Geometry	Mesh
Geometry 1 (geom1)	mesh1

Physics selection

Physics	Discretization
Transport of Diluted Species 2 (chds2)	physics
Transport of Diluted Species (chds)	physics
General Form PDE (g)	physics

2.2 Solver Configurations

2.2.1 Solver 3

Compile Equations: Time Dependent (st1)

Study and step

Name	Value
Use study	Study 2
Use study step	Time Dependent

Time-Dependent Solver 1 (t1)

General

Name	Value
Defined by study step	Time Dependent
Time	{0.01, 0.1, 1, 100, 1000, 10000, 100000}
Relative tolerance	0.00001

Thionine CoEDTA Model with Extraction 2D

1 2D model with convection (mod2)

1.1 Definitions

1.1.1 Variables

Variables 2a

Selection

Geometric entity level	Entire model

Name	Expression	Description
eps1	7.15e4[L/mol/cm]	extinction coefficient
I0	1e-3[mol/m^2/s]	Light intensity
Th0	30 [mmol/L]	Thionine concentration
STh0	1e-9[mmol/L]	Semithionine dye conc
LTh0	1e-9[mmol/L]	Leucothionine conc
R0	100[mmol/L]	Concentration of reduced species
O0	1e-9 [mmol/L]	Concentration of oxidized species
tau	16e-6[s]	Lifetime of the exited state of the dye
Abs	-log(I/I0)	Absorbance
K	10	Partition of the leucothionine
kf	kb*K	Rate of transfer to oil
kb	10[m/s]	Rate of transfer to water
krec	1e3[L/mol/s]	Recombination rate
k	1e6[L/mol/s]	Quenching rate
Kphoto	k/krec	Photoreaction equilibrium

1.1.2 Coordinate Systems

Boundary System 1

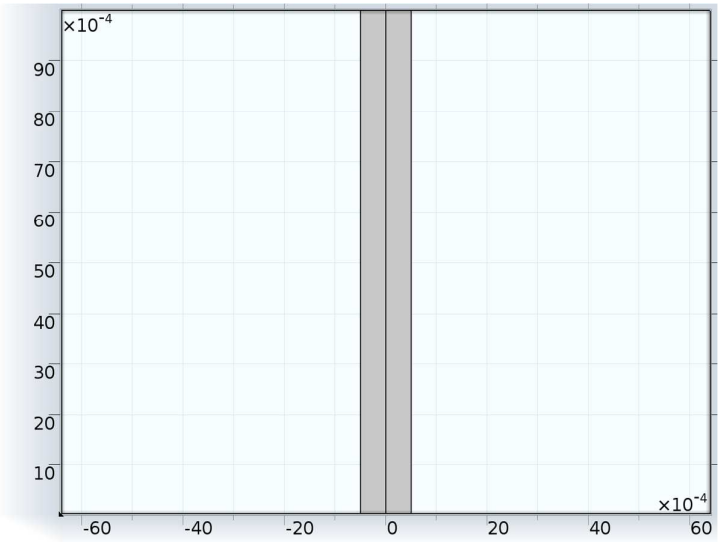
Coordinate system type	Boundary system
Identifier	sys1

Settings

Name	Value

Name	Value
Coordinate names	{t1, n, to}
Create first tangent direction from	Global Cartesian

1.2 Geometry 2



Geometry 2

Units

Length unit	m
Angular unit	deg

Geometry statistics

Property	Value
Space dimension	2
Number of domains	2
Number of boundaries	7

1.2.1 Rectangle 1 (r1)

Position

Name	Value
Position	{0, 0}
Width	0.0005
Height	0.01
Size	{0.0005, 0.01}

1.2.2 Rectangle 2 (r2)

Position

Name	Value

Name	Value
Position	{-.5e-3, 0}
Width	0.0005
Height	0.01
Size	{0.0005, 0.01}

1.3 Transport of Diluted Species Water (water)

Equations

$$\nabla \cdot \left(-D_i \nabla c_i\right) + \mathbf{u} \cdot \nabla c_i = R_i$$

$$\mathbf{N}_i = -D_i \nabla c_i + \mathbf{u} c_i$$

Settings

Description	Value
Concentration	Linear
Compute boundary fluxes	1
Apply smoothing to boundary fluxes	1
Value type when using splitting of complex variables	Real
Equation form	Study controlled
Migration in electric field	0
Convection	1
Convective term	Non - conservative form
Equation residual	Approximate residual
Streamline diffusion	1
Crosswind diffusion	1
Crosswind diffusion type	Do Carmo and Galeão
	0
Isotropic diffusion	0
Enable space-dependent physics interfaces	0
Synchronize with COMSOL Multiphysics	
	{0, 0, 0, 0, 0, 0}
	{1, 1, 1, 1, 1, 1}
Show equation assuming	std2/time

Used products

COMSOL Multiphysics
Chemical Reaction Engineering Module

1.3.1 Convection and Diffusion

Equations

$$\nabla \cdot (-D_i \nabla c_i) + \mathbf{u} \cdot \nabla c_i = R_i$$

$$\mathbf{N}_i = -D_i \nabla c_i + \mathbf{u} c_i$$

Settings

Settings

Description	Value
Velocity field	Velocity field (spf/fp1)
Electric potential	User defined
Electric potential	0
Diffusion coefficient	User defined
Diffusion coefficient	{{1e-9[m^2/s], 0, 0}, {0, 1e-9[m^2/s], 0}, {0, 0, 1e-9[m^2/s]}}
Diffusion coefficient	User defined
Diffusion coefficient	{{1e-9[m^2/s], 0, 0}, {0, 1e-9[m^2/s], 0}, {0, 0, 1e-9[m^2/s]}}
Diffusion coefficient	User defined
Diffusion coefficient	{{1e-9[m^2/s], 0, 0}, {0, 1e-9[m^2/s], 0}, {0, 0, 1e-9[m^2/s]}}
Diffusion coefficient	User defined
Diffusion coefficient	{{1e-9[m^2/s], 0, 0}, {0, 1e-9[m^2/s], 0}, {0, 0, 1e-9[m^2/s]}}
Diffusion coefficient	User defined
Diffusion coefficient	{{1e-9[m^2/s], 0, 0}, {0, 1e-9[m^2/s], 0}, {0, 0, 1e-9[m^2/s]}}
Diffusion coefficient	User defined
Diffusion coefficient	{{1e-9[m^2/s], 0, 0}, {0, 1e-9[m^2/s], 0}, {0, 0, 1e-9[m^2/s]}}
Bulk material	None

Used products

COMSOL Multiphysics

1.3.2 No Flux 1

Equations

$$-\mathbf{n} \cdot \mathbf{N}_i = 0$$

Settings

Settings

Description	Value
Apply for all species	Apply for all species

Used products

COMSOL Multiphysics

1.3.3 Initial Values 1

Settings

Settings

Description	Value
Concentration	Th0
Concentration	0
Concentration	STh0
Concentration	LTh0
Concentration	O0
Concentration	R0

Used products

COMSOL Multiphysics

1.3.4 Reactions 1

Equations

$$\nabla \cdot \left(-D_i \nabla c_i\right) + \mathbf{u} \cdot \nabla c_i = R_i$$

Settings

Settings

Description	Value
Total rate expression	{krec*STh*Ox - I*eps1*Th + Thst/tau, I*eps1*Th - Thst/tau - k*Thst*Red, k*Thst*Red - krec*STh*Ox, 0, k*Thst*Red - krec*STh*Ox, -k*Thst*Red + krec*STh*Ox}

Used products

COMSOL Multiphysics

1.3.5 Flux 1

Equations

$$-\mathbf{n} \cdot \mathbf{N}_i = N_{0,i}$$

Settings

Settings

Description	Value
Species Th	0
Species Thst	0
Species STh	1
Species LTh	0

Description	Value
Species Ox	0
Species Red	0
Inward flux	{0, 0, kb*STh_o - kf*STh, 0, 0, 0}
Flux type	General inward flux

Used products

COMSOL Multiphysics

1.3.6 Inflow 1

Equations

$$c_i = c_{0i}$$

Settings

Settings

Description	Value
Concentration	{Th0, 0, STh0, LTh0, O0, R0}
Apply reaction terms on	All physics (symmetric)
Use weak constraints	0

Used products

COMSOL Multiphysics

1.3.7 Outflow 1

Equations

$$-\mathbf{n} \cdot D_i \nabla c_i = 0$$

Used products

COMSOL Multiphysics

1.4 Transport of Diluted Species Oil (oil)

Equations

$$\nabla \cdot \left(-D_i \nabla c_i\right) + \mathbf{u} \cdot \nabla c_i = R_i$$

$$\mathbf{N}_i = -D_i \nabla c_i + \mathbf{u} c_i$$

Used products

COMSOL Multiphysics
Chemical Reaction Engineering Module

1.4.1 Convection and Diffusion 1

Equations

$$\nabla \cdot \left(-D_i \nabla c_i\right) + \mathbf{u} \cdot \nabla c_i = R_i$$

$$\mathbf{N}_i = -D_i \nabla c_i + \mathbf{u} c_i$$

Settings

Settings

Description	Value
Velocity field	Velocity field (spf/fp1)
Electric potential	User defined
Electric potential	0
Diffusion coefficient	User defined
Diffusion coefficient	{{1e-9[m^2/s], 0, 0}, {0, 1e-9[m^2/s], 0}, {0, 0, 1e-9[m^2/s]}}
Diffusion coefficient	User defined
Diffusion coefficient	{{1e-9[m^2/s], 0, 0}, {0, 1e-9[m^2/s], 0}, {0, 0, 1e-9[m^2/s]}}
Bulk material	None

Used products

COMSOL Multiphysics

1.4.2 No Flux 1

Equations

$$-\mathbf{n} \cdot \mathbf{N}_i = 0$$

Settings

Settings

Description	Value
Apply for all species	Apply for all species

Used products

COMSOL Multiphysics

1.4.3 Initial Values 1

Settings

Settings

Description	Value
Concentration	0
Concentration	0

Used products

COMSOL Multiphysics

1.4.4 Flux 1

Equations

$$-\mathbf{n} \cdot \mathbf{N}_i = N_{0i}$$

Settings

Settings

Description	Value
Species STh_o	1
Species LTh_o	0
Inward flux	{-kb*STh_o + kf*STh, 0}
Flux type	General inward flux

Used products

COMSOL Multiphysics

1.4.5 Inflow 1

Equations

$$c_i = c_{0i}$$

Settings

Settings

Description	Value
Concentration	{0, 0}
Apply reaction terms on	All physics (symmetric)
Use weak constraints	0

Used products

COMSOL Multiphysics

1.4.6 Outflow 1

Equations

$$-\mathbf{n} \cdot D_i \nabla c_i = 0$$

Used products

COMSOL Multiphysics

1.5 General Form PDE 2 (Light)

Settings

Description	Value
Shape function type	Lagrange

Description	Value
Element order	Quadratic
Compute boundary fluxes	1
Apply smoothing to boundary fluxes	1
Value type when using splitting of complex variables	Complex
Equation form	Study controlled
Dependent variable quantity	Molar flux (mol/(m^2*s))
Source term quantity	None
Unit	mol/m^3/s
Show equation assuming	0

Used products

COMSOL Multiphysics

1.5.1 General Form PDE 1

Equations

$$e_a\frac{\partial^2 I}{\partial t^2}+d_a\frac{\partial I}{\partial t}+\nabla\cdot\Gamma=f$$

$$\nabla=[\frac{\partial}{\partial x},\frac{\partial}{\partial y}]$$

Settings

Settings

Description	Value
Source term	-eps1*Th*I
Conservative flux	{I, 0}
Damping or mass coefficient	0
Mass coefficient	0

1.5.2 Zero Flux 1

Equations

$$-\mathbf{n}\cdot\Gamma=0$$

1.5.3 Initial Values 1

Settings

Settings

Description	Value
Initial value for I	0
Initial time derivative of I	0

1.5.4 Dirichlet Boundary Condition 1

Equations

$$I = r$$
$$g_{reaction} = -\mu$$

Settings

Settings

Description	Value
Value on boundary	I0
Prescribed value of I	1
Apply reaction terms on	Individual dependent variables
Use weak constraints	0

1.5.5 Flux/Source 1

Equations

$$-\mathbf{n} \cdot \Gamma = g - qI$$

Settings

Settings

Description	Value
Boundary flux/source	0
Boundary absorption/impedance term	1

1.6 Laminar Flow (spf)

Equations

$$\rho(\mathbf{u} \cdot \nabla)\mathbf{u} =$$
$$\nabla \cdot \left[-p\mathbf{I} + \mu\left(\nabla\mathbf{u} + (\nabla\mathbf{u})^T\right)\right] + \mathbf{F}$$
$$\rho\nabla \cdot \mathbf{u} = 0$$

Used products

COMSOL Multiphysics
Chemical Reaction Engineering Module

1.6.1 Fluid Properties 1

Equations

$$\rho(\mathbf{u} \cdot \nabla)\mathbf{u} =$$
$$\nabla \cdot \left[-p\mathbf{I} + \mu\left(\nabla\mathbf{u} + (\nabla\mathbf{u})^T\right)\right] + \mathbf{F}$$
$$\rho\nabla \cdot \mathbf{u} = 0$$

1.6.2 Wall 1

Equations

$$\mathbf{u} = 0$$

Settings

Settings

Description	Value
Temperature	User defined
Temperature	293.15[K]
Electric field	User defined
Electric field	{0, 0, 0}
Boundary condition	No slip
Apply reaction terms on	Individual dependent variables
Use weak constraints	0

1.6.3 Initial Values 1

Settings

Settings

Description	Value
Velocity field	{0, 0, 0}
Pressure	0

1.6.4 Inlet 1

Equations

$$L_{entr}\nabla_t \cdot \left[-p\mathbf{I} + \mu\left(\nabla_t \mathbf{u} + (\nabla_t \mathbf{u})^T\right)\right] = -p_{entr}\mathbf{n}, \quad \nabla_t \cdot \mathbf{u} = 0$$

Settings

Settings

Description	Value
Use weak constraints	0
Boundary condition	Laminar inflow
Pressure	0.02
Laminar inflow option	Average velocity
Average velocity	.01
Flow rate	0.001 [L/s]
Entrance length	1
Constrain endpoints to zero	0

Description	Value
Entrance thickness	.002
Standard pressure	1[atm]
Standard molar volume	0.0224136[m^3/mol]
Normal mass flow rate	1e-5[kg/s]
Mass flow type	Mass flow rate
Standard flow rate defined by	Standard density
Channel thickness	1.0[m]

1.6.5 Outlet 1

Equations

$$p = p_0, \quad \left[\mu\left(\nabla \mathbf{u} + (\nabla \mathbf{u})^T\right)\right]\mathbf{n} = \mathbf{0}$$

Settings

Settings

Description	Value
Apply reaction terms on	All physics (symmetric)
Use weak constraints	0
Boundary condition	Pressure, no viscous stress
Pressure	0

Used products

COMSOL Multiphysics

1.7 Mesh 2

Mesh statistics

Property	Value
Minimum element quality	0.3344
Average element quality	0.9593
Triangular elements	531358
Quadrilateral elements	1708
Edge elements	11882
Vertex elements	6

1.7.1 Size (size)

Settings

Name	Value
Calibrate for	Fluid dynamics

Name	Value
Maximum element size	4.5E-5
Minimum element size	2.0E-6
Resolution of curvature	0.3
Maximum element growth rate	1.15

1.7.2 Size 1 (size1)

Selection

Geometric entity level	Boundary
Selection	Boundaries 1, 7

Settings

Name	Value
Calibrate for	Fluid dynamics
Maximum element size	2.8E-5
Minimum element size	4.0E-7
Resolution of curvature	0.25
Predefined size	Finer

1.7.3 Size 2 (size2)

Selection

Geometric entity level	Boundary
Selection	Boundaries 2–3, 5–6

Settings

Name	Value
Calibrate for	Fluid dynamics
Maximum element size	2E-6
Minimum element size	.5E-8
Resolution of curvature	0.2
Resolution of narrow regions	1.1
Predefined size	Extremely fine
Custom element size	Custom

1.7.4 Size 3 (size3)

Selection

Geometric entity level	Boundary
Selection	Boundary 4

Settings

Name	Value
Calibrate for	Fluid dynamics
Maximum element size	1E-6
Minimum element size	.50E-8
Resolution of curvature	0.2
Resolution of narrow regions	1.05
Predefined size	Extremely fine
Custom element size	Custom

1.7.5 Corner Refinement 1 (cr1)

Selection

Geometric entity level	Domain
Selection	Domains 1–2

1.7.6 Free Triangular 1 (ftri1)

Selection

Geometric entity level	Domain
Selection	Domains 1–2

1.7.7 Boundary Layers 1 (bl1)

Selection

Geometric entity level	Domain
Selection	Domains 1–2

Settings

Name	Value
Handling of sharp corners	Trimming

Boundary Layer Properties 1 (blp1)

Selection

Geometric entity level	Boundary
Selection	Boundaries 1, 7

Settings

Name	Value
Number of boundary layers	2

1.7.8 Free Triangular 2 (ftri2)

Selection

Geometric entity level	Remaining

2 Navier Stokes ss

2.1 Stationary

Study settings

Property	Value
Include geometric nonlinearity	Off

Mesh selection

Geometry	Mesh
Geometry 1 (geom1)	mesh1
Geometry 2 (geom2)	mesh2

Physics selection

Physics	Discretization
Laminar Flow (spf)	physics

2.2 Solver Configurations

2.2.1 Solver 5

Compile Equations: Stationary (st1)

Study and step

Name	Value
Use study	Navier Stokes ss
Use study step	Stationary

Dependent Variables 1 (v1)

General

Name	Value
Defined by study step	Stationary

Initial values of variables solved for

Name	Value
Solution	Zero

Values of variables not solved for

Name	Value
Solution	Zero

3 Dye Partitioning 2D ss

3.1 Stationary

Study settings

Property	Value
Include geometric nonlinearity	Off

Mesh selection

Geometry	Mesh
Geometry 1 (geom1)	mesh1
Geometry 2 (geom2)	mesh2

Physics selection

Physics	Discretization
Transport of Diluted Species Water (phys1)	physics
Transport of Diluted Species Oil (phys2)	physics
General Form PDE 2 (g2)	physics

3.2 Solver Configurations

3.2.1 Solver 7

Compile Equations: Stationary (st1)

Study and step

Name	Value
Use study	Dye Partitioning 2D ss
Use study step	Stationary

Stationary Solver 1 (s1)

General

Name	Value
Defined by study step	Stationary
Relative tolerance	0.000010