Supporting Information

Dynamic mapping of electrochemiluminescence reactivity in space: application to bead-based assays

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1. Supplementary figures

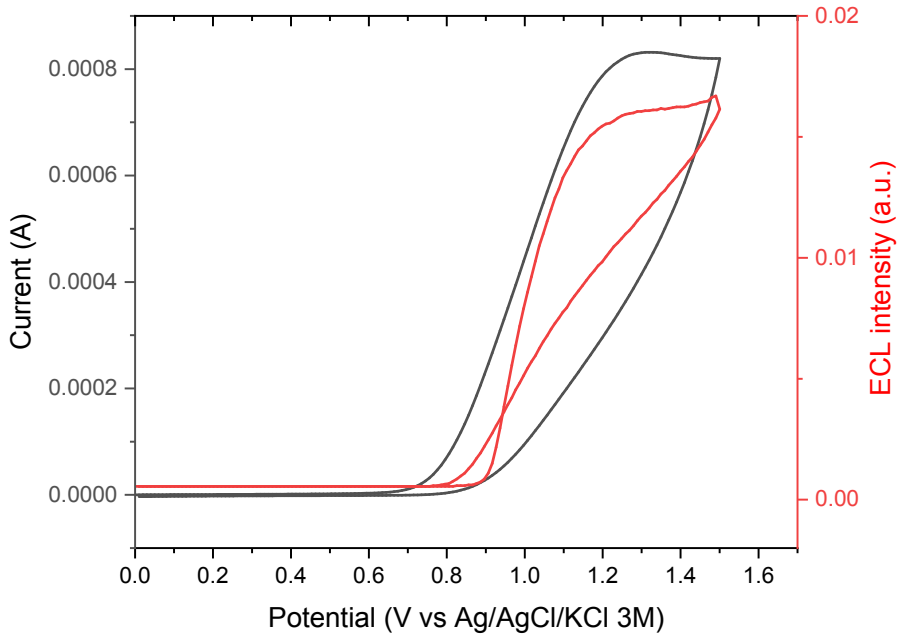


Figure S1. Variations of the current (black curve) and of the ECL signal (red curve) recorded during a cyclic voltammogram experiments performed with a GC electrode on which 12-µm labelled beads were deposited. The solution was PBS containing 100 mM TPA (pH 7.4).

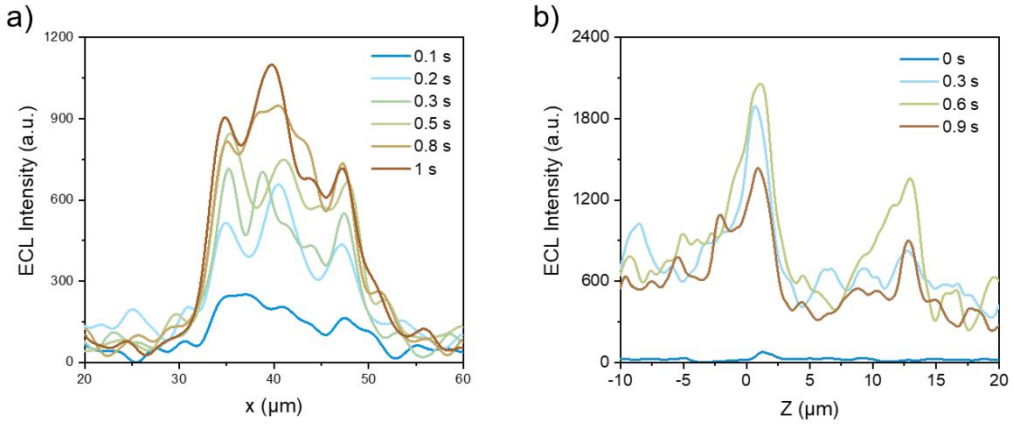


Figure S2. Dynamic ECL profiles extracted from a 12-μm bead in top (a) and side-view (b) configurations within the first second of the anodic treatment. ECL was generated by imposing a constant potential of 1.4 V with a GC electrode in a PBS solution containing 100 mM TPA (pH 7.4).

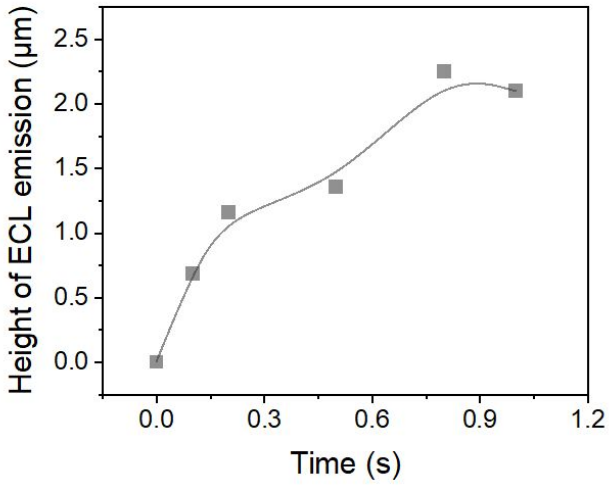


Figure S3. Variations of the height of ECL emission layer with time extracted from dynamic ECL imaging from a 12-μm bead in top-view configuration.

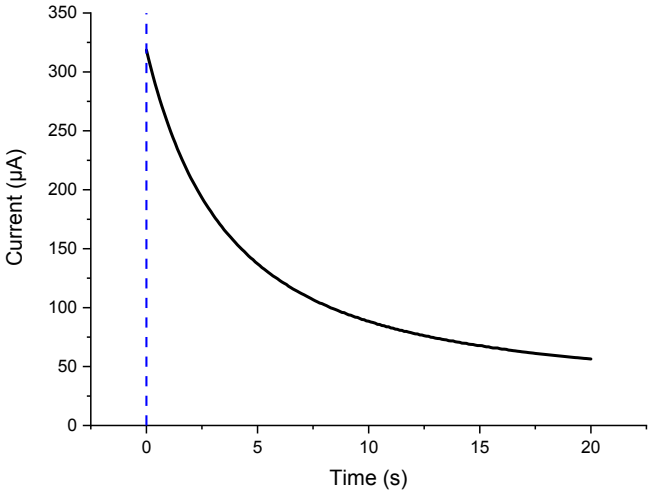


Figure S4. Evolution of the current upon the imposition of a constant potential of 1.4 V at t = 0 s (dashed blue line) to a GC electrode in a PBS solution containing 100 mM TPA (pH 7.4).

2. Finite element simulation details and parameters

The reactions simulated with finite element here were fully described in the main text see scheme 1. For the simulation software COMSOL Multiphysics 5.5 was used (package "Transport of Diluted Species" and "Surface Reactions"). The heterogeneous electron-transfer reactions were simulated in the boundary (flux electrode section) since those occur at the electrode surface. The reaction with the $Ru(bpy)_3^{2+}$ attached to the beads were simulated in the surface reaction section. Otherwise chemical reactions are considered in the subdomain settings. Dependent variables are TPA (named A in the simulation), TPA° (named E in the simulation), $TPA^{\circ+}$ (named I in the simulation), HTPA (named C in the simulation), other products (named X in the simulation), H+ (named H in the simulation) for the transport diluted species section and $[Ru(bpy)_3]^{2+}$

(named G in the simulation), $[Ru(bpy)_3]^+$ (named G1 in the simulation), $[Ru(bpy)_3]^{2+*}$ (named F in the simulation), and photons (named L in the simulation).

Simulation details are described below.

1.1 Global Definition

Table S1. Global definition: Simulation parameters

Name	Expression	Value	Description
alpha	0.5	0.5	electron transfer coefficient
F	96485	96485	Faraday constant [C mol-1]
R	8.314	8.314	Gas constant [J mol-1 K-1]
T	298.15	298.15	temperature [K]
fa	38.92	38.92	F/RT [V-1]
E0	0.9	0.9	forward TPA oxidation
D	5e-6[cm^2/s]	5E−10 m^2/s	Diffusion coefficient for TPA
DH	5e-5[cm^2/s]	5E−9 m^2/s	Diffusion coefficient for H
k0	0.01[cm/s]	1E−4 m/s	heterogeneous ET const [ms-1]
Na	6.022e23	6.022E23	avogadro number[mol-1]
n	1	1	n° of electrons exchanged
Ea	1.2	1.2	anodic switching potential [V]
k3_	3.5e3[1/s]	3500 1/s	forward constant for deprotonation of RCtpa
k3	1e6[1/(s*M)]	1000 $m^3/(s·mol)$	backward constant for deprotonation of RCtpa
k1	1e7[1/(s*M)]	10000 $m^3/(s·mol)$	pka of Ctpa
k1_	8e-3[1/s]	0.008 1/s	pkb of TPA
H0	1e-7[M]	1E−4 mol/m^3	ph 7
E0d	-1	−1	
k5	1e6[1/M/s]	1000 $m^3/(s·mol)$	
k_5	1e-3	0.001	
kem	1e8[1/s]	1E8 1/s	constant for emission
DRu	5e-10[cm^2/s]	5E−14 m^2/s	

Name	Expression	Value	Description
C0	0	0	
Dmin	1e-50	1E−50	
dC	0.000001	1E−6	
dt	0.1	0.1	
A0t	0.180[M]	180 mol/m^3	Initial concentration of TPA
Ru0	1	1	Initial concentration of Ru
K	k1/k1_	1.25E6 m^3/mol	
CC0	A0t/(1 + 1/(K*H0))	178.57 mol/m^3	
A0	A0t - CC0	1.4286 mol/m^3	
Rb	6[um]	6E−6 m	bead radius

Table S2. Global definition Variables

Name	Expression	Unit	Description
kI	k0*exp(-alpha*fa*(Ea - E0))	m/s	forward constant for TPA oxidation
kA	k0*exp((1 - alpha)*fa*(Ea - E0))	m/s	backward constant for TPA oxidation
kX	k0*exp(-alpha*fa*(Ea - E0d))	m/s	forward constant for TPA radical oxidation
kE	k0*exp((1 - alpha)*fa*(Ea - E0d))	m/s	backward constant for TPA radical oxidation

1.2 Model

Table S3. Model, Definitions Variables

Name	Expression	Unit	Description
t1	0.1		""
t2	0.2		""
dt	0.01		""
f1	flc2hs(t - t1, dt)		""
f2	flc2hs(t - t2, dt)		""
r_k1	(-k1*A*H0 + k1_*C)	mol/(m^3·s)	reaction
r_k3	(k3_*I - k3*E*H0)	mol/(m^3·s)	reaction
fs_E	k5*s_G*E	mol/(m^2·s)	flux on beads
fs_I	k5*s_G1*I	mol/(m^2·s)	flux on beads

Name	Expression	Unit	Description
r_G	(-fs_E+kem2*s_L)	mol/(m^2·s)	reaction on beads
r_G1	(-fs_I + fs_E)	mol/(m^2·s)	reaction on beads
r_L	(-kem2*s_L + fs_I)	mol/(m^2·s)	reaction on beads
r_F	(+kem2*s_L)	mol/(m^2·s)	reaction on beads
kem2	kem*1	1/s	
fe_A	(-kA*A + kI*I)	mol/(m^2·s)	flux on electrode
fe_E	(-kE*E*(E>=0))	mol/(m^2·s)	flux on electrode
fe_I	(-kI*I + kA*A)	mol/(m^2·s)	flux on electrode
fe_X	(kE*E*(E>=0))	mol/(m^2·s)	flux on electrode
r_kd	k1*I*E*(E>=0)	mol/(m^3·s)	

1.3 Geometry

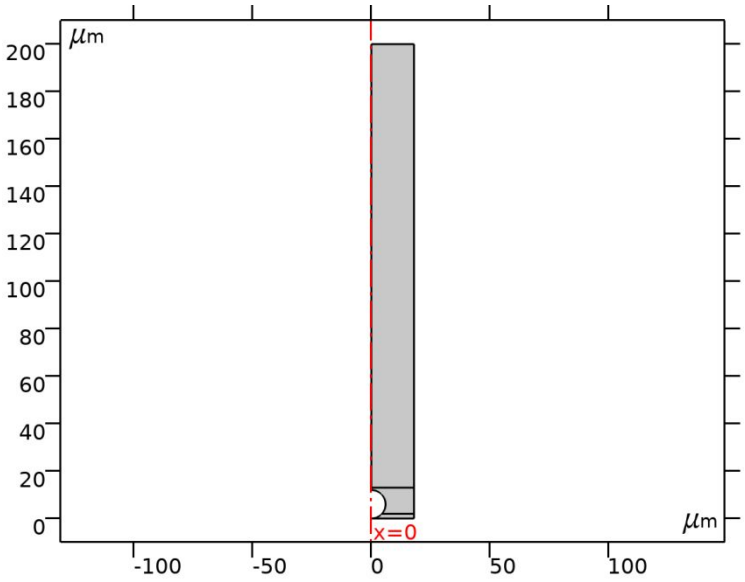


Figure S5. Model geometry. The model geometry used for the simulation is reported in the figure.

1.4 Transport of diluted species

Under transport diluted species: Diffusion, Axial Symmetry, No flux, Initial values, Reaction, Bulk, Flux electrode, Flux beads

Table S4. Diffusion domain 1-3

Description	Value
Diffusion coefficient A	{{D, 0, 0}, {0, D, 0}, {0, 0, D}}
Diffusion coefficient E	{{D, 0, 0}, {0, D, 0}, {0, 0, D}}
Diffusion coefficient I	{{D, 0, 0}, {0, D, 0}, {0, 0, D}}
Diffusion coefficient C	{{D, 0, 0}, {0, D, 0}, {0, 0, D}}
Diffusion coefficient X	{{D, 0, 0}, {0, D, 0}, {0, 0, D}}
Diffusion coefficient H	{{DH, 0, 0}, {0, DH, 0}, {0, 0, DH}}

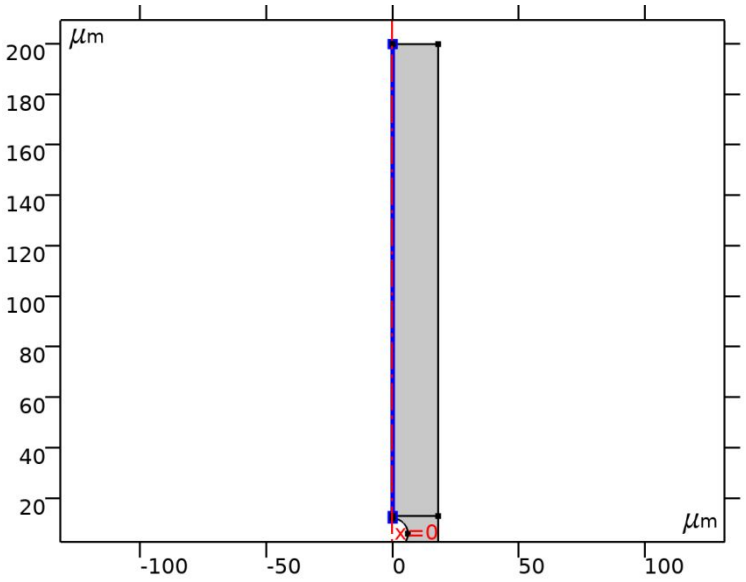


Figure S6. Model Domains: Axial symmetry. Blue line represent the axial symmetry in the model domains

No flux

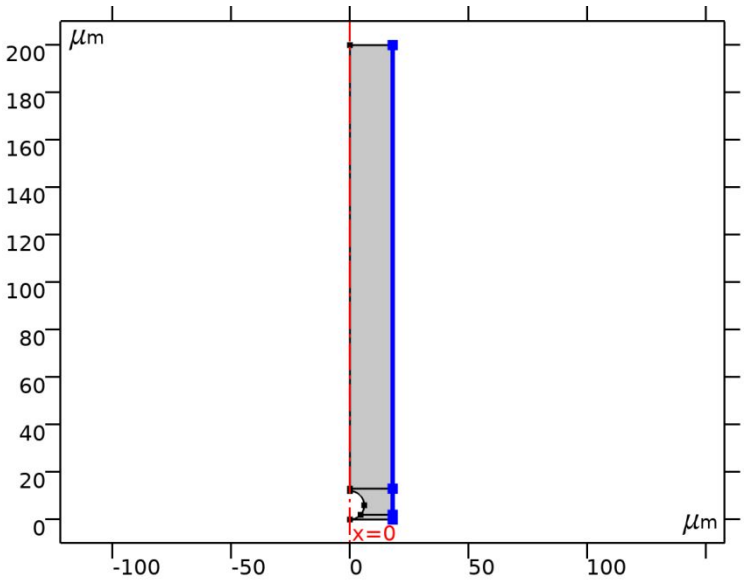
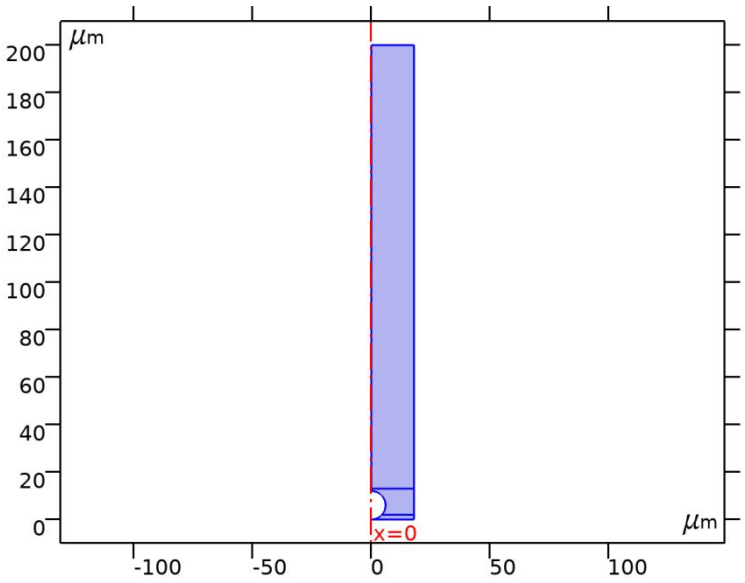


Figure S7. Model Domains: No flux. Blue line is the no flux domain in the model

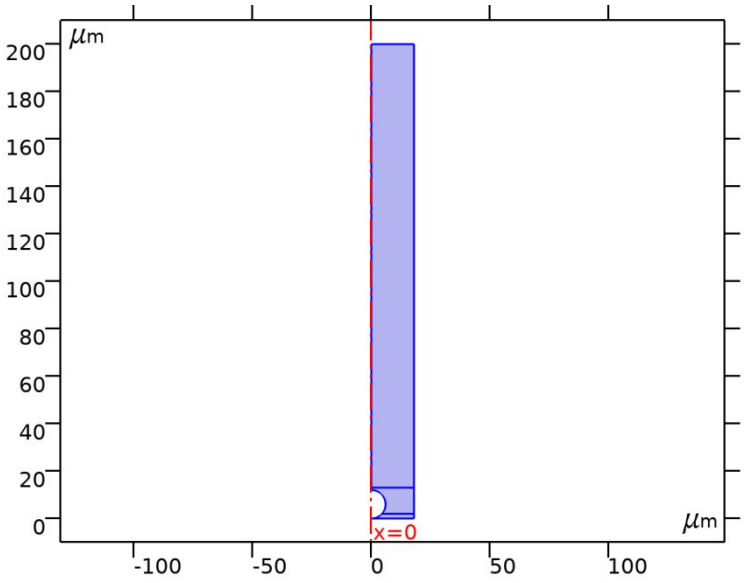
Initial values



Description	Value
Concentration	{A0, C0, C0, CC0, C0, H0}

Figure S8. Model Domains: Initial values. Blue area is the model domains where initial values are defined.

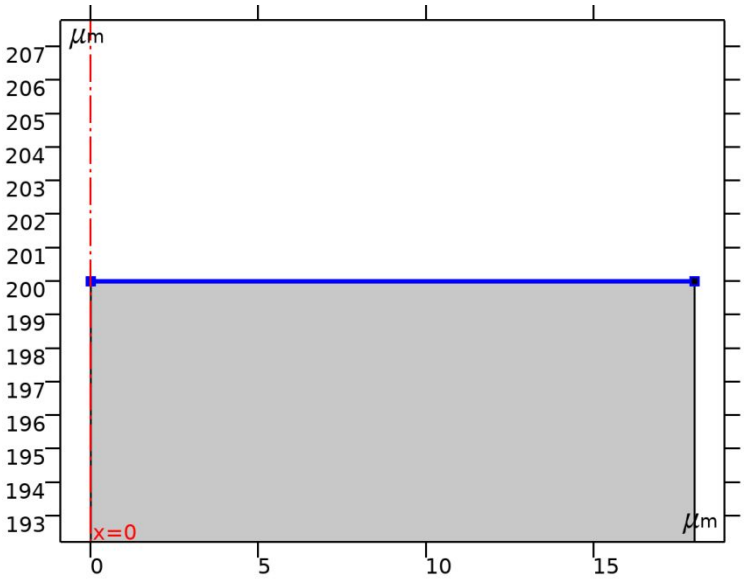
Reaction



Description	Value
Total rate expression A	r_k1 + r_kd
Total rate expression E	r_k3 - r_kd
Total rate expression I	-r_k3 - r_kd
Total rate expression C	-r_k1
Total rate expression X	r_kd
Total rate expression H	(r_k1 + r_k3)*0

Figure S9. Model Domains: reactions. Blue area is the model domains where the chemical reactions are defined.

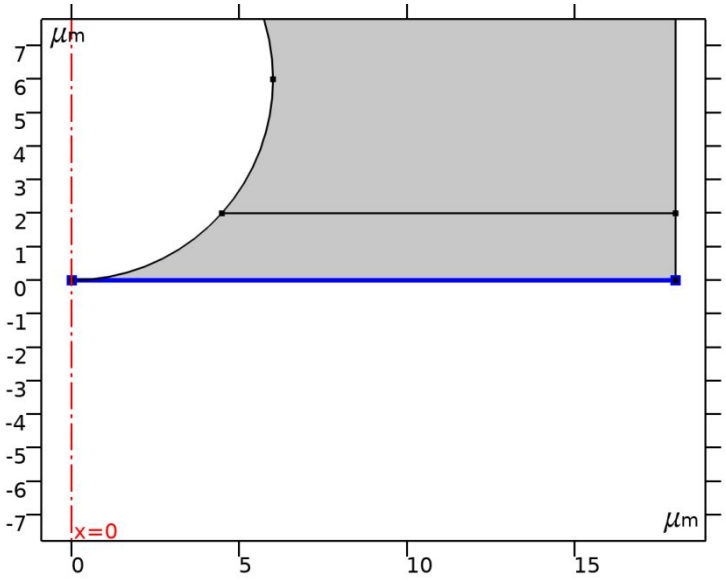
Bulk



Description	Value
Species A	A0t - C
Species E	C0
Species I	C0
Species C	(A0t)/(1 + 1/(K*H0))
Species X	C0
Species H	H0
Concentration	{A0t - C, C0, C0, (A0t)/(1 + 1/(K*H0)), C0, H0}

Figure S10. Model Domains: Bulk. Blue line is the bulk of the solution in the model domains

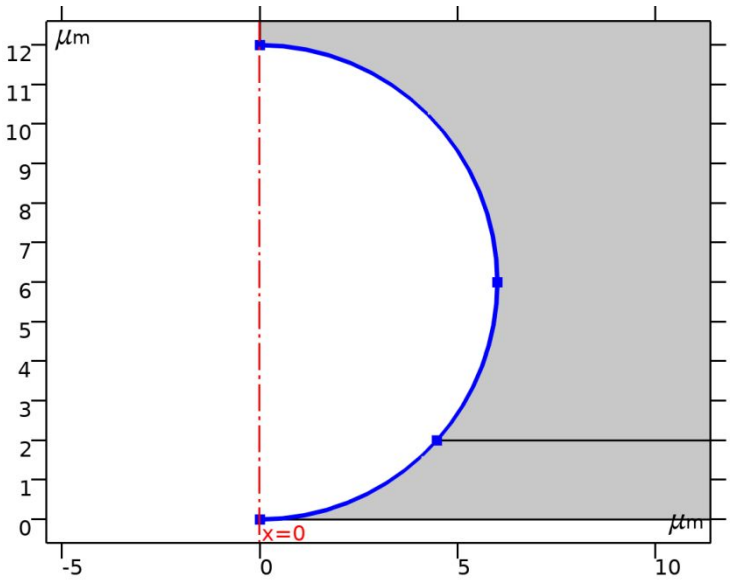
Flux electrode



Description	Value
Flux type	General inward flux
Species A	fe_A
Species E	fe_E
Species I	fe_I
Species C	0
Species X	fe_X
Species H	0
	{fe_A, fe_E, fe_I, 0, fe_X, 0}

Figure S11. Model Domains: flux electrode. Blue line is the electrode surface where electrochemical reactions occurs in the model

Flux beads

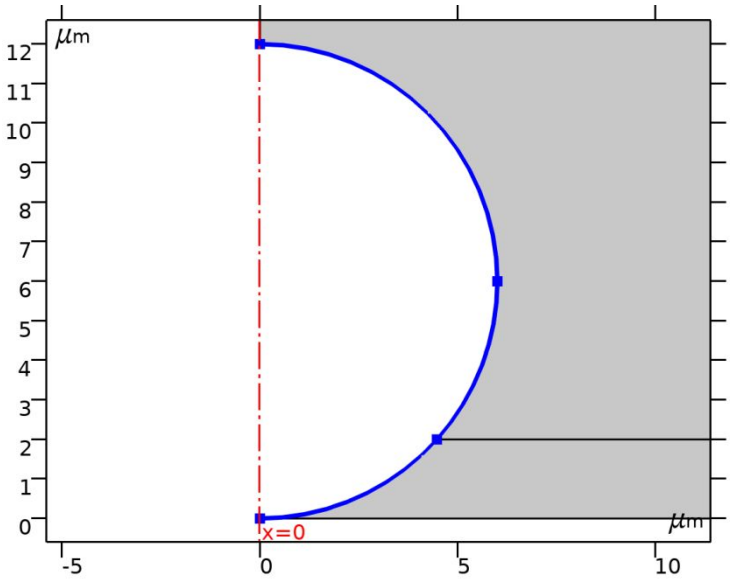


Description	Value
Flux type	General inward flux
Species A	fs_I
Species E	-fs_E
Species I	-fs_I
Species C	0
Species X	fs_E
Species H	0
	{fs_I, -fs_E, -fs_I, 0, fs_E, 0}

Figure S12. Model Domains: flux beads. Blue line is the beads surface

1.5 Surfaces reactions

Under surface reaction: Surface proprieties, Axial Symmetry, No flux, Initial values, Reaction



Description	Value
Density of sites	2e-5[mol/m^2]
Site occupancy number	{1, 1, 1, 1}

Description	Value
Surface material	None
Diffusion coefficient G	{{Dmin, 0, 0}, {0, Dmin, 0}, {0, 0, Dmin}}
Diffusion coefficient G1	{{Dmin, 0, 0}, {0, Dmin, 0}, {0, 0, Dmin}}
Diffusion coefficient F	{{Dmin, 0, 0}, {0, Dmin, 0}, {0, 0, Dmin}}
Diffusion coefficient L	{{Dmin, 0, 0}, {0, Dmin, 0}, {0, 0, Dmin}}

Figure S13. Surfaces reactions. Blue line is the beads surface where the luminophore is bound

Axial Symmetry

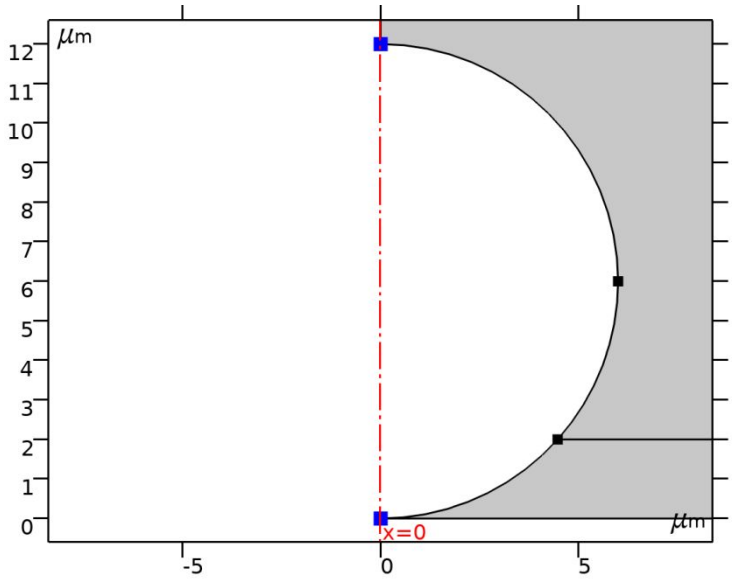


Figure S14. Surfaces reactions: axial symmetry. Blue points are axial symmetry

No flux

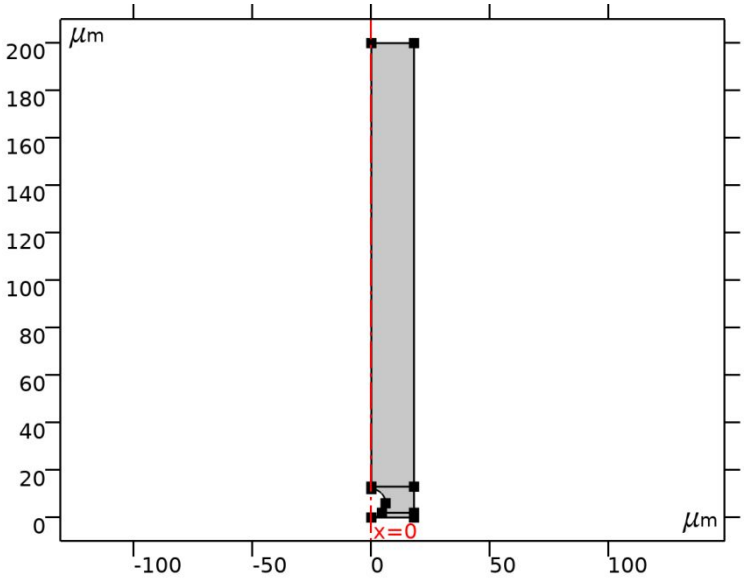
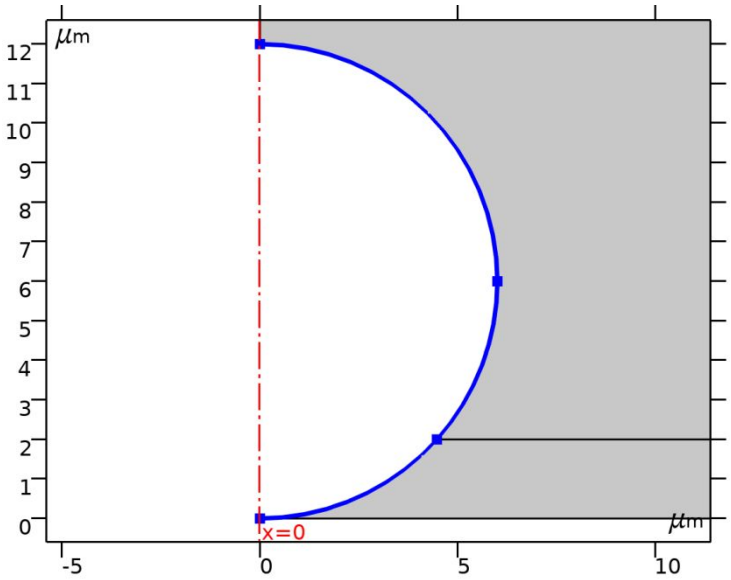


Figure S15. Surfaces reactions: Noflux

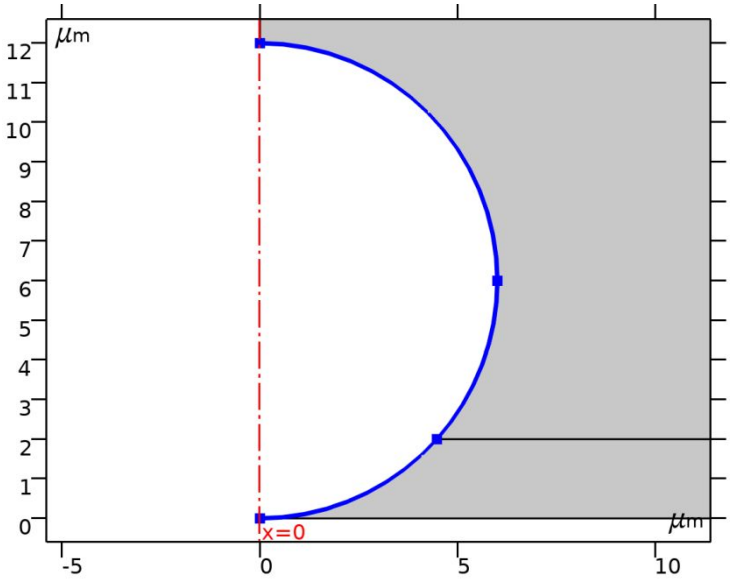
Initial values



Description	Value
Surface concentration	{1e-3, 0, 0, 0}

Figure S16. Surfaces reactions: Initial value

Reaction



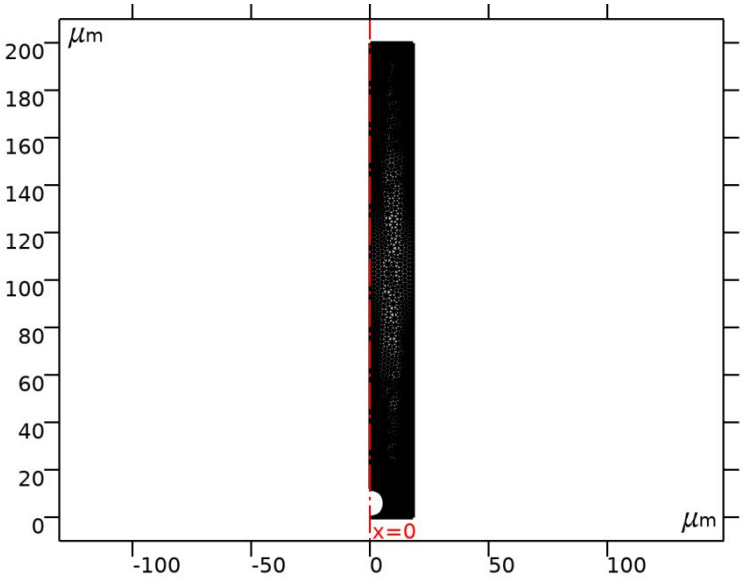
Description	Value
Reaction rate for surface species G	r_G
Reaction rate for surface species G1	r_G1
Reaction rate for surface species F	r_F
Reaction rate for surface species L	r_L

Figure S17. Surfaces reactions: Reactions. Blue line is the beads surface where the

luminophore reactions occurs

1.6 Mesh

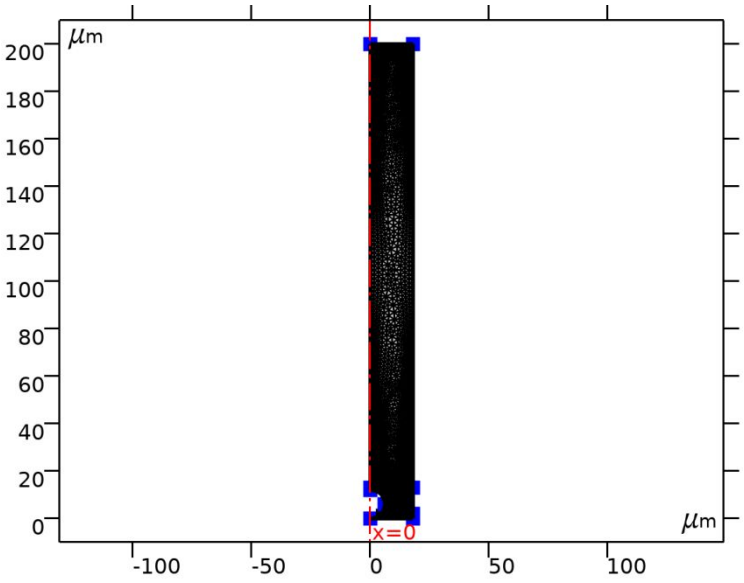
Size:



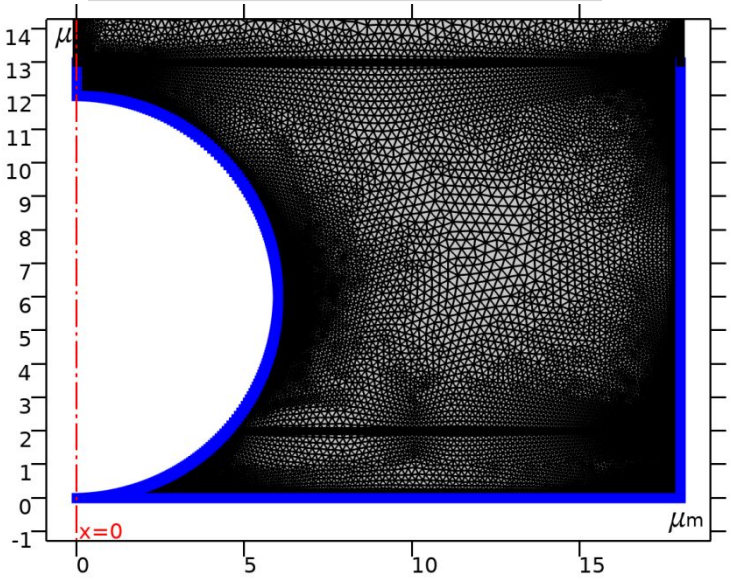
Description	Value
Maximum element size	15
Minimum element size	0.03
Curvature factor	0.3
Maximum element growth rate	1.2
Custom element size	Custom

Figure S18. Model mesh: mesh size

Free triangular:

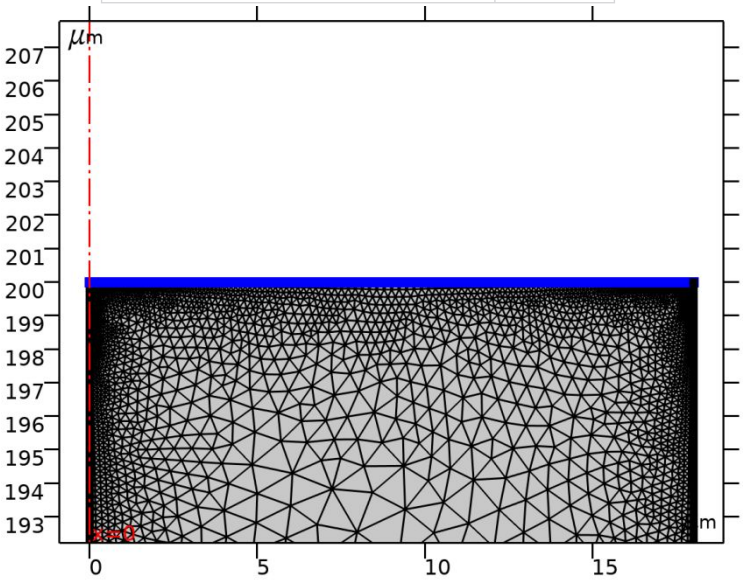


Description	Value
Maximum element size	0.05
Minimum element size	0.0012
Minimum element size	Off
Curvature factor	0.3
Curvature factor	Off
Resolution of narrow regions	Off
Maximum element growth rate	1.02
Custom element size	Custom



Description	Value
Maximum element size	0.268

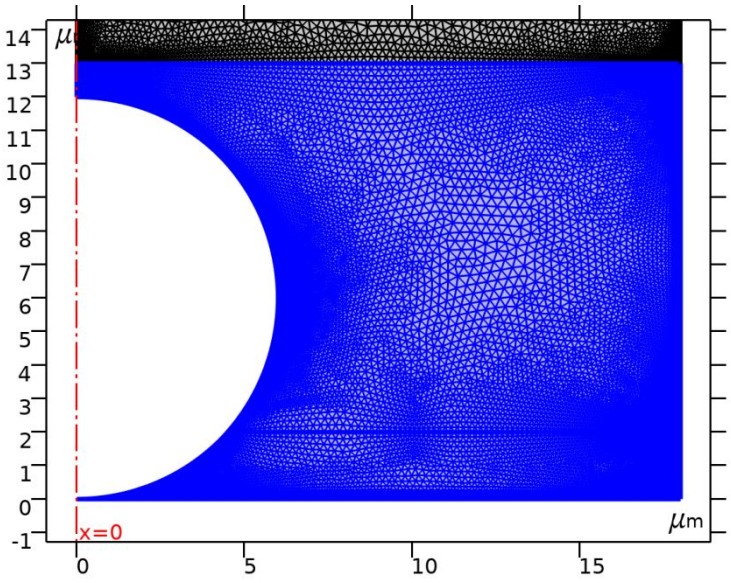
Description	Value
Maximum element size	Off
Minimum element size	0.01
Curvature factor	0.3
Curvature factor	Off
Resolution of narrow regions	Off
Maximum element growth rate	1.05
Custom element size	Custom

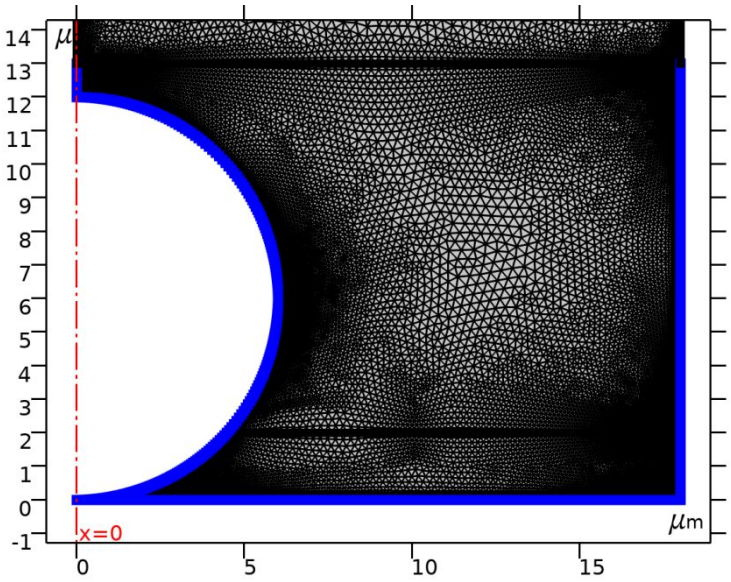


Description	Value
Maximum element size	6.7
Maximum element size	Off
Minimum element size	0.03
Minimum element size	Off
Curvature factor	0.3
Curvature factor	Off
Resolution of narrow regions	Off
Maximum element growth rate	1.05
Custom element size	Custom

Figure S19. Model mesh: Free triangular

Boundary layers:





Description	Value
Number of boundary layers	10
Boundary layer stretching factor	1.02
Thickness of first layer	Manual
Thickness	0.02

Figure S20. Model mesh: Boundary layers

1.7 Study

Time-dependent solution has been optimized with different solution times in the time range: very fine when the potential is applied which then gradually increases when the

potential remains constant.

Table S5. Time dependent solver

Times	Unit
0 10^{range(-7,1,-2)} range(0.05,0.05,1)	s

Description	Value
Times	{0, 1.0E-7, 1.0E-6, 1.0E-5, 1.0E-4, 0.001, 0.01, 0.05, 0.1, 0.15000000000000002, 0.2, 0.25, 0.3, 0.35000000000000003, 0.4, 0.45, 0.5, 0.55, 0.6000000000000001, 0.6500000000000001, 0.7000000000000001, 0.7500000000000001, 0.8, 0.8500000000000001, 0.9000000000000001, 0.9500000000000001, 1}
Tolerance	User controlled
Relative tolerance	0.1

3. Supplementary Video

Video S1. Top-view ECL microscopy of a single bead recorded when imposing a constant potential of 1.4 V at t = 1 s (dashed blue line) to a GC electrode in a PBS solution containing 100 mM TPA (pH 7.4). Exposure time: 100ms.

Video S2. Simulation of the ECL signal emitted by a single bead in the side-view configuration.

Video S3. Simulation of the ECL signal emitted by a single bead in the top-view configuration.