Supporting Information

Edge-to-Center Propagation of Photochemical Reaction during Single-Crystal-to-Single-Crystal Photomechanical Transformation of 2,5-Distyrylpyrazine Crystals

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Experimental methods.

Materials.

2,5-Distyrylpyrazine (**DSP**) was synthesized according to the procedures reported previously.[S1] Micrometer-size single crystals were prepared by sublimating the powder crystals to the glass slide at 160 °C for 3 hours.

Microscopic observation of crystals.

Optical microphotographs of **DSP** crystals were recorded using a Nikon ECLIPSE E600POL polarizing optical microscope equipped with a video camera system. UV light irradiation to the crystals was carried out using a super high-pressure mercury lamp (100 W; UV-1A filter (365 nm light excitation) attached to the polarizing optical microscope. The irradiation power of the incident light was measured by using a Neoark PM-335A power meter. The change in the fluorescence intensity was analyzed by using Image J software.

Numerical simulation.

For quantitative analysis of the edge-to-center propagation of photochemical reaction on optical length scale in **DSP** crystals, numerical simulation was performed with a home-built program written in Igor Pro ver. 8.0.4.2. The details of the program are described below.

Change in cell parameters accompanying photopolymerization reaction in DSP crystals

Table S1. Change in cell parameters accompanying photopolymerization reaction in **DSP** crystals.[S2]

	Monomer crystal	Polymer crystal	Rate of change / %
a / Å	9.6111	10.842	+12.8
b / Å	7.6534	7.411	−3.17
c / Å	20.6232	18.12	−12.1

Thermal effect on the edge-to-center propagation of photochemical reaction in DSP crystals

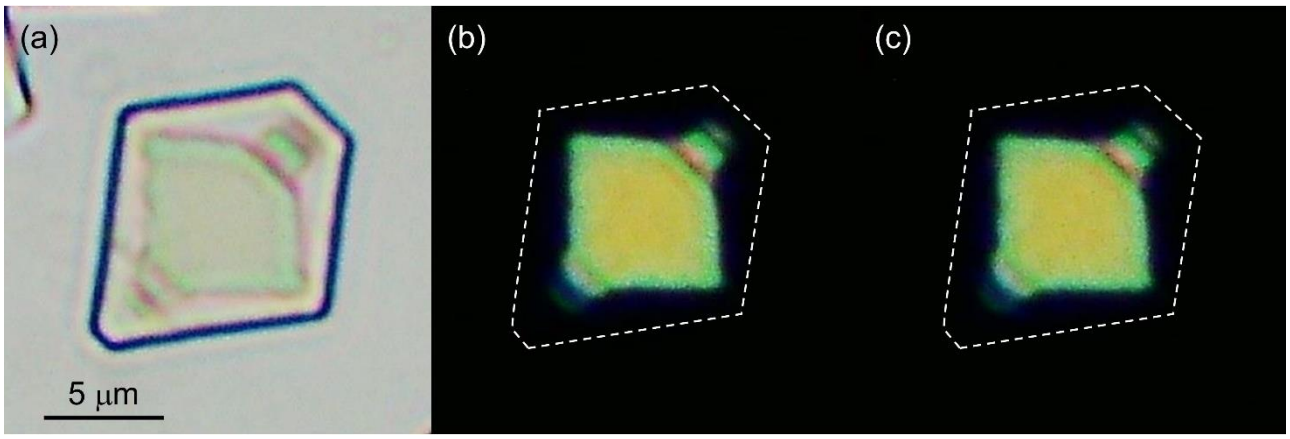

Figure S1. DSP crystal under (a) no Nicols and (b) crossed Nicols when UV light was just stopped. (c) The area exhibiting interference color was kept after 3 minutes, indicating no thermal effect on the edge-to-center propagation photochemical reaction in **DSP** crystals.

Change in conversion ratio in DSP single crystals

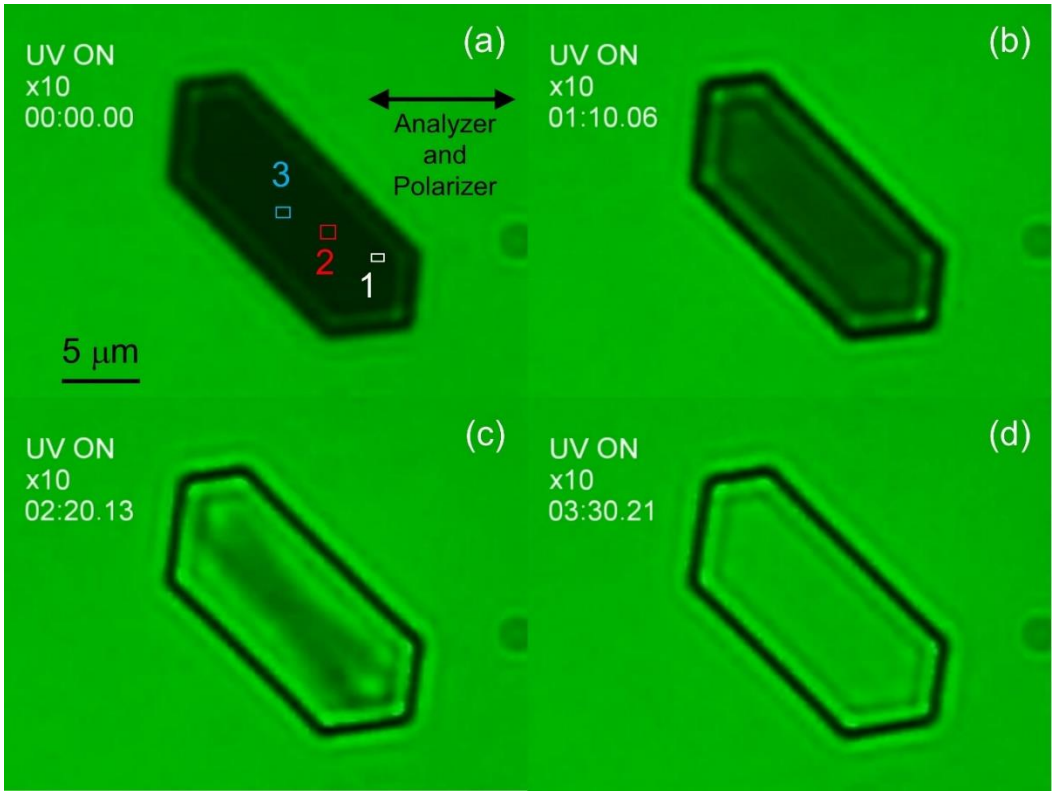

Figure S2. Dynamic interference color change originating from the birefringence change of a **DSP** single crystal under excitation with 365 nm light (4.0 mW cm^{-2}). Note that this observation was performed under 546 nm light with a monochromatic filter over a white light source under parallel Nicols. The different positions from the edge of the crystal to the center are marked as 1, 2, and 3.

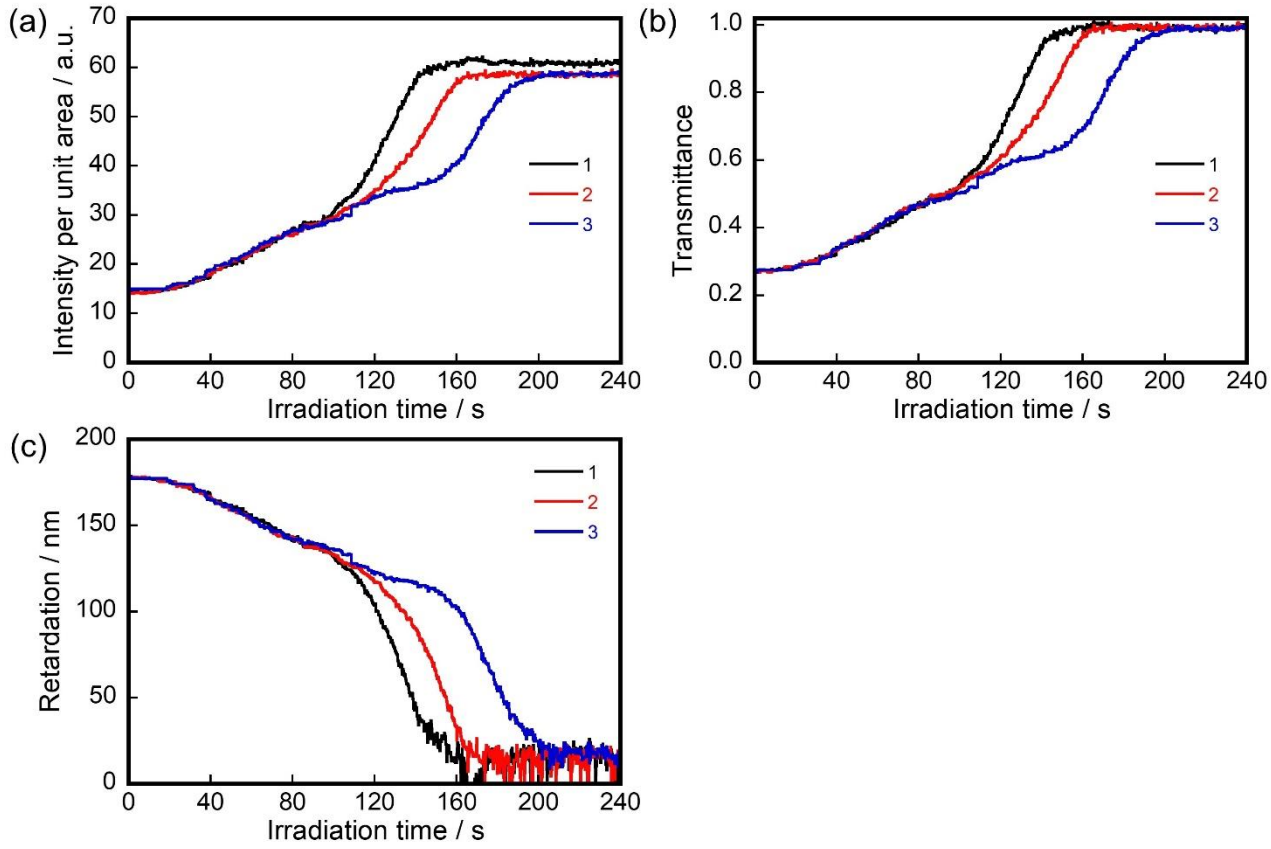

Figure S3. (a) Change in intensity per unit area at the position marked in Figure S2 calculated by using Image J program. (b) and (c) are the change in transmittance and retardation, respectively, calculated by the following method.

The conversion ratio of the photochemical reaction in **DSP** crystal was calculated based on the interference color change originating from the birefringence change. First, the interference color change at positions of 1, 2, and 3 shown in Figure S2 was converted into the intensity change using image J program (Figure S3a). Next, considering a retardation measured by Sénarmont compensator (Nikon P-CS) under monochromatic light at 546 nm generated by a color filter before the start of the reaction and after the completion of the reaction, the intensity was converted into the transmittance.

The transmittance before the start of the reaction and after the completion of the reaction (Table S2) was calculated by the equation (S1).

Table S2. Retardation measured by Sénarmont compensator and transmittance calculated by equation (S1).

	Before reaction	After completing the reaction
Retardation / nm	177	18
Transmittance	0.274	0.99

$$T = \cos^2 \frac{\pi R}{\lambda_0} \quad \text{(S1)}$$

where T is the transmittance, R is the retardation, and λ_0 is the wavelength used for the observation. In this observation, λ_0 is 546 nm. The intensity change (Figure S3a) was converted into the transmittance change (Figure S3b) by equation (S2).

$$T = \frac{Int. - Int._{\min}}{Int._{\max} - Int._{\min}} (T_{\text{after}} - T_{\text{before}}) + T_{\text{before}} \quad \text{(S2)}$$

where $Int.$ is intensity, $Int._{\min}$ is the intensity before reaction, $Int._{\max}$ is the intensity after completing the reaction, T_{before} is the calculated transmittance before reaction, T_{after} is the calculated transmittance after completing the reaction.

Next, the relationship between the transmittance and the retardation at the parallel Nicols was derived, and the transmittance (Figure S3b) was converted into the retardation (Figure S3c). Generally, transmittance under crossed Nicols is written as follows.

$$\frac{I_c}{I_0} = \sin^2 \frac{\pi d \Delta n}{\lambda_0} \tag{S3}$$

where I_0 is the sum of the light intensity, I_c is light intensity under crossed Nicols, d is the thickness of the crystal, and Δn is birefringence. When under parallel Nicols,

$$\frac{I_p}{I_0} = \frac{I_0 - I_c}{I_0} = 1 - \sin^2 \frac{\pi d \Delta n}{\lambda_0} = \cos^2 \frac{\pi d \Delta n}{\lambda_0} \tag{S4}$$

where I_p is light intensity under parallel Nicols. Then, the relationship between the transmittance (I_p/I_0) and the retardation (R) at the parallel Nicols is derived as follows,

$$R = d\Delta n = \frac{\lambda_0}{\pi} \cos^{-1} \sqrt{\frac{I_p}{I_0}} \tag{S5}$$

Using equation (S5), the transmittance (Figure S3b) was converted into the retardation (Figure S3c). In our previous work, birefringence changes linearly with respect to the conversion ratio.[S3,S4] Therefore, equation (S6) is derived.

$$conversion \propto \Delta n \propto \cos^{-1} \sqrt{\frac{I_p}{I_0}} \tag{S6}$$

where *conversion* is the conversion ratio. From this relationship, the retardation (Figure S3c) was converted into the conversion ratio (Figure 4c).

Fluorescence observation of a DSP crystal intentionally cut with a razor

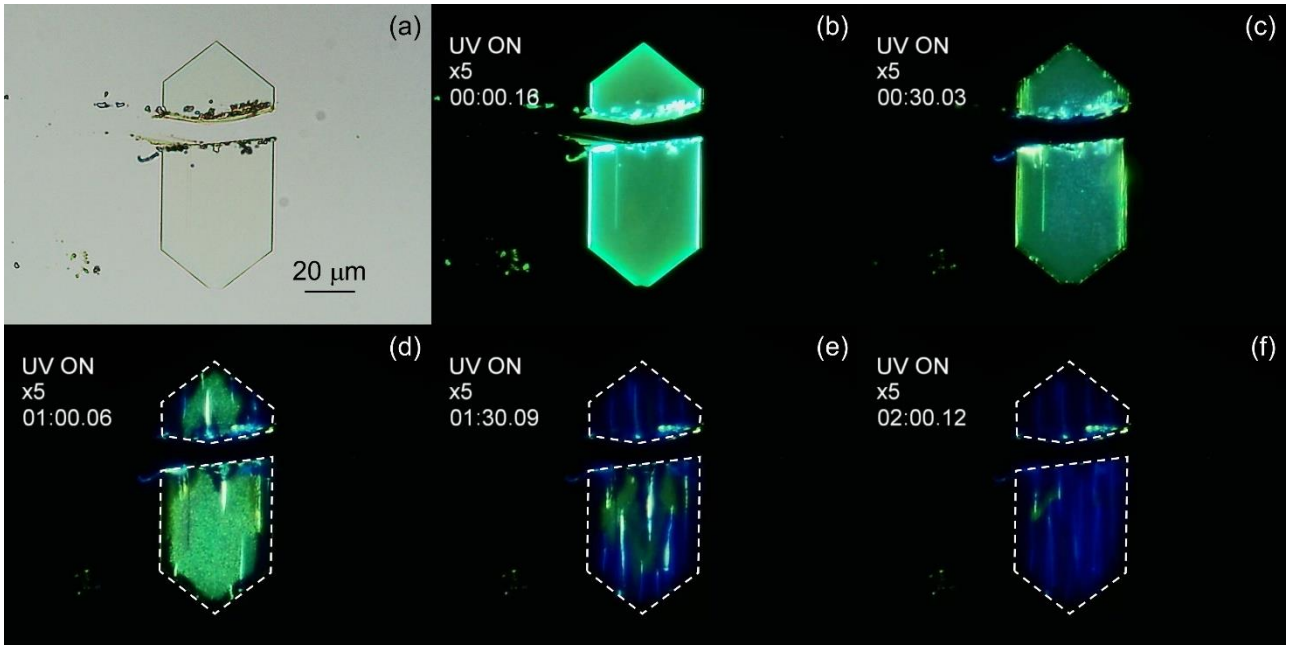

Figure S4. (a) Microphotograph of a **DSP** crystal observed under white light. (b-f) Dynamic fluorescent intensity change of a **DSP** single crystal under excitation with 365 nm light (14 mW cm^{-2}).

Details of numerical simulations

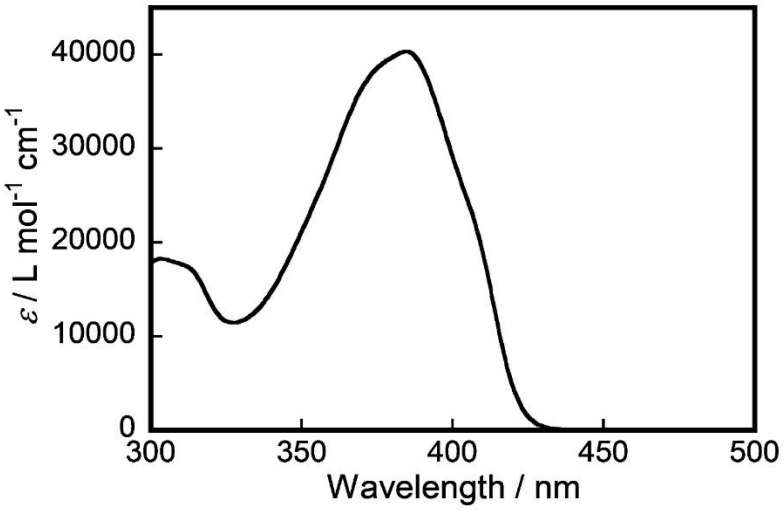

Figure S5. Molar extinction coefficient of **DSP** in THF.

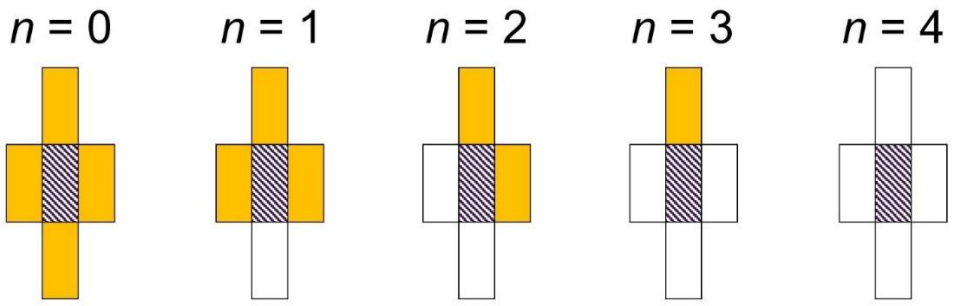

Figure S6. Number of reacted pixels (*n*) when focusing on a certain pixel (dotted pixel). Yellow and white pixels indicate unreacted and reacted pixels, respectively.

Table S3. Definition for simulations.

Parameter	Symbol	Value	Unit
Lattice constants of **DSP** crystal	a	9.6111	Å
	b	7.6534	Å
	c	20.6232	Å
Number of molecules in a unit cell of **DSP** crystal	Z	4	
Density of **DSP** crystal	*Density*	4.3785	mol L^{-1}
Number of unit cells in one direction	N_{cells}		
Number of pixels arranged in the width direction (along x-axis)	$N_{Pixels(x)}$		
Number of pixels arranged in the thickness direction (along z-axis)	$N_{Pixels(z)}$		
Number of molecules in a pixel	$N_{Molecules/Pixel}$		
Width of crystal	*Width*		μm
Thickness of crystal	*Thickness*		μm

Irradiated area in cross section	*Irradiated area*		cm^2
Molar extinction coefficient of **DSP**	ε		$L\ mol^{-1}\ cm^{-1}$
Absorbance before reaction	*Absorbance*		
Number of reacted pixels	n		
n when quantum yield increases stepwise	n_s		
Reaction quantum yield with the cooperative effect of the adjacent reacted n pixels	Phi_{nc}		
Range of crystal surface showing the special reactivity	*Edge*		
Reaction quantum yield with the surface effect	Phi_{edge}		
Constant parameter to show the contrast of the photoreactivity between the surface and bulk of the crystal	C_{edge}	0.8	
Coordinate of a pixel	(x, z)		

Actual reaction quantum yields at a position	Phi_n	
Number of repeated times in numerical simulation	N_{Loops}	
Number of *Loops* when the reaction is completed	$N_{Loops(final)}$	
Number of photons when the reaction is completed	$N_{Photons(final)}$	photons
Number of photons at *Irradiated area* when the reaction is completed	$N_{Photons(final)}/Irradiated\ area$	photons cm^{-2}

$$N_{Molecules/Pixel} = Z \cdot N_{cells}^2 \quad \text{(S7)}$$

$$Width = a \cdot N_{cells} \cdot N_{Pixels(x)} \cdot 10^{-4} \quad \text{(S8)}$$

$$Thickness = c \cdot N_{cells} \cdot N_{Pixels(z)} \cdot 10^{-4} \quad \text{(S9)}$$

$$Irradiated\ area = b \cdot Width \cdot 10^{-12} \quad \text{(S10)}$$

$$Absorbance = \varepsilon \cdot Density \cdot Thickness \cdot 10^{-4} \quad \text{(S11)}$$

$$N_{Photons(final)} = N_{Loops(final)} \cdot N_{Molecules/Pixel} \quad \text{(S12)}$$

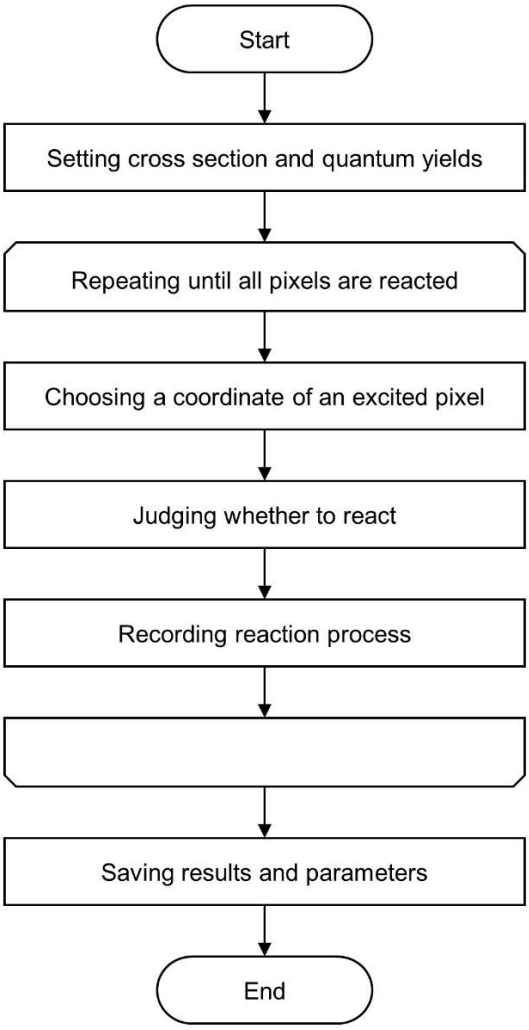

Figure S7. Flowchart of the program for the numerical simulation.

Table S4. Setup of the parameters and results of simulations.

Simulation number	n_s	Phi_{0c}	Phi_{nc}	*Edge*	N_{Loops}	$N_{Photons(final)}$/*Irradiated area**
1	1	0.0001	0.5	0.1	5.86×10^5	7.96×10^{17}
2	1	0.0001	0.5	1	5.57×10^5	7.57×10^{17}
3	1	0.0001	1	0.1	2.91×10^5	3.95×10^{17}
4	1	0.0001	1	1	2.89×10^5	3.93×10^{17}
5	1	0.001	0.5	0.1	5.60×10^5	7.61×10^{17}
6	1	0.001	0.5	1	5.81×10^5	7.91×10^{17}
7	1	0.001	1	0.1	2.77×10^5	3.77×10^{17}
8	1	0.001	1	1	2.87×10^5	3.90×10^{17}
9	1	0.01	0.5	0.1	5.85×10^5	7.96×10^{17}
10	1	0.01	0.5	1	5.71×10^5	7.76×10^{17}
11	1	0.01	1	0.1	2.85×10^5	3.87×10^{17}
12	1	0.01	1	1	3.03×10^5	4.12×10^{17}

13	2	0.0001	0.5	0.1	7.68×10^{6}	1.04×10^{19}
14	2	0.0001	0.5	1	6.88×10^{6}	9.35×10^{18}
15	2	0.0001	1	0.1	3.86×10^{6}	5.25×10^{18}
16	2	0.0001	1	1	3.42×10^{6}	4.65×10^{18}
17	2	0.001	0.5	0.1	6.28×10^{6}	8.54×10^{18}
18	2	0.001	0.5	1	5.73×10^{6}	7.78×10^{18}
19	2	0.001	1	0.1	3.57×10^{6}	4.85×10^{18}
20	2	0.001	1	1	3.35×10^{6}	4.56×10^{18}
21	2	0.01	0.5	0.1	2.14×10^{6}	2.92×10^{18}
22	2	0.01	0.5	1	2.01×10^{6}	2.73×10^{18}
23	2	0.01	1	0.1	1.49×10^{6}	2.03×10^{18}
24	2	0.01	1	1	1.41×10^{6}	1.92×10^{18}
25	3	0.0001	0.5	0.1	2.21×10^{7}	3.00×10^{19}
26	3	0.0001	0.5	1	2.21×10^{7}	3.00×10^{19}

27	3	0.0001	1	0.1	2.21×10^{7}	3.00×10^{19}
28	3	0.0001	1	1	2.21×10^{7}	3.00×10^{19}
29	3	0.001	0.5	0.1	2.21×10^{7}	3.00×10^{19}
30	3	0.001	0.5	1	2.21×10^{7}	3.00×10^{19}
31	3	0.001	1	0.1	2.21×10^{7}	3.00×10^{19}
32	3	0.001	1	1	2.21×10^{7}	3.00×10^{19}
33	3	0.01	0.5	0.1	1.59×10^{7}	2.17×10^{19}
34	3	0.01	0.5	1	1.54×10^{7}	2.09×10^{19}
35	3	0.01	1	0.1	1.65×10^{7}	2.24×10^{19}
36	3	0.01	1	1	1.52×10^{7}	2.06×10^{19}
37	4	0.0001	0.5	0.1	2.21×10^{7}	3.00×10^{19}
38	4	0.0001	0.5	1	2.21×10^{7}	3.00×10^{19}
39	4	0.0001	1	0.1	2.21×10^{7}	3.00×10^{19}
40	4	0.0001	1	1	2.21×10^{7}	3.00×10^{19}

41	4	0.001	0.5	0.1	2.21×10^{7}	3.00×10^{19}
42	4	0.001	0.5	1	2.21×10^{7}	3.00×10^{19}
43	4	0.001	1	0.1	2.21×10^{7}	3.00×10^{19}
44	4	0.001	1	1	2.21×10^{7}	3.00×10^{19}
45	4	0.01	0.5	0.1	2.21×10^{7}	3.00×10^{19}
46	4	0.01	0.5	1	2.21×10^{7}	3.00×10^{19}
47	4	0.01	1	0.1	2.21×10^{7}	3.00×10^{19}
48	4	0.01	1	1	2.21×10^{7}	3.00×10^{19}
49	2	0.0001	0.5	0.05	1.86×10^{6}	1.01×10^{19}
50	2	0.0001	0.5	0.1	8.20×10^{6}	1.11×10^{19}
51	2	0.0001	0.5	0.1	7.30×10^{6}	9.92×10^{18}
52	2	0.0001	0.5	0.1	9.09×10^{6}	1.24×10^{19}
53	2	0.0001	0.5	0.05	7.03×10^{6}	1.91×10^{19}

*Note that when the value is 3.0×10^{19}, the simulation is stopped on the way because there is a large difference between the simulated and the experimental results. Therefore, the values of $N_{\text{Photons(final)}}$/*Irradiated area* are out of the definition.

Table S5. Setup of the other parameters

Simulation number	N_{cells}	$N_{Pixels(x)}$	$N_{Pixels(z)}$	$N_{Molecules/Pixel}$	*Width*	*Thickness*	*Irradiated area*	ε	*Abs*	C_{edge}
1–48	5	2000	100	100	9.6111	1.0312	7.36×10^{11}	30000	13.545	0.8
49	10	1000	50	400	9.6111	1.0312	7.36×10^{11}	30000	13.545	0.8
50	5	2000	100	100	9.6111	1.0312	7.36×10^{11}	20000	9.0299	0.8
51	5	2000	100	100	9.6111	1.0312	7.36×10^{11}	40000	18.06	0.8
52	5	2000	200	100	9.6111	2.0623	7.36×10^{11}	30000	27.09	0.8
53	10	2000	100	400	19.222	2.0623	1.47×10^{10}	30000	27.09	0.8

Figures S8–S60. Setups and results of Simulation number 1–53. (a) Cross-sectional view of Phi_0 in the cross section. (b,c) Change in Phi_n relative to x and z, respectively (d) Change in Phi_{nc} relative to n. (e–g) Cross-sectional view of the progress of the photochemical reaction. (h) Change in the conversion ratio relative to the value of N_{Loops}. The solid lines indicate the change in the average conversion ratio at a certain range of x.

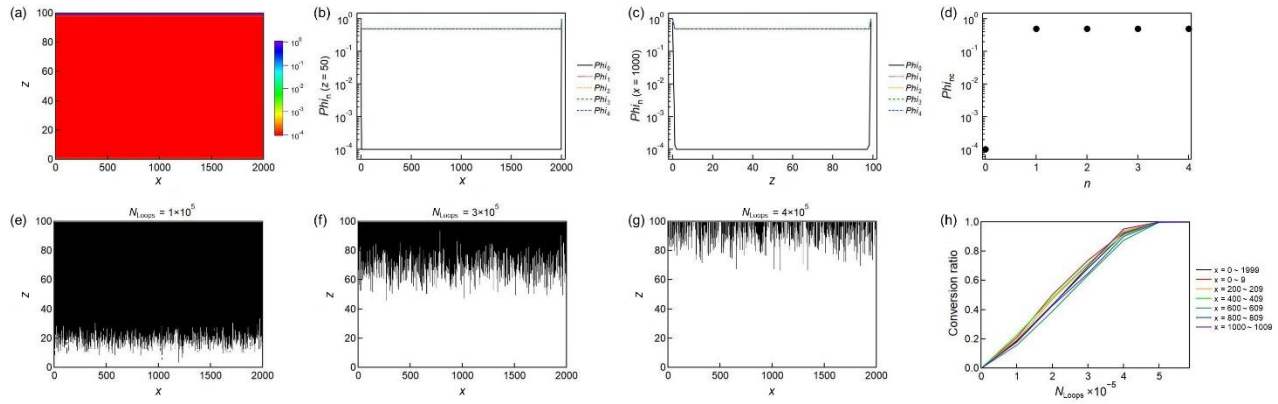

Figure S8. Setups and results of Simulation number 1.

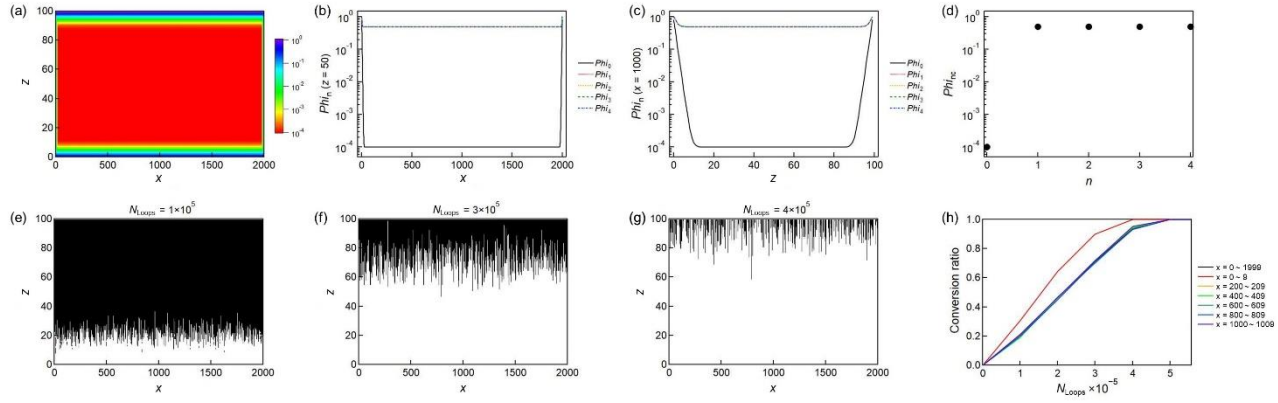

Figure S9. Setups and results of Simulation number 2.

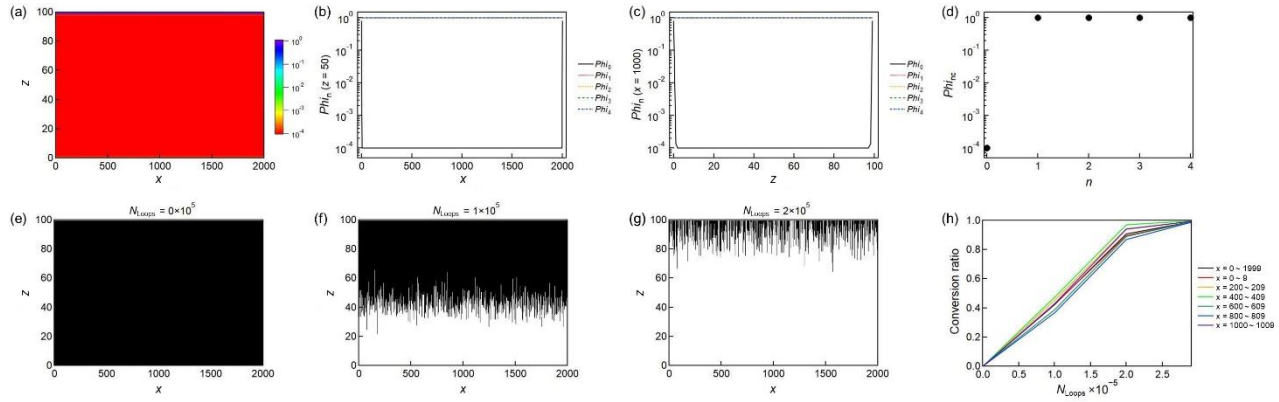

Figure S10. Setups and results of Simulation number 3.

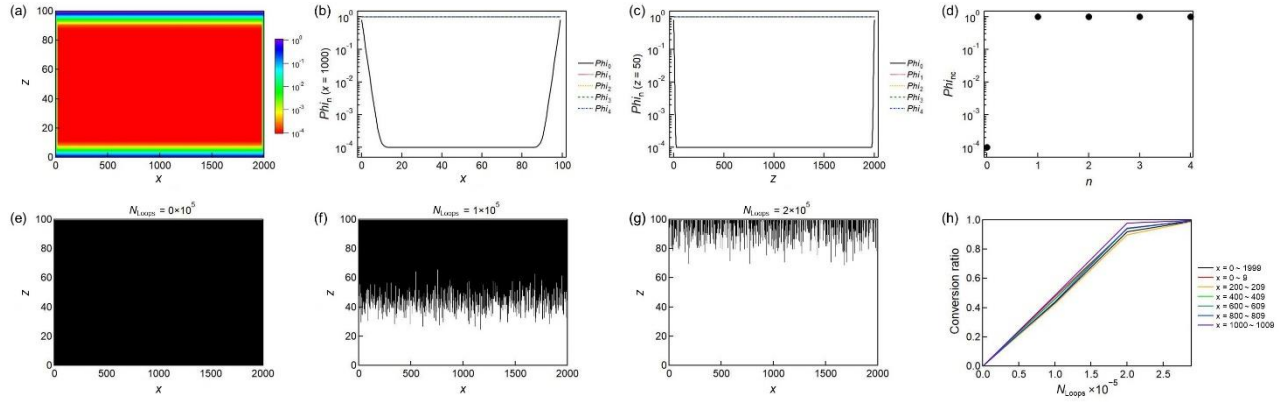

Figure S11. Setups and results of Simulation number 4.

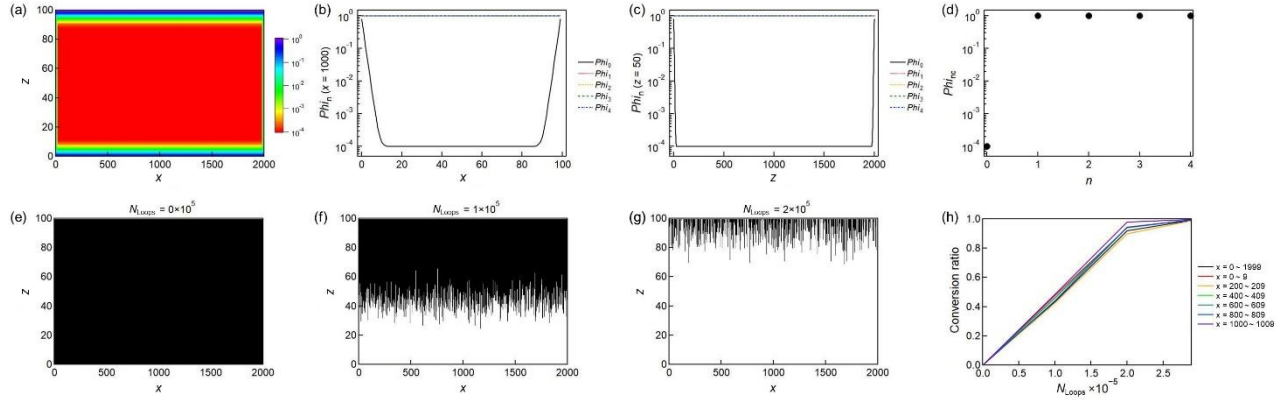

Figure S12. Setups and results of Simulation number 5.

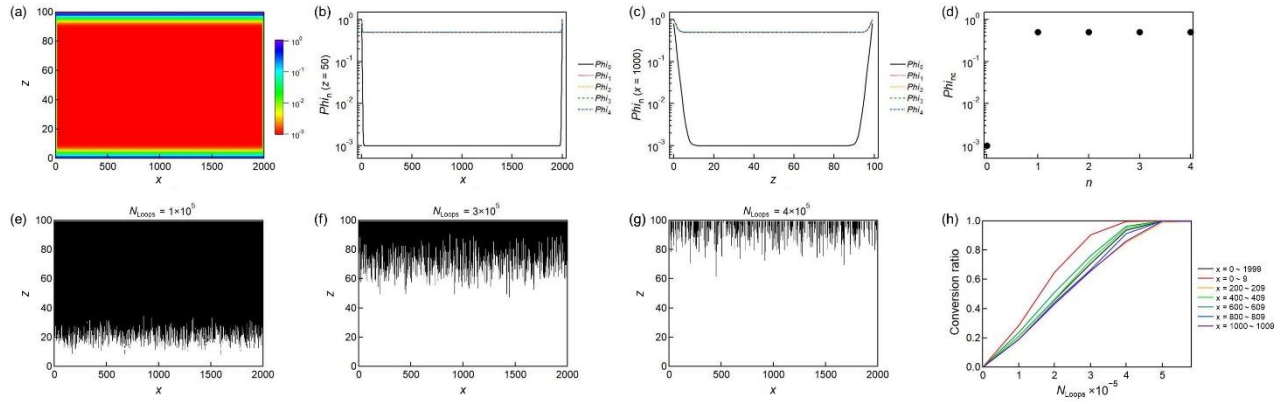

Figure S13. Setups and results of Simulation number 6.

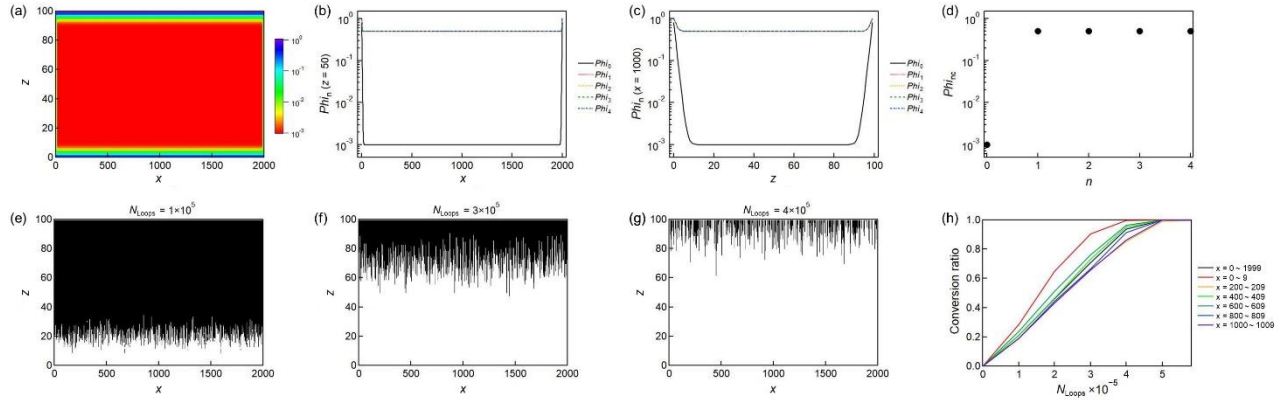

Figure S14. Setups and results of Simulation number 7.

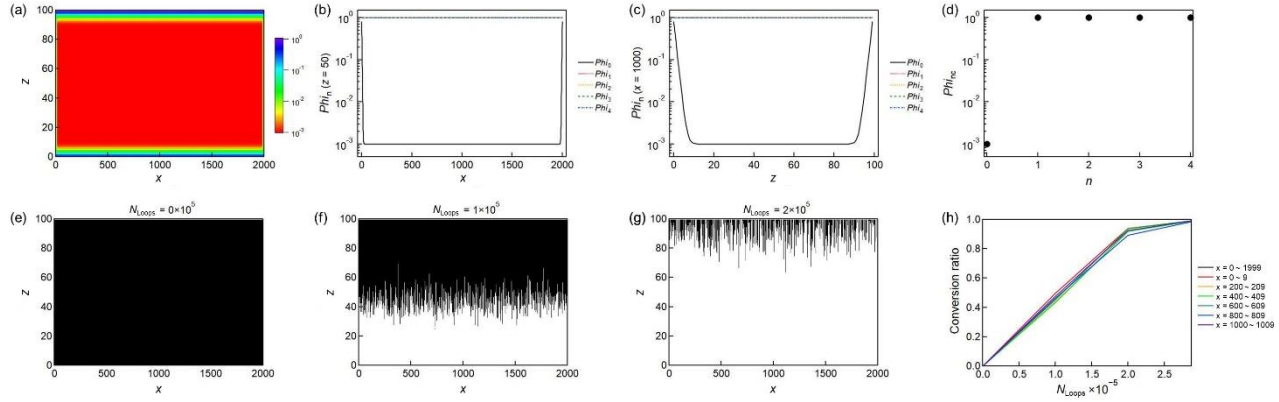

Figure S15. Setups and results of Simulation number 8.

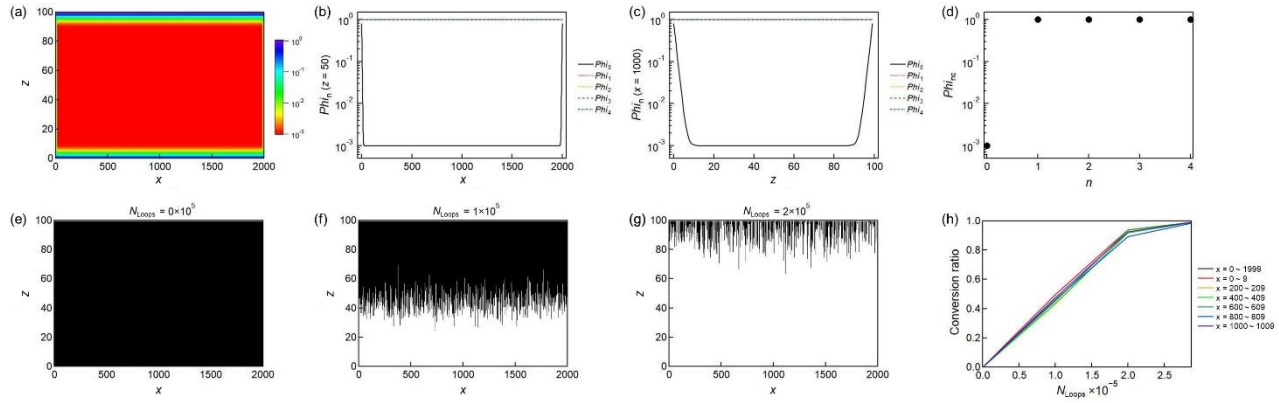

Figure S16. Setups and results of Simulation number 9.

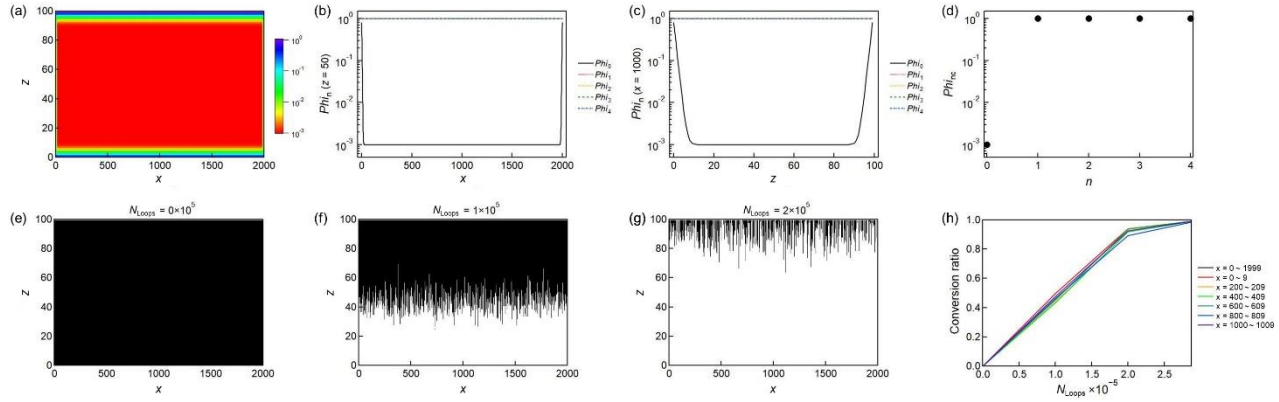

Figure S17. Setups and results of Simulation number 10.

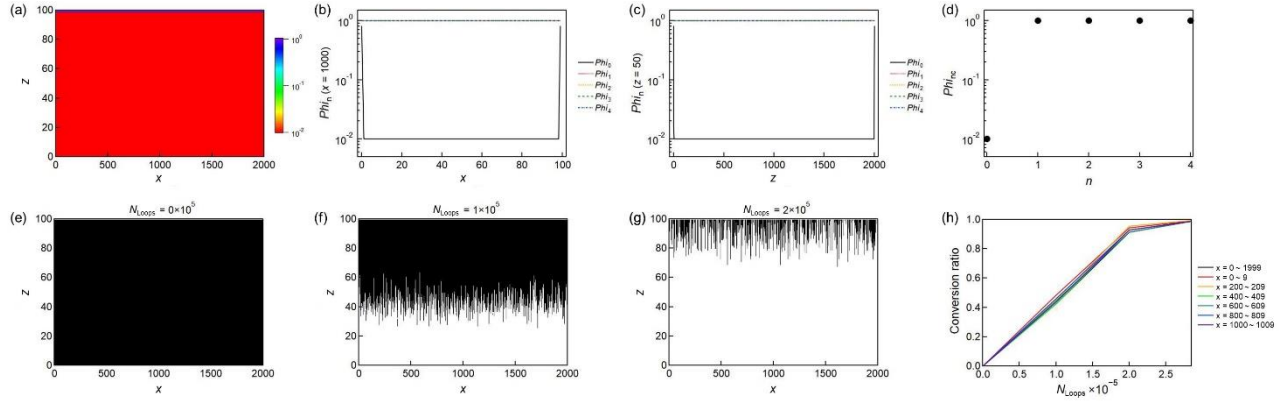

Figure S18. Setups and results of Simulation number 11.

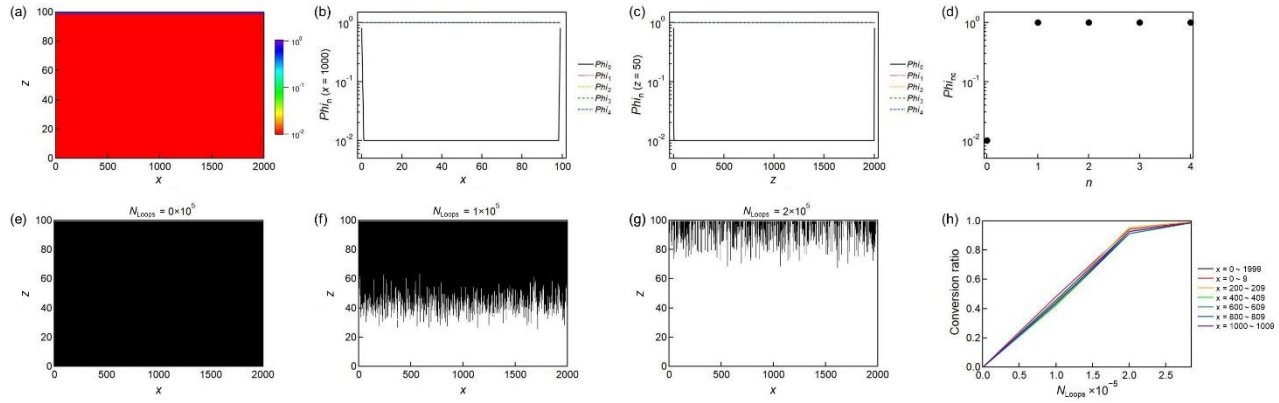

Figure S19. Setups and results of Simulation number 12.

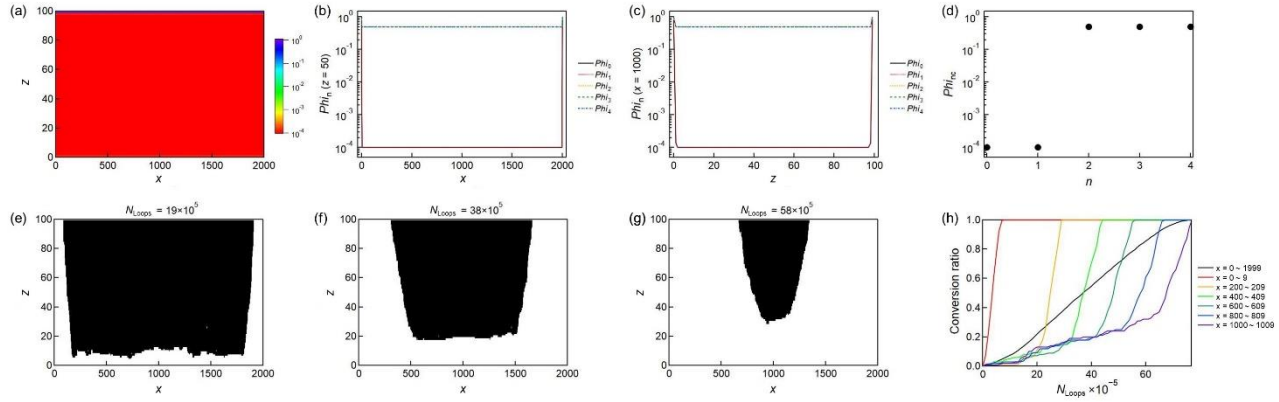

Figure S20. Setups and results of Simulation number 13.

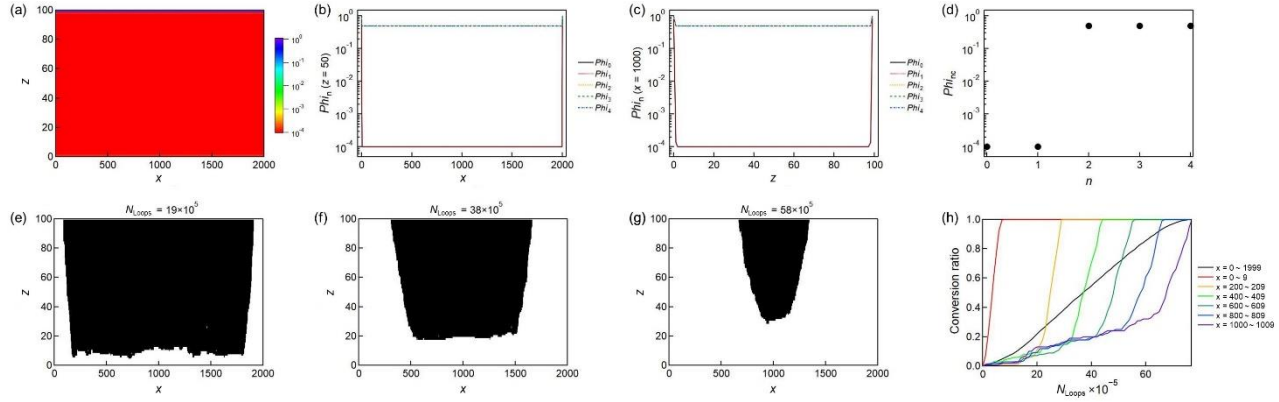

Figure S21. Setups and results of Simulation number 14.

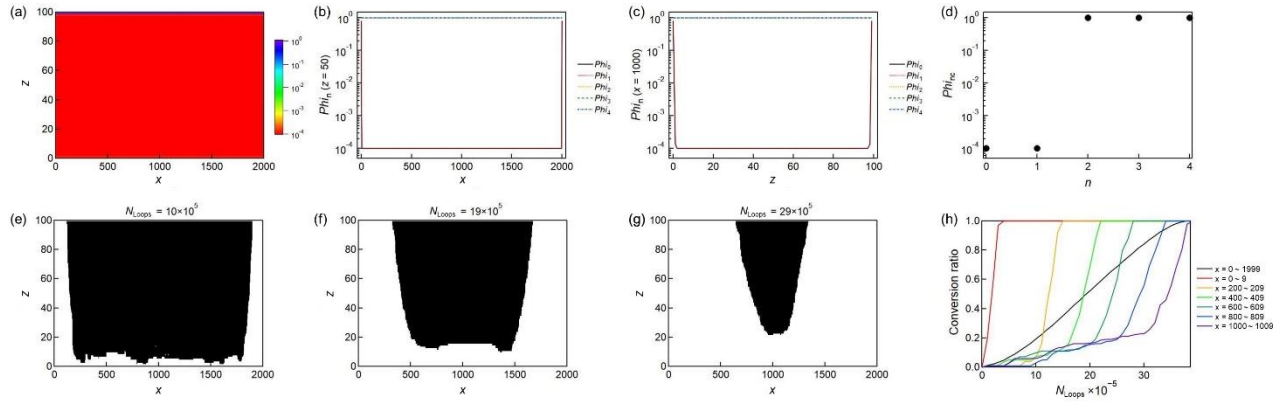

Figure S22. Setups and results of Simulation number 15.

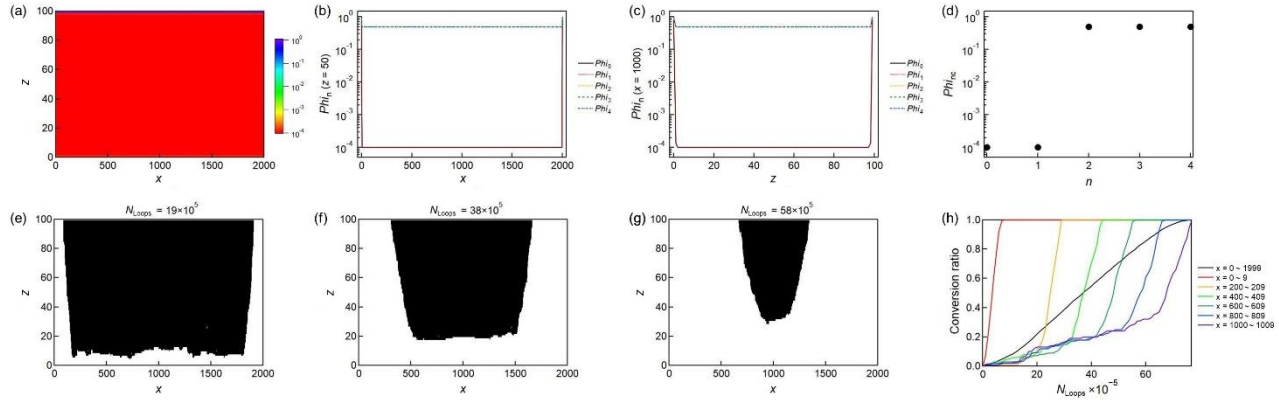

Figure S23. Setups and results of Simulation number 16.

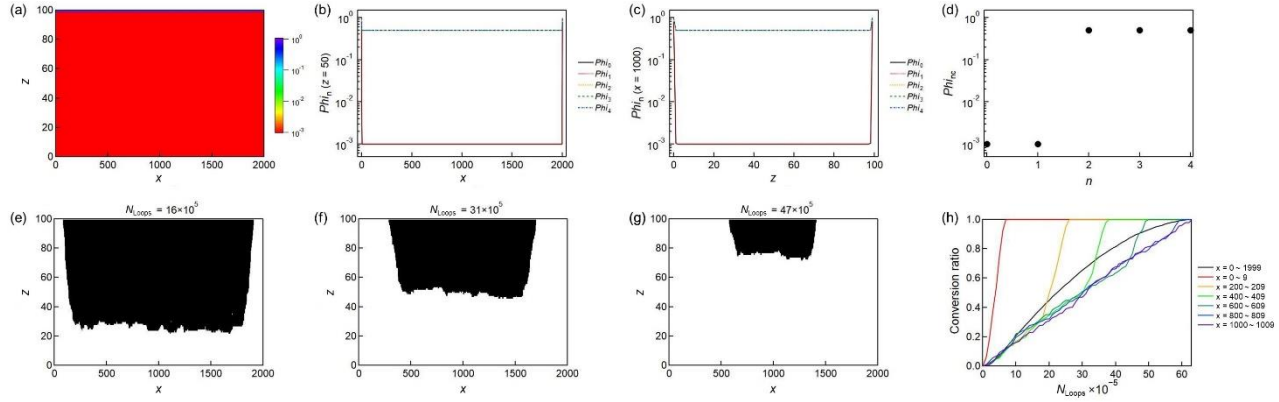

Figure S24. Setups and results of Simulation number 17.

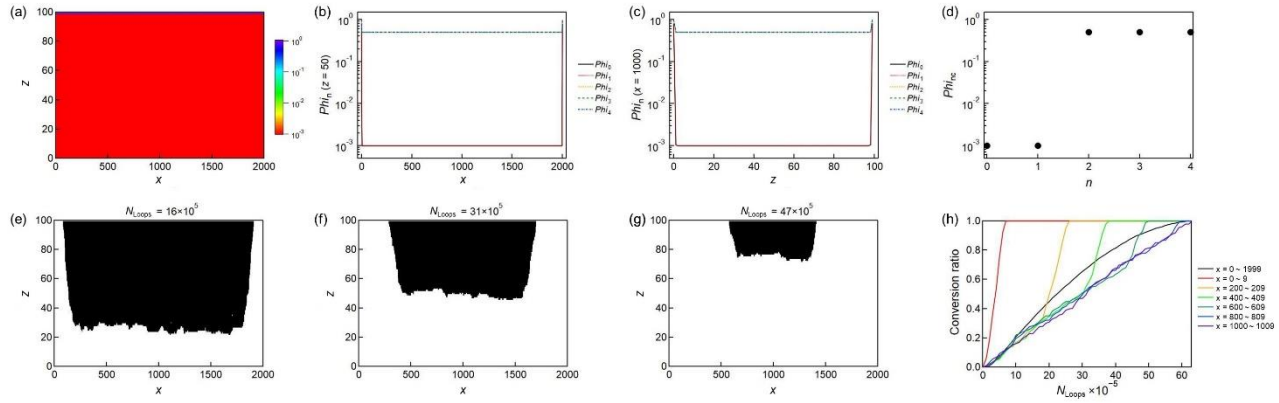

Figure S25. Setups and results of Simulation number 18.

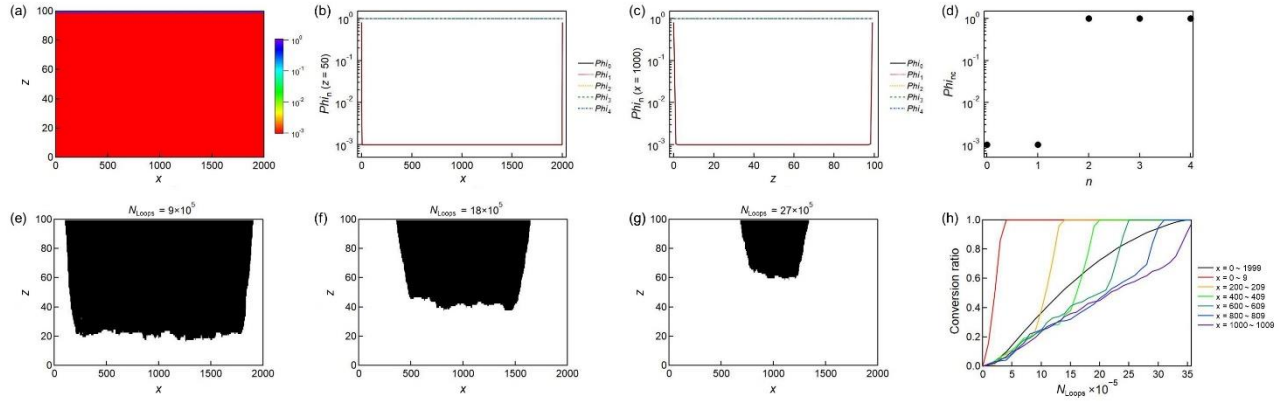

Figure S26. Setups and results of Simulation number 19.

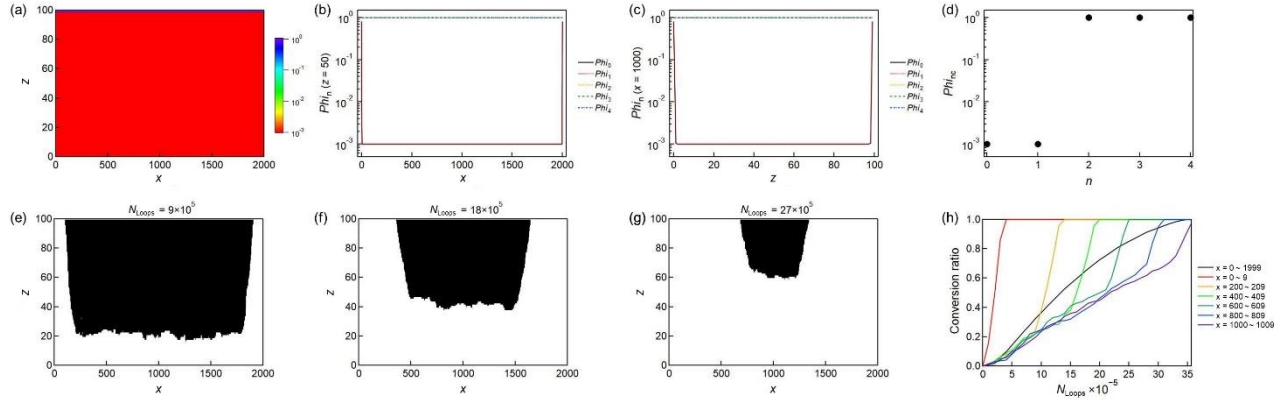

Figure S27. Setups and results of Simulation number 20.

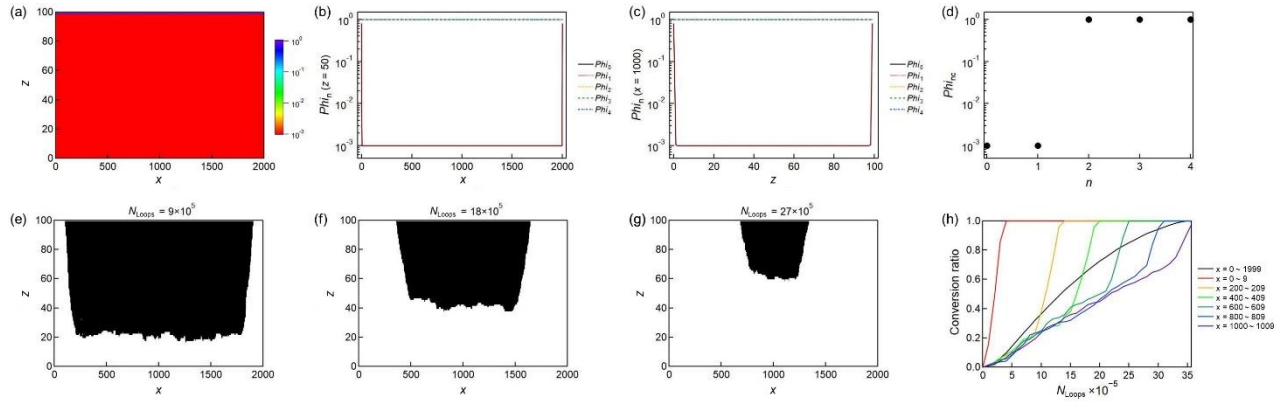

Figure S28. Setups and results of Simulation number 21.

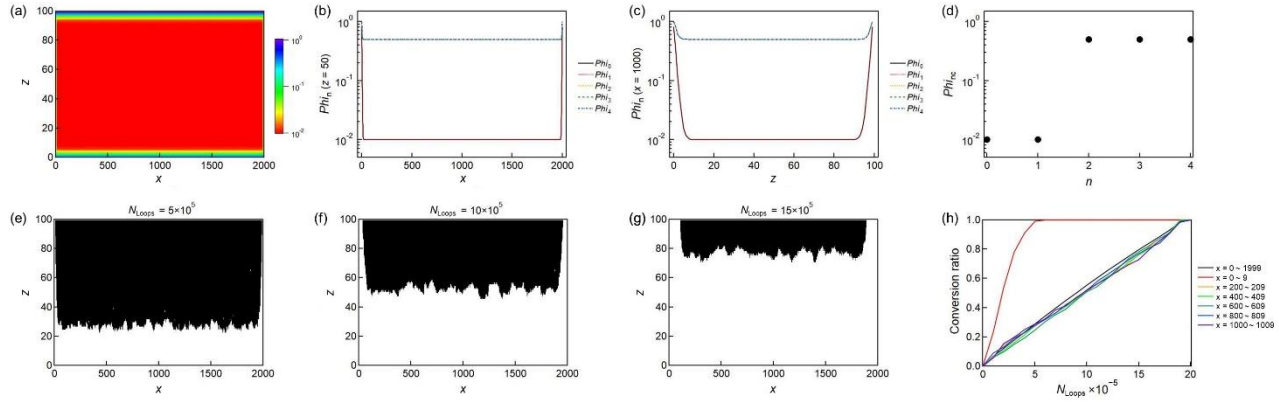

Figure S29. Setups and results of Simulation number 22.

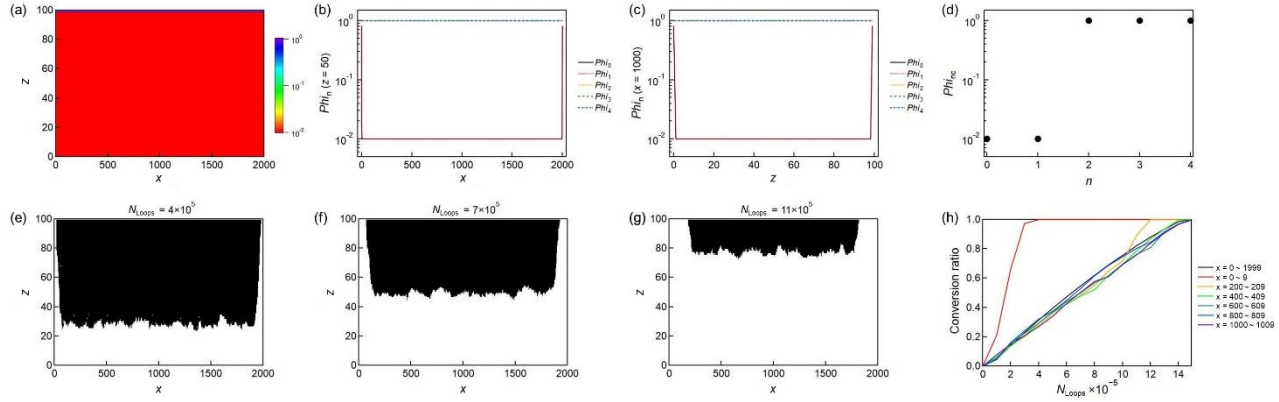

Figure S30. Setups and results of Simulation number 23.

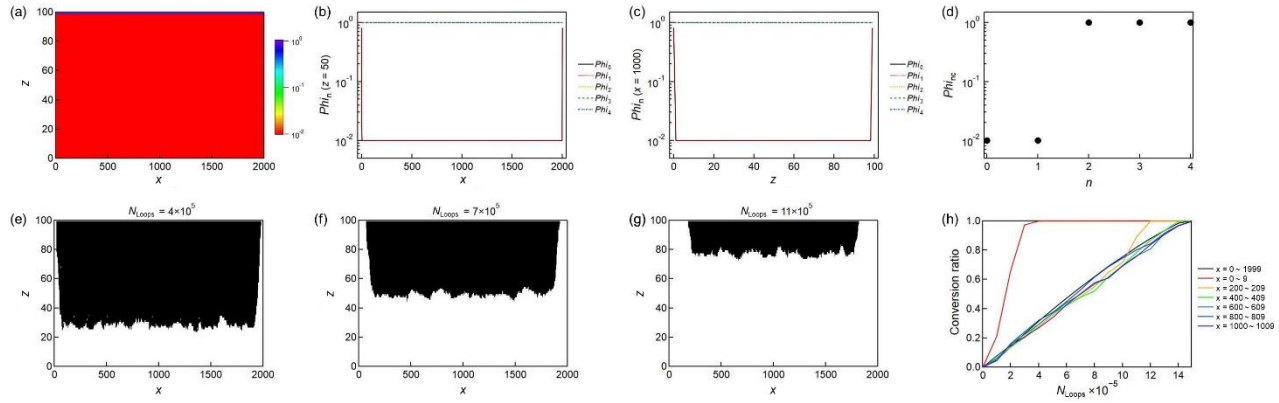

Figure S31. Setups and results of Simulation number 24.

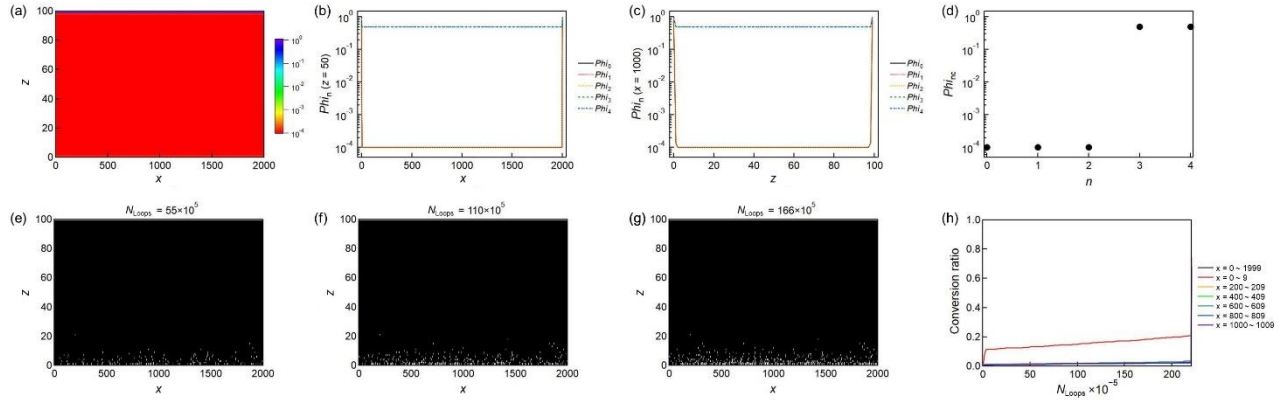

Figure S32. Setups and results of Simulation number 25.

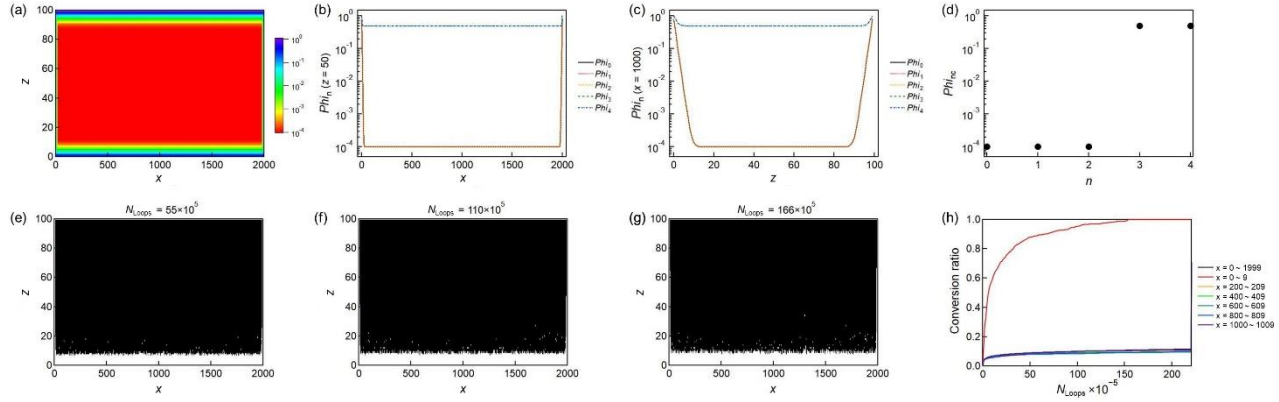

Figure S33. Setups and results of Simulation number 26.

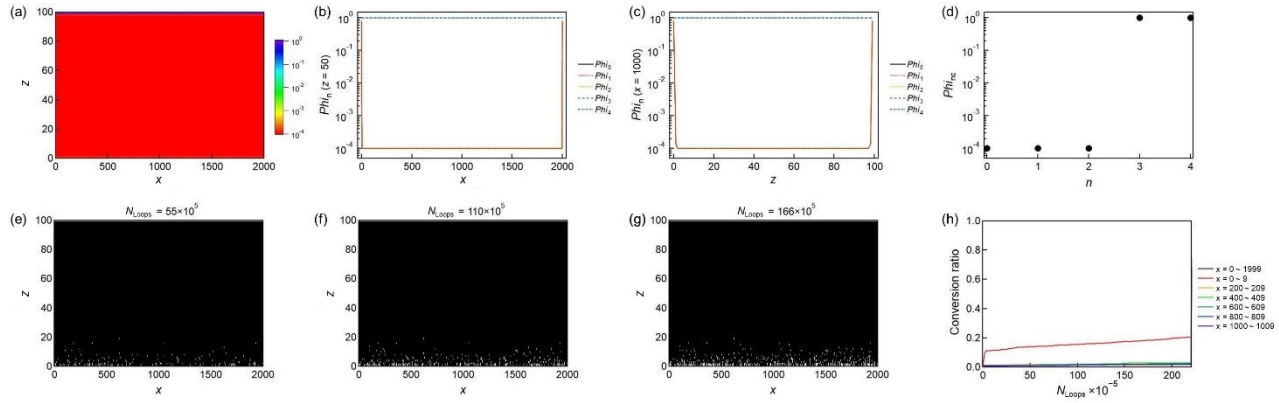

Figure S34. Setups and results of Simulation number 27.

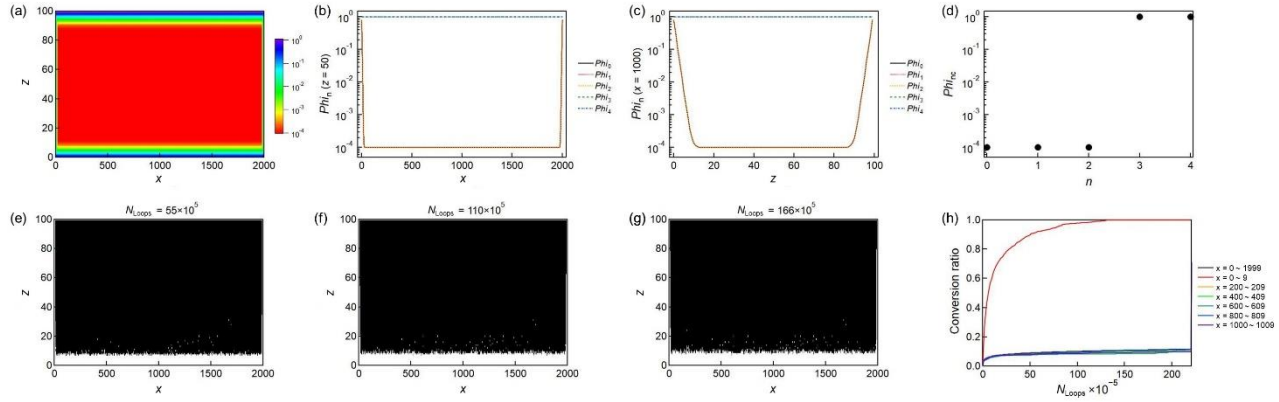

Figure S35. Setups and results of Simulation number 28.

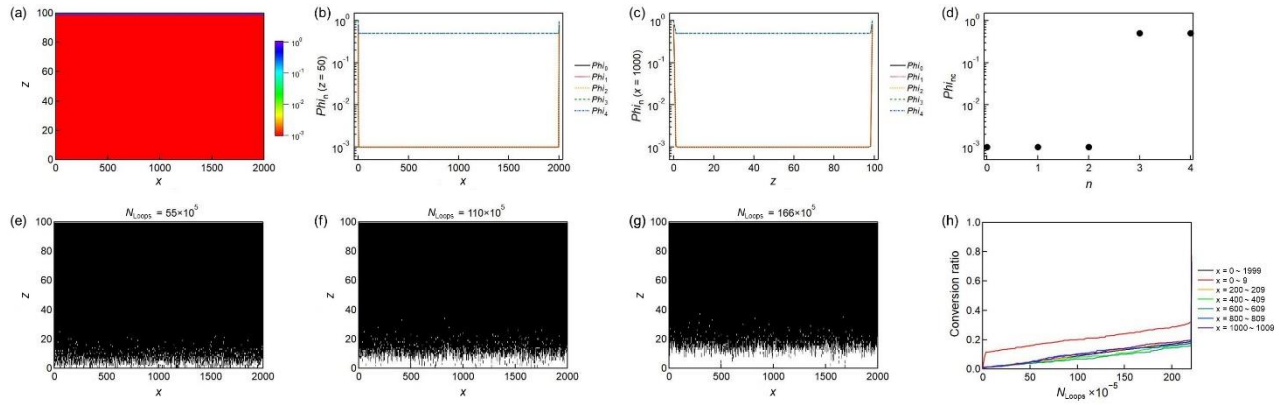

Figure S36. Setups and results of Simulation number 29.

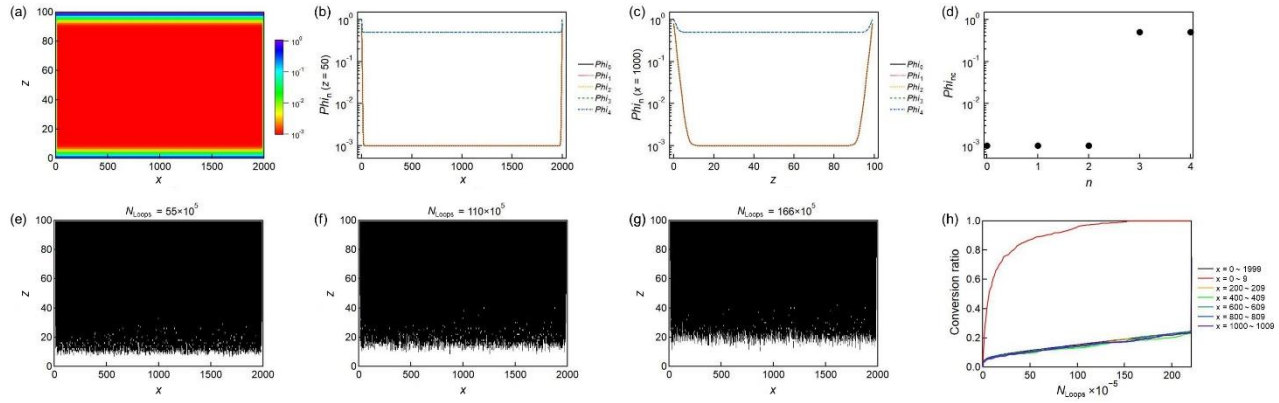

Figure S37. Setups and results of Simulation number 30.

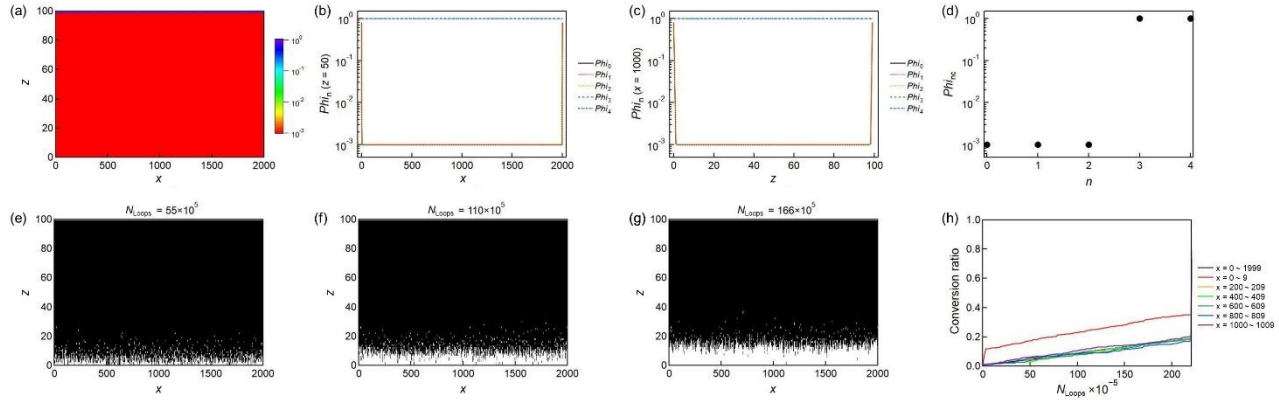

Figure S38. Setups and results of Simulation number 31.

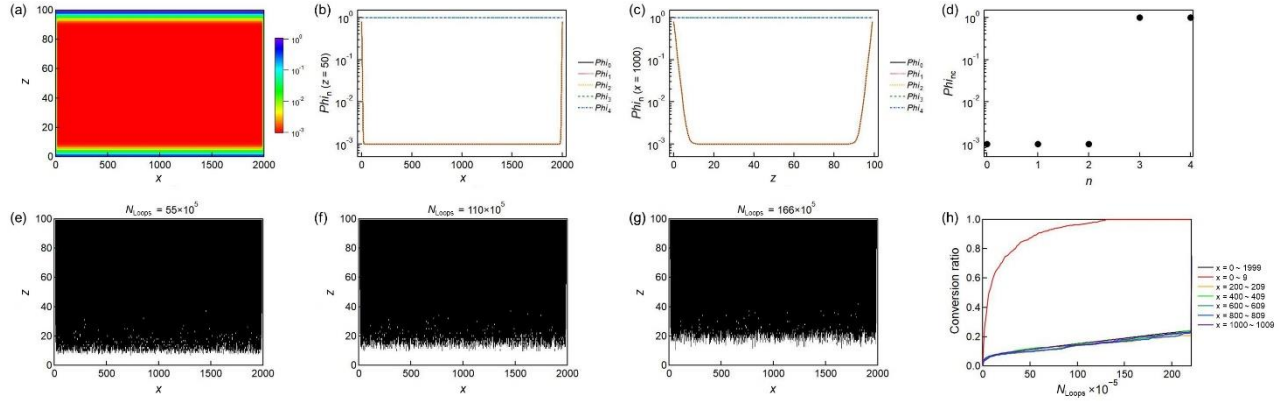

Figure S39. Setups and results of Simulation number 32.

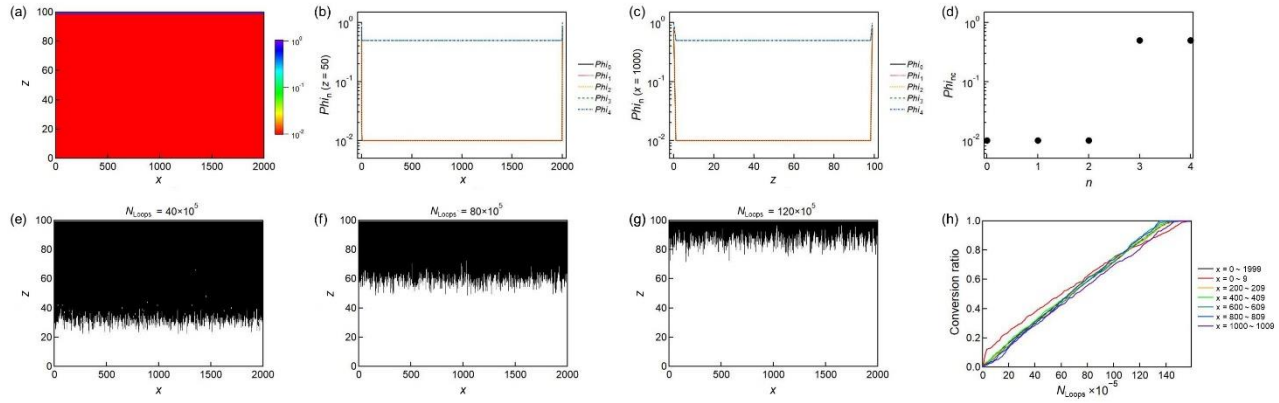

Figure S40. Setups and results of Simulation number 33.

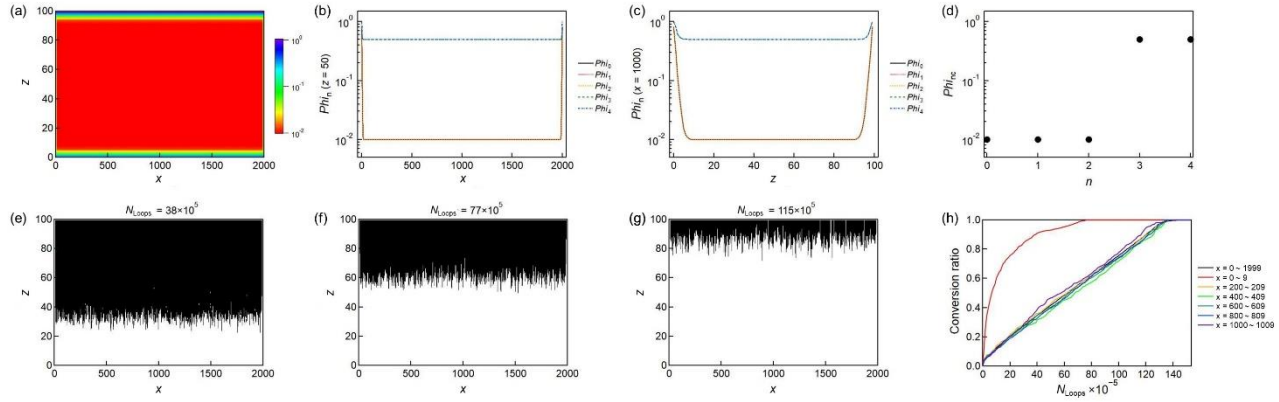

Figure S41. Setups and results of Simulation number 34.

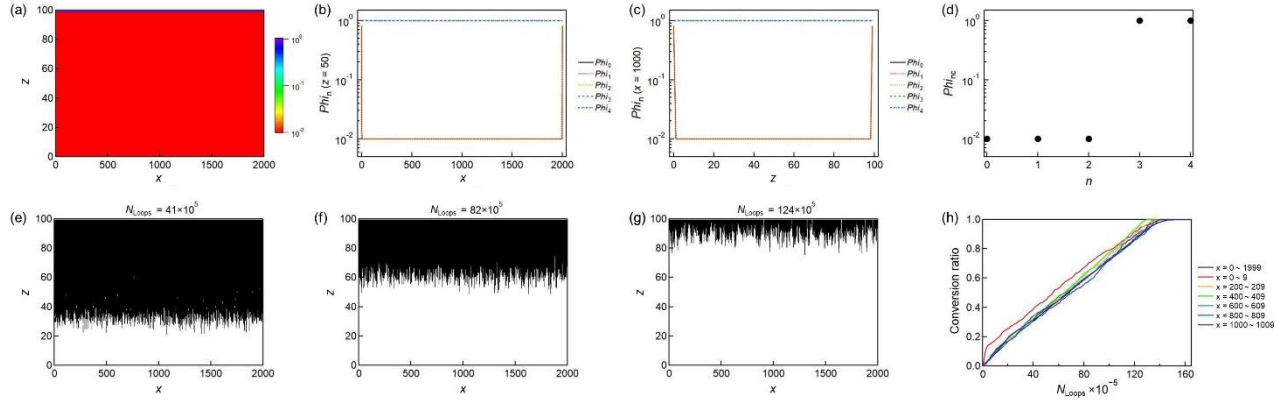

Figure S42. Setups and results of Simulation number 35.

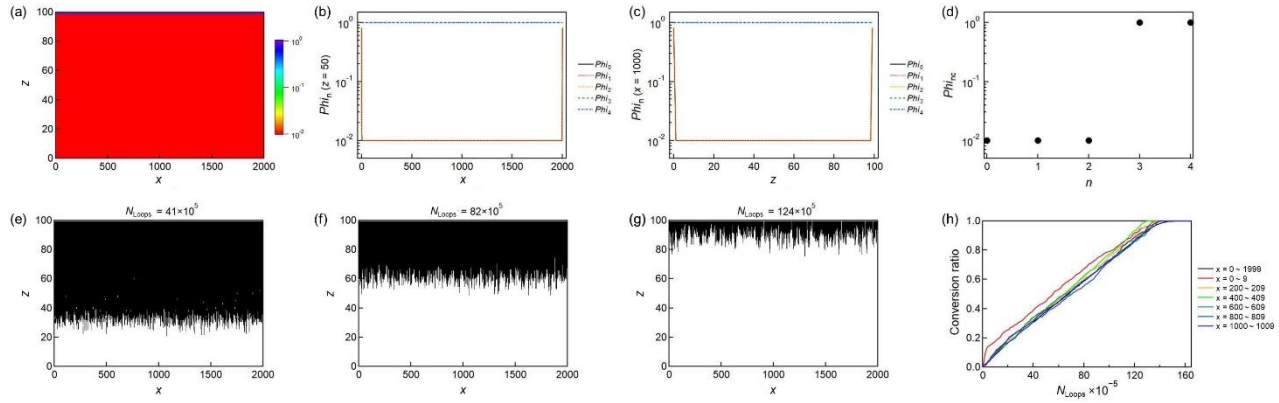

Figure S43. Setups and results of Simulation number 36.

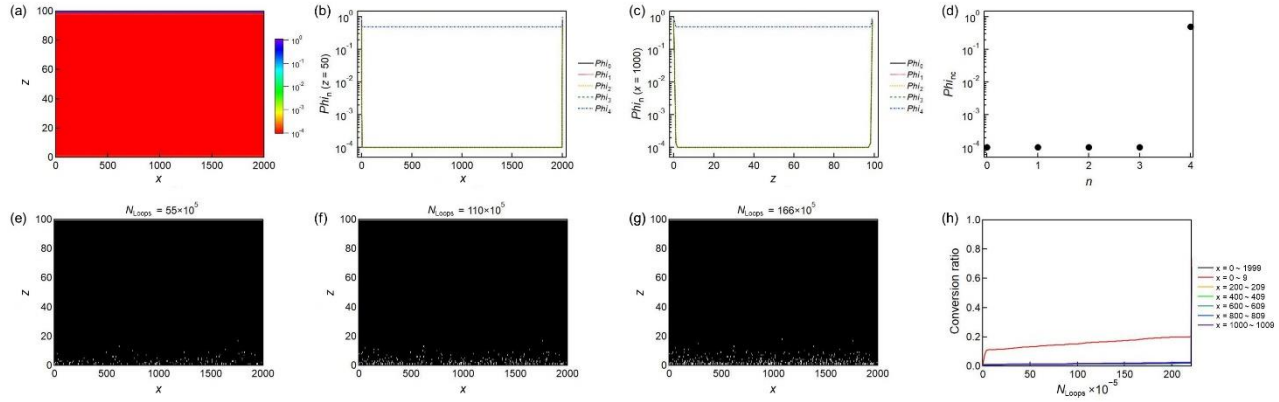

Figure S44. Setups and results of Simulation number 37.

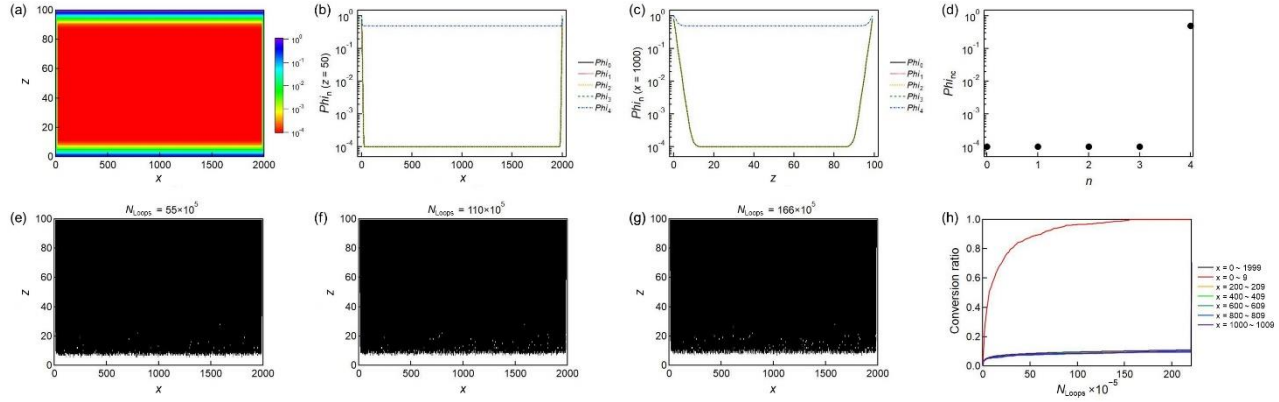

Figure S45. Setups and results of Simulation number 38.

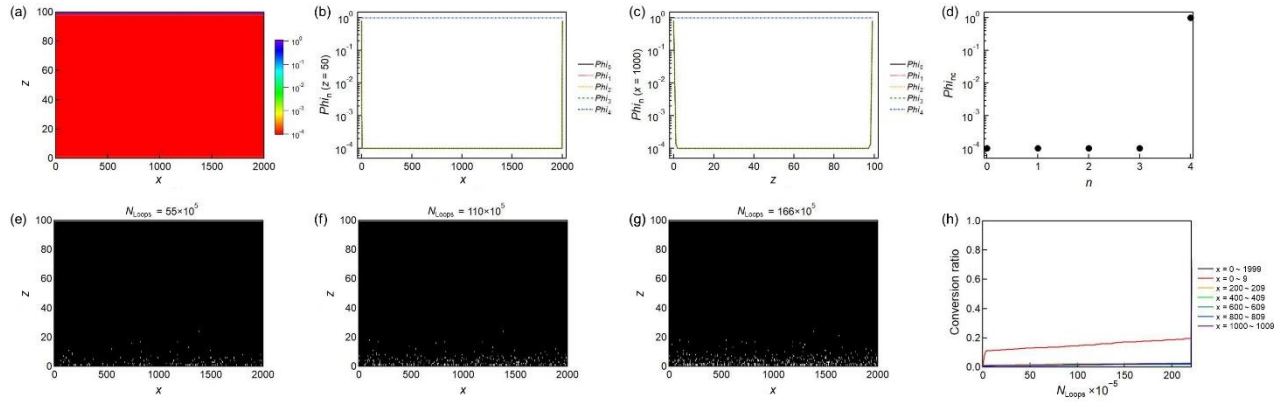

Figure S46. Setups and results of Simulation number 39.

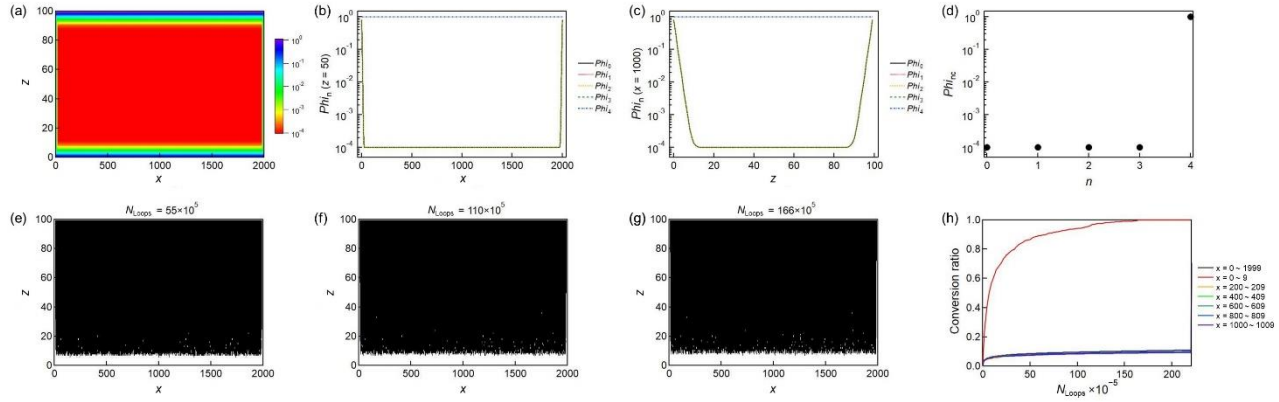

Figure S47. Setups and results of Simulation number 40.

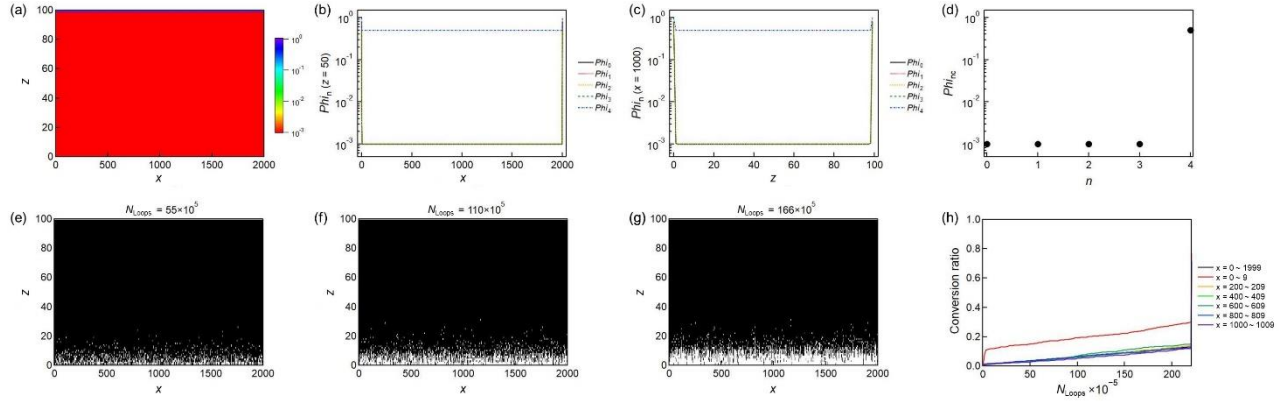

Figure S48. Setups and results of Simulation number 41.

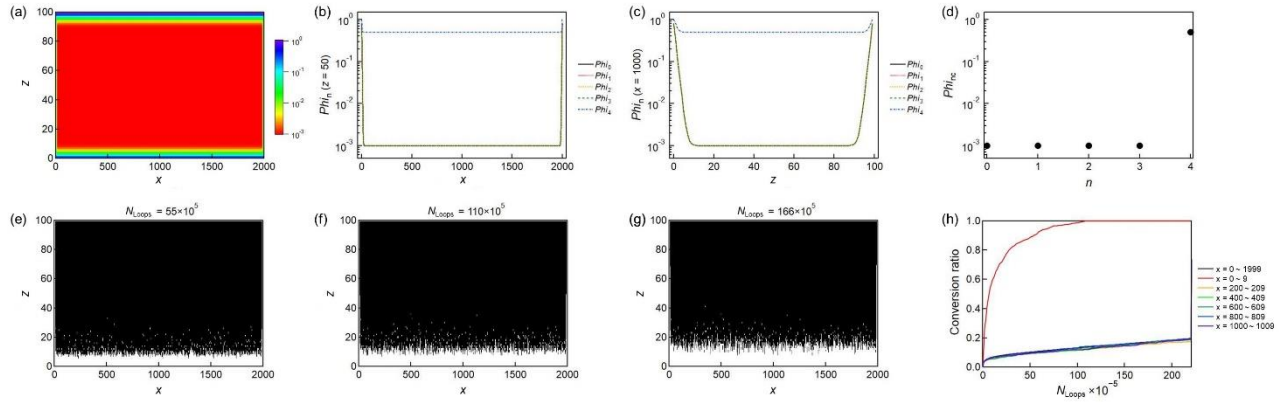

Figure S49. Setups and results of Simulation number 42.

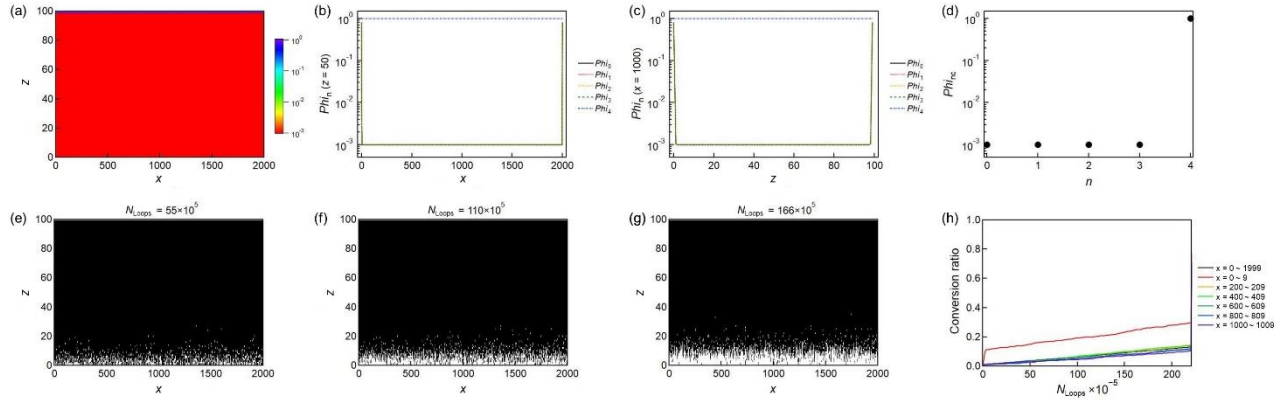

Figure S50. Setups and results of Simulation number 43.

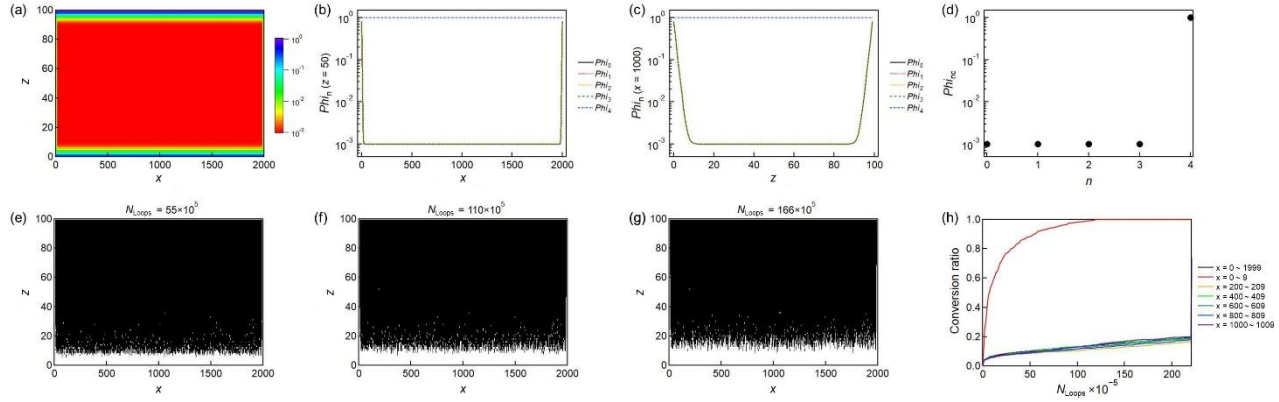

Figure S51. Setups and results of Simulation number 44.

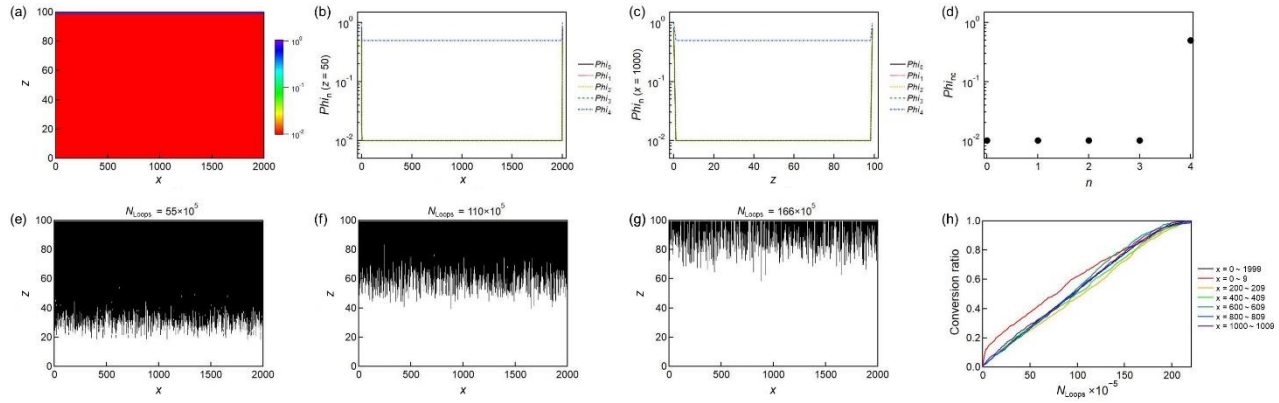

Figure S52. Setups and results of Simulation number 45.

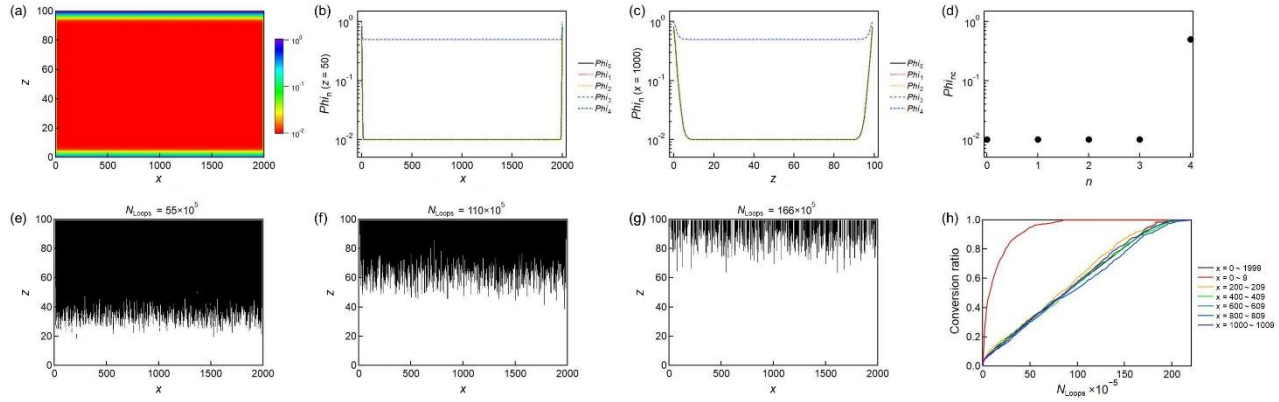

Figure S53. Setups and results of Simulation number 46.

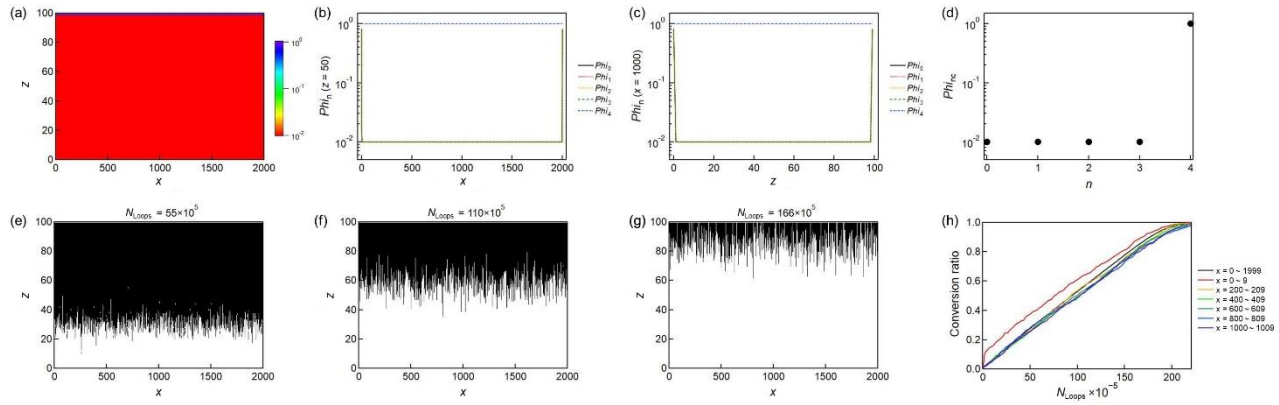

Figure S54. Setups and results of Simulation number 47.

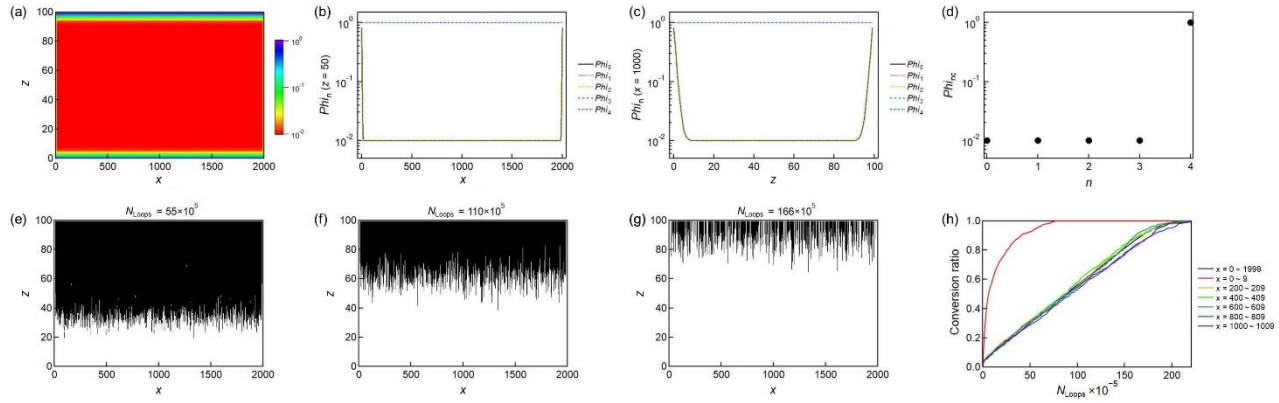

Figure S55. Setups and results of Simulation number 48.

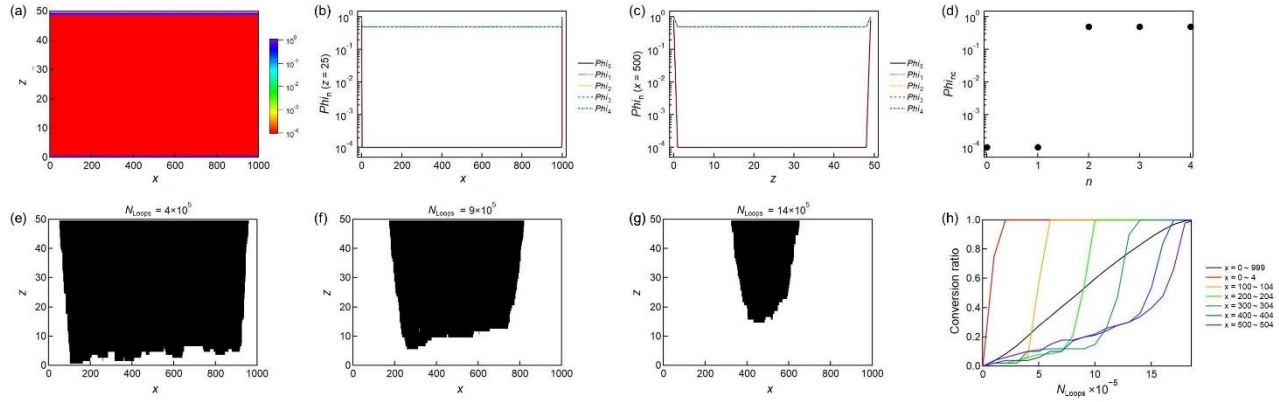

Figure S56. Setups and results of Simulation number 49.

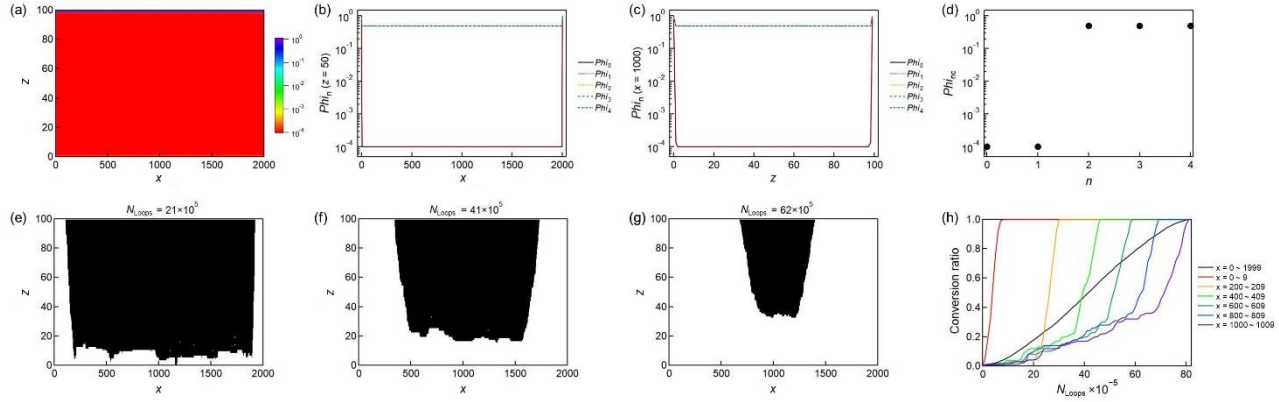

Figure S57. Setups and results of Simulation number 50.

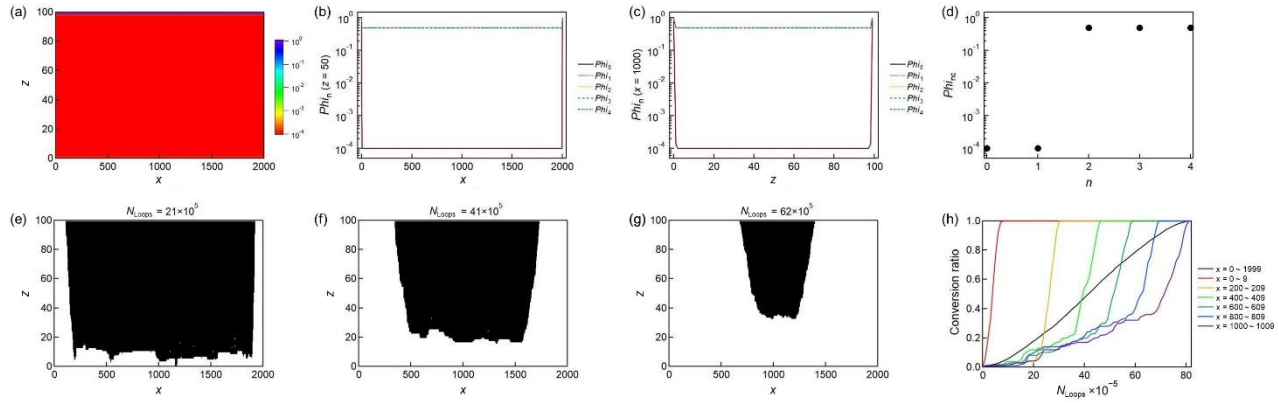

Figure S58. Setups and results of Simulation number 51.

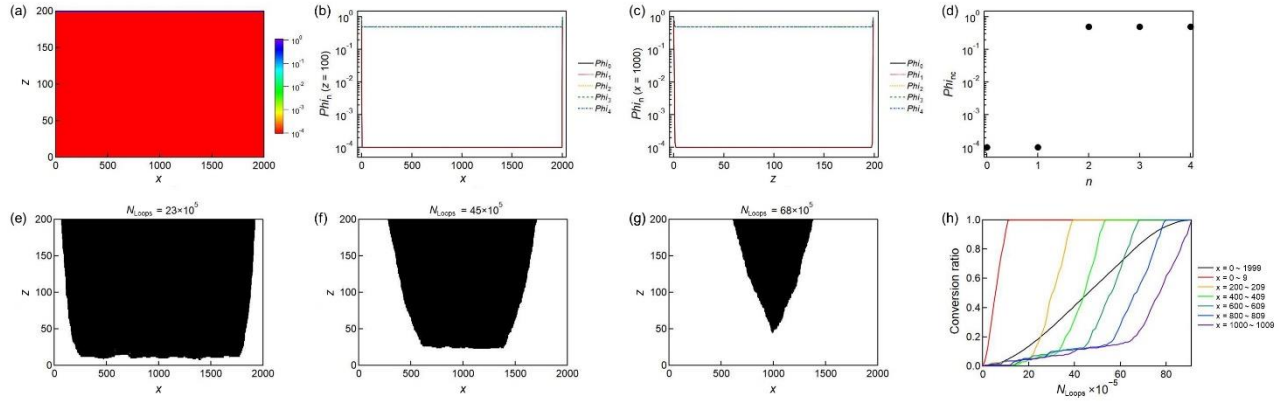

Figure S59. Setups and results of Simulation number 52.

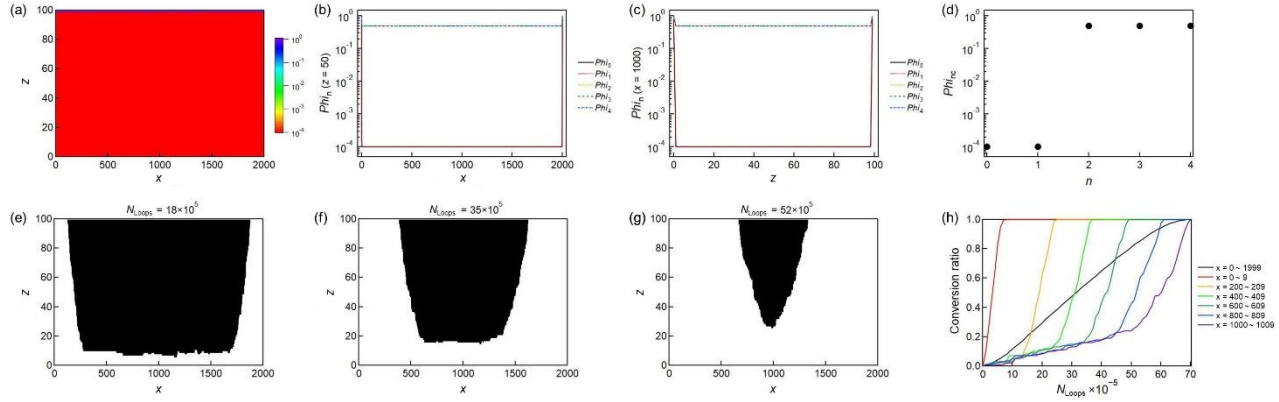

Figure S60. Setups and results of Simulation number 53.

Numerical simulation program that can be run by Igor Pro

```
#pragma TextEncoding = "UTF-8"
#pragma rtGlobals=1
//////////////////////////////////////////////////////////////
Macro simulation(name, Ncells, NPixelsx, NPixelsz, epsilon, Phi0c, Phinc, Edge, Cedge, ns)
String name = "test1"
Variable Ncells = 5
Variable NPixelsx=2000
Variable NPixelsz=100
Variable epsilon = 30000
Variable Phi0c = 0.0001
Variable Phinc = 0.5
Variable Edge = 0.1
Variable Cedge = 0.8
Variable Save_interval = 100000
Variable ns = 2
Silent 1
PauseUpdate

calculation(name, Ncells, NPixelsx, NPixelsz, epsilon, Phi0c, Phinc, Edge, Cedge, Save_interval,
ns)

End

//////////////////////////////////////////////////////////////
Function calculation(name, Ncells, NPixelsx, NPixelsz, epsilon, Phi0c, Phinc, Edge, Cedge,
Save_interval, ns)
String name
Variable Ncells, NPixelsx, NPixelsz, epsilon, Phi0c, Phinc, Edge, Cedge, Save_interval, ns
```

```
Variable Z = 4
Variable a = 9.6111
Variable b = 7.6534
Variable c = 20.6232
variable Density = 4.3785

Variable molecules_pixels_2 = Z*Ncells*Ncells
Variable Width = a*Ncells*NPixelsx*10^-4
Variable Thickness = c*Ncells*NPixelsz*10^-4
Variable Irradiated_area = b*Width*10^-12
Variable Absorbance = epsilon*Density*10^-4*Thickness

Variable start = datetime
string filename = "simulation(" + name + ")"
NewPath/C/O temporary "C:Users:****:" + filename + ":"

Silent 1
PauseUpdate

// Setting cross section and quantum yields

Make /D/O/N=(NPixelsx, NPixelsz) Cross_section = 0

Make /D/O/N=(10000, 7) Conversion = 1

Make /D/O/N=(NPixelsx, NPixelsz) Phi_edge_cross_section = Cedge*(exp(-x/(2.14*Edge)) +
exp(-(NPixelsx-1-x)/(2.14*Edge)) + exp(-y/Edge) + exp(-(NPixelsz-1-y)/Edge))
```

```
Make /D/O/N=(NPixelsx, NPixelsz, 5) Phi_nc_cross_section = 0
        Phi_nc_cross_section[][][0] = Phi0c

        if(ns == 1)
        Phi_nc_cross_section[][][1] = Phinc
        Phi_nc_cross_section[][][2] = Phinc
        Phi_nc_cross_section[][][3] = Phinc
        Phi_nc_cross_section[][][4] = Phinc

        elseif(ns == 2)
        Phi_nc_cross_section[][][1] = Phi0c
        Phi_nc_cross_section[][][2] = Phinc
        Phi_nc_cross_section[][][3] = Phinc
        Phi_nc_cross_section[][][4] = Phinc

        elseif(ns == 3)
        Phi_nc_cross_section[][][1] = Phi0c
        Phi_nc_cross_section[][][2] = Phi0c
        Phi_nc_cross_section[][][3] = Phinc
        Phi_nc_cross_section[][][4] = Phinc

        elseif(ns == 4)
        Phi_nc_cross_section[][][1] = Phi0c
        Phi_nc_cross_section[][][2] = Phi0c
        Phi_nc_cross_section[][][3] = Phi0c
        Phi_nc_cross_section[][][4] = Phinc

        endif
```

```
Make /D/O/N=(NPixelsx, NPixelsz, 5) Phi_n_cross_section = 0

        Phi_n_cross_section[][][0] = Phi_edge_cross_section[x][y] +
Phi_nc_cross_section[x][y][0]

        Phi_n_cross_section[][][1] = Phi_edge_cross_section[x][y] +
Phi_nc_cross_section[x][y][1]

        Phi_n_cross_section[][][2] = Phi_edge_cross_section[x][y] +
Phi_nc_cross_section[x][y][2]

        Phi_n_cross_section[][][3] = Phi_edge_cross_section[x][y] +
Phi_nc_cross_section[x][y][3]

        Phi_n_cross_section[][][4] = Phi_edge_cross_section[x][y] +
Phi_nc_cross_section[x][y][4]


        Variable x0 = 0, y0 = 0, z0 = 0

        for(z0 = 0; z0 < 5; z0 += 1)

                for(y0 = 0; y0 < NPixelsz; y0 += 1)

                        for(x0 = 0; x0 < NPixelsx; x0 += 1)

                                if(Phi_n_cross_section[x0][y0][z0] > 1)

                                        Phi_n_cross_section[x0][y0][z0] = 1

                                endif

                        endfor

                endfor

        endfor


Make /D/O/N=(5) n_versus_Phi_nc = 0

        n_versus_Phi_nc[0] = Phi_nc_cross_section[0][0][0]

        n_versus_Phi_nc[1] = Phi_nc_cross_section[0][0][1]

        n_versus_Phi_nc[2] = Phi_nc_cross_section[0][0][2]

        n_versus_Phi_nc[3] = Phi_nc_cross_section[0][0][3]

        n_versus_Phi_nc[4] = Phi_nc_cross_section[0][0][4]


Variable NLoops, x1, z1, z2, k
```

```
Variable counter

For(NLoops = 0; sum(Cross_section, -inf, inf)/(NPixelsx*NPixelsz) < 1 ; NLoops += 1)

// Choosing a coordinate of an excited pixel

if (NLoops > 0)

        x1 = floor((enoise(1) + 1)/2*NPixelsx)
        z1 = floor((-NPixelsz/Absorbance*log((enoise(1) + 1)/2)))

        k = 0
        counter = 0

        Do

                If(Cross_section[x1][k] == 1)
                        counter += 1
                Else
                        counter += 0
                Endif

        k += 1
        While(k < z1)

        z2 = z1 + counter

        if(z2 < NPixelsz)
```

```
                do
                        if(Cross_section[x1][z2] == 0)
                                break
                        endif
                        z2 += 1
                        if(z2 >= NPixelsz)
                                break
                        endif
                while(1)

        Endif

// Judging whether to react

if(z2 < NPixelsz)

                if(Cross_section[x1-1][z2] + Cross_section[x1+1][z2] + Cross_section[x1][z2-1]
+ Cross_section[x1][z2+1] >= 4)

                        If((enoise(1) + 1)/2 <= Phi_n_cross_section[x1][z2][4])
                                Cross_section[x1][z2] = 1
                        Endif

                Elseif(Cross_section[x1-1][z2] + Cross_section[x1+1][z2] +
Cross_section[x1][z2-1] + Cross_section[x1][z2+1] >= 3)

                        If((enoise(1) + 1)/2 <= Phi_n_cross_section[x1][z2][3])
                                Cross_section[x1][z2] = 1
                        Endif
```

```
                Elseif(Cross_section[x1-1][z2] + Cross_section[x1+1][z2] +
Cross_section[x1][z2-1] + Cross_section[x1][z2+1] >= 2)

                    If((enoise(1) + 1)/2 <= Phi_n_cross_section[x1][z2][2])

                        Cross_section[x1][z2] = 1

                    Endif

                Elseif(Cross_section[x1-1][z2] + Cross_section[x1+1][z2] +
Cross_section[x1][z2-1] + Cross_section[x1][z2+1] >= 1)

                    If((enoise(1) + 1)/2 <= Phi_n_cross_section[x1][z2][1])

                        Cross_section[x1][z2] = 1

                    Endif

                Else

                    If((enoise(1) + 1)/2 <= Phi_n_cross_section[x1][z2][0])

                        Cross_section[x1][z2] = 1

                    Endif

                Endif

Endif

endif

// Recording reaction process

if(mod(NLoops, Save_interval) == 0)
```

```
Variable ave_n = floor(9/2000*NPixelsx)

Variable interval = NPixelsx/10

Matrixop/O/FREE/O destwave = sum(subrange(Cross_section,0,NPixelsx-
1,0,NPixelsz-1))

Conversion[NLoops/Save_interval][0] = destwave[0][0]/(NPixelsz*NPixelsx)

Matrixop/O/FREE/O destwave =
sum(subrange(Cross_section,interval*0,interval*0+ave_n,0,NPixelsz-1))

Conversion[NLoops/Save_interval][1] = destwave[0][0]/(NPixelsz*(ave_n+1))

Matrixop/O/FREE/O destwave =
sum(subrange(Cross_section,interval*1,interval*1+ave_n,0,NPixelsz-1))

Conversion[NLoops/Save_interval][2] = destwave[0][0]/(NPixelsz*(ave_n+1))

Matrixop/O/FREE/O destwave =
sum(subrange(Cross_section,interval*2,interval*2+ave_n,0,NPixelsz-1))

Conversion[NLoops/Save_interval][3] = destwave[0][0]/(NPixelsz*(ave_n+1))

Matrixop/O/FREE/O destwave =
sum(subrange(Cross_section,interval*3,interval*3+ave_n,0,NPixelsz-1))

Conversion[NLoops/Save_interval][4] = destwave[0][0]/(NPixelsz*(ave_n+1))

Matrixop/O/FREE/O destwave =
sum(subrange(Cross_section,interval*4,interval*4+ave_n,0,NPixelsz-1))

Conversion[NLoops/Save_interval][5] = destwave[0][0]/(NPixelsz*(ave_n+1))

Matrixop/O/FREE/O destwave =
sum(subrange(Cross_section,interval*5,interval*5+ave_n,0,NPixelsz-1))

Conversion[NLoops/Save_interval][6] = destwave[0][0]/(NPixelsz*(ave_n+1))


Display/N=Cross_section ;AppendImage Cross_section

    ModifyImage Cross_section ctab= {0,1,Grays,0}

    textbox/C/N=NLoops/F=0/A=MT/E=2/B=1/X=5.00/Y=1.00
"\\F'Arial'\\Z18\\f02N\\BLoops\\f00\\Z18 = " + num2str(NLoops/Save_interval) + "×" + "10\\S" +
num2str(log(Save_interval))

    SetAxis left 0,NPixelsz

    SetAxis bottom 0,NPixelsx
```

```
                ModifyGraph
margin(top)=36,Width=360,height={Aspect,0.7},tick=2,mirror=2,fSize=18,axThick=1.5,lblMargin
(left)=15,lblMargin(bottom)=10,standoff=0,font="Arial";DelayUpdate

                Label left "\\Z20\\f02z";DelayUpdate

                Label bottom "\\Z20\\f02x"

            SavePICT/O/E=-7/P=temporary as "Cross_section_"+
num2str(NLoops/Save_interval)+ "_" + filename + ".tiff"

            killwindow Cross_section0


endif


if(NLoops*molecules_pixels_2/Irradiated_area >= 3.0*10^19)

    break

endif


Endfor


// Saving results and parameters


Display/N=Conversion Conversion[][0], Conversion[][1], Conversion[][2], Conversion[][3],
Conversion[][4], Conversion[][5], Conversion[][6]

    SetAxis left 0,1

    SetAxis bottom 0,NLoops/Save_interval

    ModifyGraph Width=360, margin(right)=144, rgb(Conversion)=(0,0,0),
rgb(Conversion#2)=(65535,43690,0),rgb(Conversion#3)=(0,65535,0),
rgb(Conversion#4)=(1,39321,19939),rgb(Conversion#5)=(1,16019,65535),rgb(Conversion#6)=(26
411,1,52428),lsize=1.5,
tick=2,mirror=2,fSize=18,axThick=1.5,lblMargin(left)=15,lblMargin(bottom)=15,standoff=0,font=
"Arial",height={Aspect,0.7};DelayUpdate

    Legend/C/N=text0/J/F=0/B=1/A=RC/E=2/X=1/Y=5 "\\Z14\\s(Conversion)\\f02x \\f00= 0
~ " + num2str(NPixelsx-1) + "\r\\s(Conversion#1)\\f02x \\f00= " + num2str(interval*0) + " ~ " +
num2str(interval*0+ave_n) + "\r\\s(Conversion#2)\\f02x \\f00= " + num2str(interval*1) + " ~ " +
num2str(interval*1+ave_n) + "\r\\s(Conversion#3)\\f02x \\f00= " + num2str(interval*2) + " ~ " +
num2str(interval*2+ave_n) + "\r\\s(Conversion#4)\\f02x \\f00= " + num2str(interval*3) + " ~ " +
num2str(interval*3+ave_n) + "\r\\s(Conversion#5)\\f02x \\f00= " + num2str(interval*4) + " ~ " +
```

```
num2str(interval*4+ave_n) + "\r\\s(Conversion#6)\\f02x \\f00= " + num2str(interval*5) + " ~ " +
num2str(interval*5+ave_n);DelayUpdate

        Label left "\\Z20 Conversion ratio";DelayUpdate

        Label bottom "\\Z20\\f02N\\BLoops\\f00\\Z20×10\\S−" + num2str(log(Save_interval))

SavePICT/O/E=-7/P=temporary as "Conversion_" + filename + ".tiff"

killwindow Conversion0

Save/O/J/P=temporary Conversion as "Conversion_" + filename + ".txt"


Save/O/J/P=temporary Phi_n_cross_section as "Phi_n_cross_section_" + filename + ".txt"


display/N=Phinx Phi_n_cross_section[][NPixelsz/2][0], Phi_n_cross_section[][NPixelsz/2][1],
Phi_n_cross_section[][NPixelsz/2][2], Phi_n_cross_section[][NPixelsz/2][3],
Phi_n_cross_section[][NPixelsz/2][4]

        SetAxis left Phi0c/2,1.5

        SetAxis bottom -NPixelsx*0.02,NPixelsx+NPixelsx*0.02

        ModifyGraph    Width=360,
margin(right)=108,log(left)=1,lsize=1.5,rgb(Phi_n_cross_section)=(0,0,0),
rgb(Phi_n_cross_section#2)=(65535,43690,0),rgb(Phi_n_cross_section#3)=(2,39321,1),rgb(Phi_n_
cross_section#4)=(1,16019,65535),lstyle(Phi_n_cross_section#1)=1,
lstyle(Phi_n_cross_section#2)=2, lstyle(Phi_n_cross_section#3)=3,
lstyle(Phi_n_cross_section#4)=4,
height={Aspect,0.7},tick=2,mirror=2,fSize=18,axThick=1.5,lblMargin(left)=20,lblMargin(bottom)
=10,standoff=0,font="Arial",logLabel(left)=0,logHTrip(left)=1,logLTrip(left)=1;DelayUpdate

        Legend/C/N=text0/J/F=0/B=1/A=RC/E=2/X=5/Y=5
"\\Z14\\s(Phi_n_cross_section)\\f02Phi\\f00\\B0 \r\\Z14\\s(Phi_n_cross_section#1)\\f02Phi\\f00\\B1
\r\\Z14\\s(Phi_n_cross_section#2)\\f02Phi\\f00\\B2\r\\Z14\\s(Phi_n_cross_section#3)\\f02Phi\\f00\\
B3\r\\Z14\\s(Phi_n_cross_section#4)\\f02Phi\\f00\\B4"

        Label left "\\Z20\\f02Phi\\f00\\Bn\\M (\\f02z\\f00 = " + num2str(NPixelsz/2) + ")"

        Label bottom "\\Z20\\f02x"

SavePICT/O/E=-7/P=temporary as "Phinx_" + filename + ".tiff"

killwindow Phinx


display/N= Phinz Phi_n_cross_section[NPixelsx/2][][0], Phi_n_cross_section[NPixelsx/2][][1],
Phi_n_cross_section[NPixelsx/2][][2], Phi_n_cross_section[NPixelsx/2][][3],
Phi_n_cross_section[NPixelsx/2][][4]
```

```
		SetAxis left Phi0c/2,1.5

		SetAxis bottom -NPixelsz*0.02,NPixelsz+NPixelsz*0.02

		ModifyGraph Width=360, margin(right)=108,height={Aspect,0.7},
log(left)=1,lsize=1.5,rgb(Phi_n_cross_section)=(0,0,0),
rgb(Phi_n_cross_section#2)=(65535,43690,0),rgb(Phi_n_cross_section#3)=(2,39321,1),rgb(Phi_n_
cross_section#4)=(1,16019,65535),lstyle(Phi_n_cross_section#1)=1,
lstyle(Phi_n_cross_section#2)=2, lstyle(Phi_n_cross_section#3)=3,
lstyle(Phi_n_cross_section#4)=4,
height={Aspect,0.7},tick=2,mirror=2,fSize=18,axThick=1.5,lblMargin(left)=20,lblMargin(bottom)
=10,standoff=0,font="Arial",logLabel(left)=0,logHTrip(left)=1,logLTrip(left)=1;DelayUpdate

		Legend/C/N=text0/J/F=0/B=1/A=RC/E=2/X=5/Y=5
"\\Z14\\s(Phi_n_cross_section)\\f02Phi\\f00\\B0 \r\\Z14\\s(Phi_n_cross_section#1)\\f02Phi\\f00\\B1
\r\\Z14\\s(Phi_n_cross_section#2)\\f02Phi\\f00\\B2\r\\Z14\\s(Phi_n_cross_section#3)\\f02Phi\\f00\\
B3\r\\Z14\\s(Phi_n_cross_section#4)\\f02Phi\\f00\\B4"

		Label left "\\Z20\\f02Phi\\f00\\Bn\\M (\\f02x\\f00 = " + num2str(NPixelsx/2) + ")"

		Label bottom "\\Z20\\f02z"

SavePICT/O/E=-7/P=temporary as "Phinz_" + filename + ".tiff"

killwindow	Phinz


Display/N=Phi_0_cross_section;AppendImage Phi_n_cross_section

		ModifyImage Phi_n_cross_section log=1, ctab= {*,*,Rainbow,0}

		SetAxis left 0,NPixelsz

		SetAxis bottom 0,NPixelsx

		ModifyGraph
margin(right)=108,tick=2,mirror=2,height={Aspect,0.7},fSize=18,axThick=1.5,lblMargin(left)=15,
lblMargin(bottom)=10,standoff=0,font="Arial",Width=360

		ColorScale/C/N=text0/F=0/A=RC/E
image=Phi_n_cross_section,font="Arial",fsize=14,log=1,logLTrip=1,logHTrip=1

		Label left "\\Z20\\f02z";DelayUpdate

		Label bottom "\\Z20\\f02x"

SavePICT/O/E=-7/P=temporary as "Phi_0_cross_section_" + filename + ".tiff"

killwindow Phi_0_cross_section


display/N=n_versus_Phi_nc n_versus_Phi_nc
```

```
		setaxis left Phi0c/2,1.5

		setaxis bottom -0.05, 4.05

		ModifyGraph Width=360, log(left)=1, lsize=1.5, rgb(n_versus_Phi_nc)=(0,0,0),
height={Aspect,0.7},tick=2,mirror=2,fSize=18,axThick=1.5,lblMargin(left)=20,lblMargin(bottom)
=10,standoff=0,font="Arial",logLabel(left)=0,logHTrip(left)=1,logLTrip(left)=1,mode=3,marker=1
9, msize=5;DelayUpdate

		Label left "\\Z20\\f02Phi\\f00\\Bnc";DelayUpdate

		Label bottom "\\Z20\\f02n"

SavePICT/O/E=-7/P=temporary as "n_versus_Phi_nc_" + filename + ".tiff"

killwindow n_versus_Phi_nc0

Save/O/J/P=temporary n_versus_Phi_nc as "n_versus_Phi_nc_" + filename + ".txt"


Make /D/T/O/N=(18,2) Parameters

Parameters[0][0] = "name"

Parameters[0][1] = name

Parameters[1][0] = "Ncells"

Parameters[1][1] = num2str(Ncells)

Parameters[2][0] = "NPixelsx"

Parameters[2][1] = num2str(NPixelsx)

Parameters[3][0] =
"NPixelsz"

Parameters[3][1] = num2str(NPixelsz)

Parameters[4][0] = "Molecules/Pixels^2"

Parameters[4][1] = num2str(Molecules_pixels_2)

Parameters[5][0] = "Width"

Parameters[5][1] = num2str(Width)

Parameters[6][0] = "Thickness"

Parameters[6][1] = num2str(Thickness)

Parameters[7][0] = "Irradiated_area"

Parameters[7][1] = num2str(Irradiated_area)
```

```
Parameters[8][0] = "Epsilon"
Parameters[8][1] = num2str(Epsilon)
Parameters[9][0] = "Absorbance"
Parameters[9][1] = num2str(Absorbance)
Parameters[10][0] = "ns"
Parameters[10][1] = num2str(ns)
Parameters[11][0] = "Phi0c"
Parameters[11][1] = num2str(Phi0c)
Parameters[12][0] = "Phinc"
Parameters[12][1] = num2str(Phinc)
Parameters[13][0] = "Edge"
Parameters[13][1] = num2str(Edge)
Parameters[14][0] = "Cedge"
Parameters[14][1] = num2str(Cedge)
Parameters[15][0] = "Save_interval"
Parameters[15][1] = num2str(Save_interval)
Parameters[16][0] = "NLoops"
Parameters[16][1] = num2str(NLoops)
Parameters[17][0] = "Photons/Irradiated_area"
Parameters[17][1] = num2str(NLoops*molecules_pixels_2/Irradiated_area)

Save/O/J/P=temporary Parameters as "Parameters_" + filename + ".txt"

variable timeElapsed = dateTime - start
print "This procedure took " + num2str(timeElapsed) + " in seconds."
beep

End
////////////////////////////////////////////////////////////
```

References

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[S2] K. Tashiro, H. Yamamoto, K. Sugimoto, T. Takahama, M. Tanaka, M. Hasegawa, *Macromolecules* **2019**, *52*, 2189–2202.

[S3] K. Morimoto, H. Tsujioka, D. Kitagawa, S. Kobatake, *Bull. Chem. Soc. Jpn.* **2019**, *92*, 1299–1304.

[S4] K. Morimoto, D. Kitagawa, F. Tong, K. Chalek, L. J. Mueller, C. J. Bardeen, S. Kobatake, *Angew. Chem. Int. Ed.* **2022**, *61*, e202114089; *Angew. Chem.* **2022**, *134*, e202114089.