Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B

Shape-controlled fabrication of micron-scale surface chemical gradients via electrochemically activated copper(I) “click” chemistry

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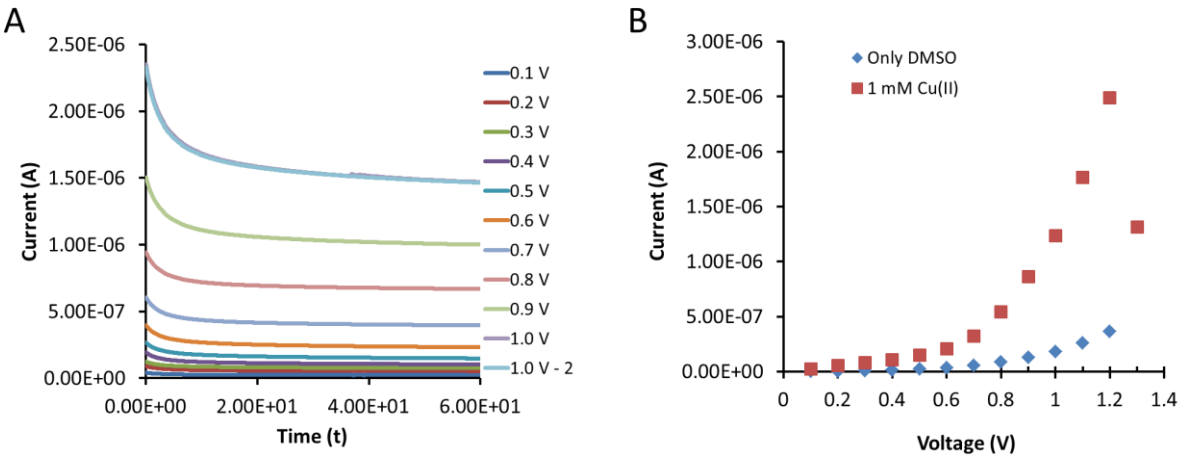
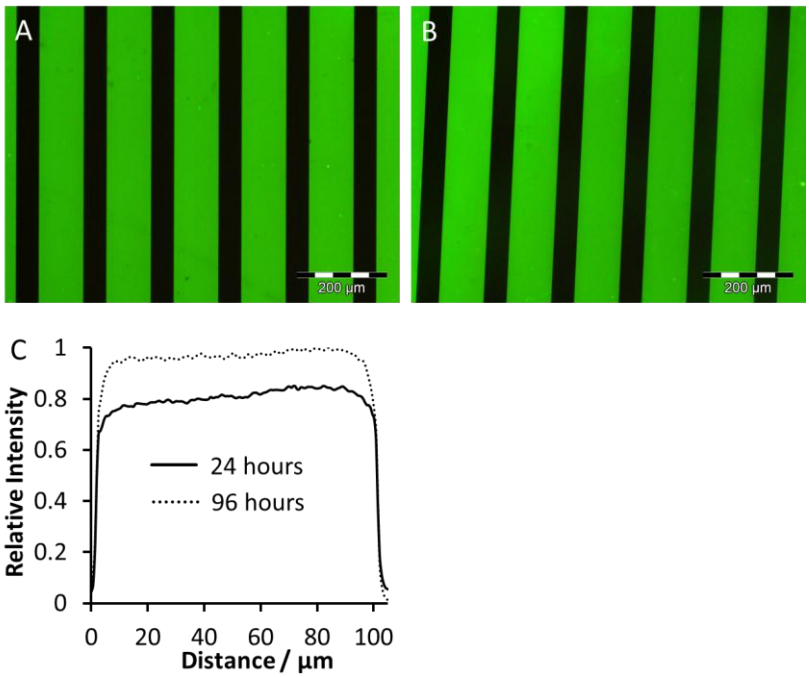
Supporting Information



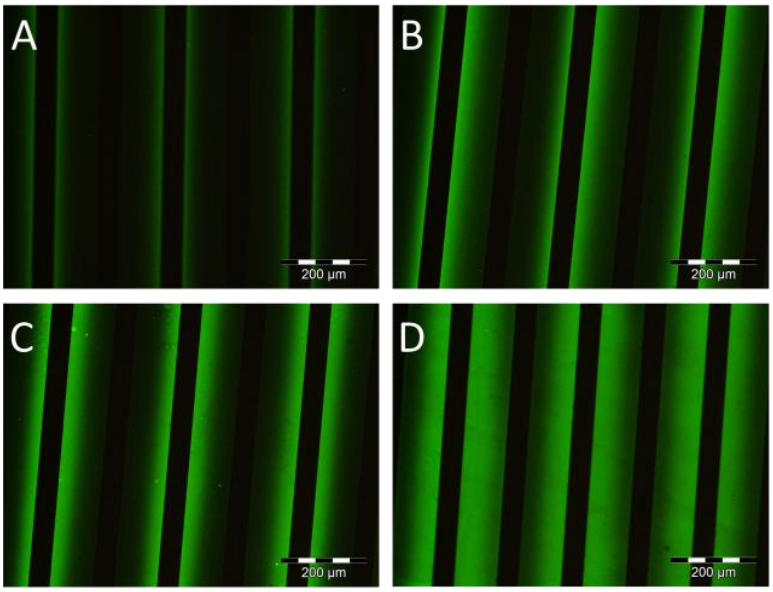
S1 Graphs of A) Current vs. Time for a solution of 1mM $CuSO_4$ in DMSO and B) current vs. potential for a solution of 1mM $CuSO_4$ in DMSO (▪) and only DMSO (♦).



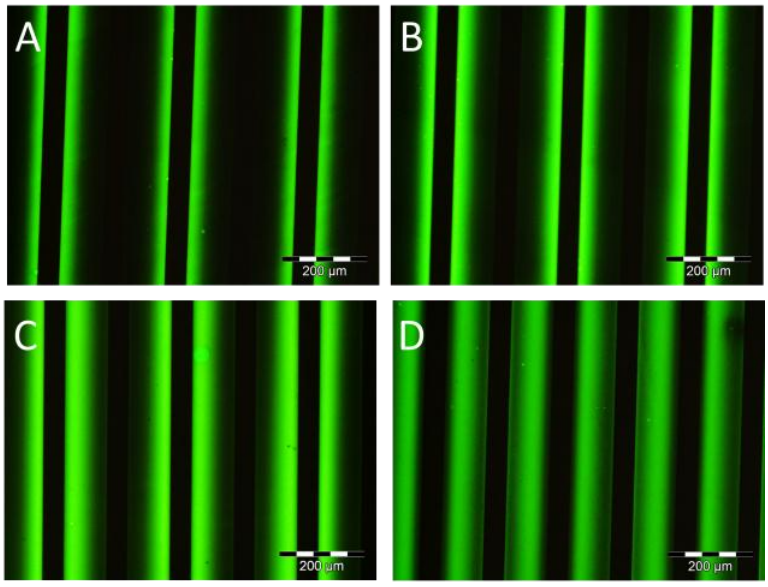
S2 Fluorescence microscopy images after A) 24 hours and B) 96 hours incubation of an azide functionalized substrate in 1mM solution of **1**, 10uM $CuSO_4$ and 1mM ascorbic acid in tert-butanol/water=1/2. C) Intensity profile of the images A) and B).

[Cu(II)] (mM)	Ligand / [ligand] (mM)	Supporting electrolyte (mM)	Potential (V)	Reaction time (min)	Gap size (µm)	*m* (μm^{-1})	R^2	Linear range [µm]	I_{max}
1. 0.2	TBTA/0.2	Na_2SO_4 0.8	1.0	4	100	0.042	0.995	13.7	0.917
2. 0.2	TBTA/0.2	Na_2SO_4 0.8	1.0	8	100	0.052	0.998	16.3	1.142
3. 1.0	TBTA/1.0	/	1.0	1	100	0.030	0.998	22.8	0.920
4. 1.0	/	/	1.0	4	100	0.007	0.993	42.3	0.477
5. 1.0	/	/	1.0	2	100	0.006	0.983	34.5	0.416
6. 1.0	/	/	1.0	1	100	0.004	0.975	24.7	0.188
7. 0.2	TBTA/0.2	Na_2SO_4 0.8	1.0	2	50	0.045	0.999	9.8	0.710
8. 0.2	TBTA/0.2	Na_2SO_4 0.8	1.0	1	50	0.028	0.993	8.5	0.363
9. 1.0	TBTA/1.0	/	1.0	1	50	0.026	0.984	16.3	0.620
10. 0.2	TBTA/0.2	Na_2SO_4 0.8	1.0	1	25	0.014	0.984	10.4	0.382
11. 0.2	TBTA/0.2	Na_2SO_4 0.8	1.0	2	25	0.029	0.991	8.5	0.575
12. 0.2	TBTA/0.2	Na_2SO_4 0.8	1.0	1	10/50	0.036	0.987	6.5	0.436
13. 0.2	TBTA/0.2	Na_2SO_4 0.8	1.0	1	10/5	0.072	0.968	3.2	0.455
14. 1.0	2,6-lut./100	/	0.4	4	100	0.013	0.996	13.0	0.304
15. 1.0	2,6-lut./100	/	0.6	4	100	0.023	0.991	14.3	0.604
16. 1.0	2,6-lut./100	/	0.8	4	100	0.017	0.997	40.3	1.114
17. 1.0	2,6-lut./100	/	1.0	4	100	0.018	0.998	47.5	1.130
18. 1.0	2,6-lut./100	/	0.4	4+8	100	0.017	0.997	22.8	0.622
19. 1.0	2,6-lut./100	/	0.4	4+8+16	100	0.022	0.998	26.0	0.997
20. 1.0	2,6-lut./100	/	0.4	28	100	0.022	0.998	32.5	1.095
21. 1.0	2,6-lut./100	/	0.6	4+8	100	0.020	0.996	32.5	1.043
22. 0.2	2,6-lut./20	Na_2SO_4 0.8	1.0	4	100	0.020	0.972	7.8	0.291
23. 0.2	2,6-lut./20	Na_2SO_4 0.8	1.0	8	100	0.044	0.967	4.6	0.522
24. 0.2	2,6-lut./20	Na_2SO_4 0.8	1.0	16	100	0.032	0.995	9.8	0.558
25. 5.0	2,6-lut./500	/	1.0	1	100	0.018	0.998	20.8	0.713
26. 5.0	2,6-lut./500	/	1.0	2	100	0.024	0.997	34.5	1.163
27. 5.0	2,6-lut./500	/	1.0	4	100	0.021	0.998	47.5	1.267
28. 1.0	2,6-lut./100	nBu_4NBF_4 100	1.0	2	100	0.007	0.997	12.4	0.160
29. 1.0	2,6-lut./100	nBu_4NBF_4 100	1.0	4	100	0.007	0.994	29.9	0.329
30. 1.0	2,6-lut./100	nBu_4NBF_4 100	1.0	8	100	0.010	0.998	39.7	0.563
31. 1.0	2,6-lut./100	nBu_4NBF_4 100	1.0	16	100	0.011	0.996	31.9	0.610
32. 1.0	2,6-lut./100	nBu_4NBF_4 100	1.0	32	100	0.013	0.997	37.1	0.828
33. 1.0	2,6-lut./100	/	1.0	4	100	0.034	0.997	5.9	0.318
34. 1.0	2,6-lut./100	/	1.0	4	100	0.008	0.998	65.1	0.702

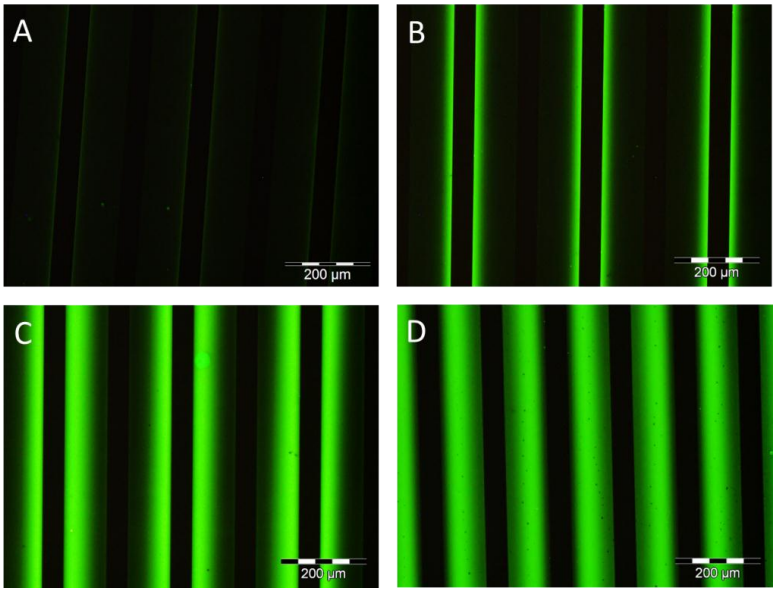
Table S1 Table of the slope, correlation coefficient (R^2), linear range and maximum of intensity near the cathode (Imax) as function of the reaction conditions.



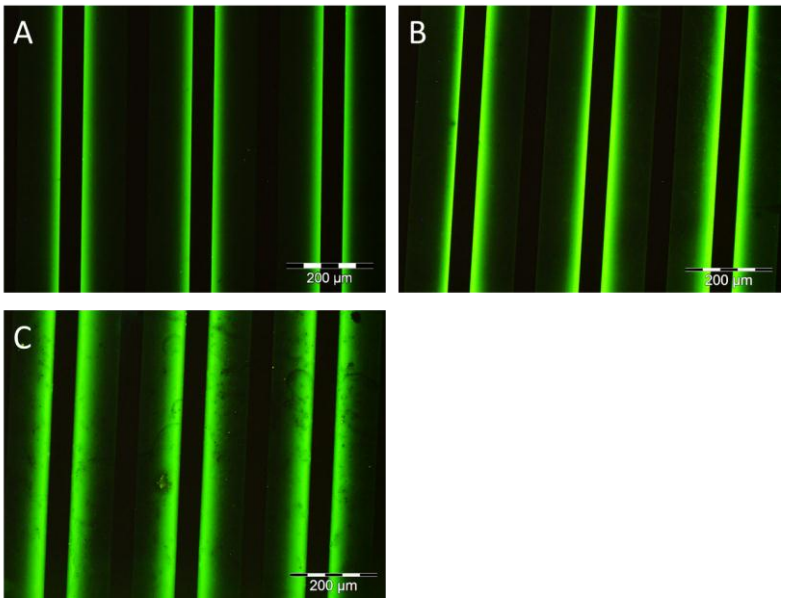
S3 Fluorescence microscopy images of surface chemical gradients of **1** obtained using 1mM of **1** and 1 mM $CuSO_4$ in DMSO, at the potential difference of 1.0 V for various reaction time: A) 1 min; B) 2 min; C) 4 min; and D) 8 min.



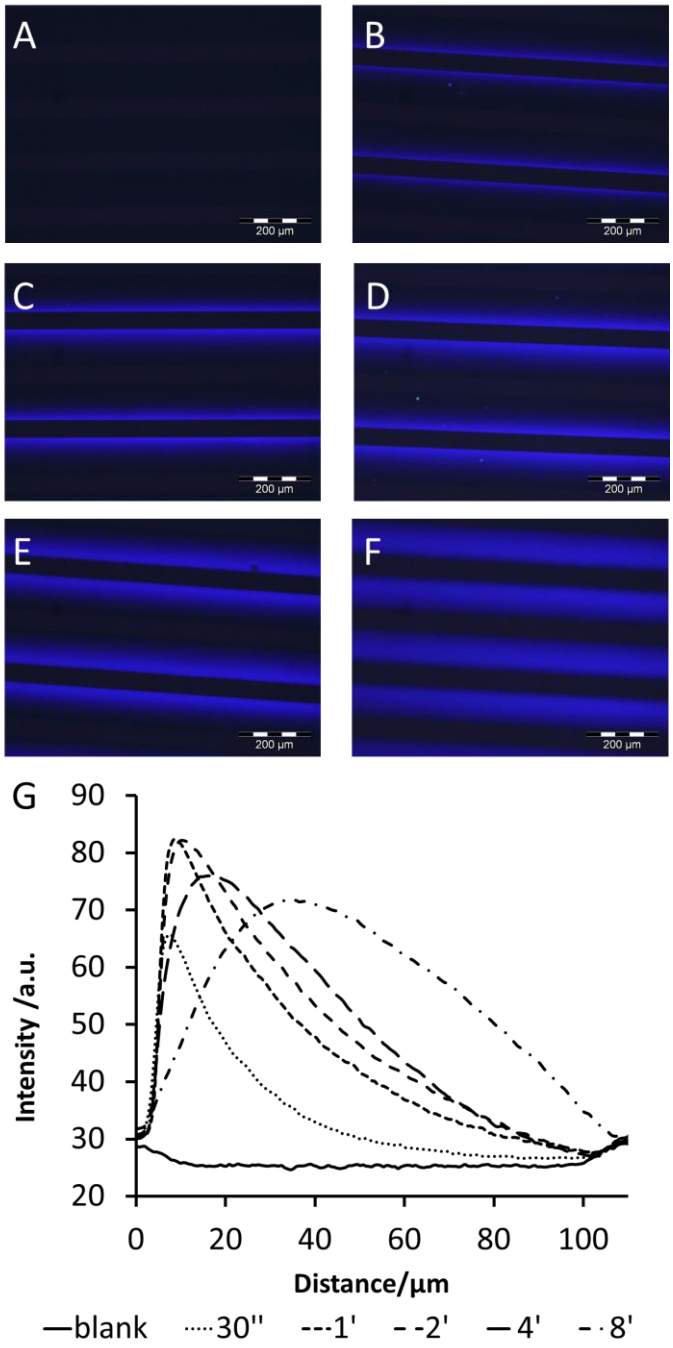
S4 Fluorescence microscopy images of surface chemical gradients of **1** obtained using 1mM of **1** and 1 mM $CuSO_4$/TBTA in DMSO, at the potential difference of 1.0 V for various reaction time: A) 1 min; B) 2 min; C) 4 min; and D) 8 min.



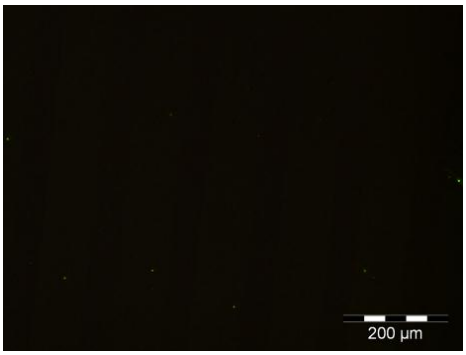
S5 Fluorescence microscopy images of surface chemical gradients of **1** obtained using 1mM of **1** in DMSO, at the potential difference of 1.0 V for 4 min reaction time and different $CuSO_4$/TBTA concentrationc; A) 0.05 mM $CuSO_4$/TBTA and 0.95 mM Na_2SO_4; B) 0.2 mM $CuSO_4$/TBTA and 0.8 mM Na_2SO_4; C) 1.0 mM $CuSO_4$/TBTA; D) 5.0 mM $CuSO_4$/TBTA.



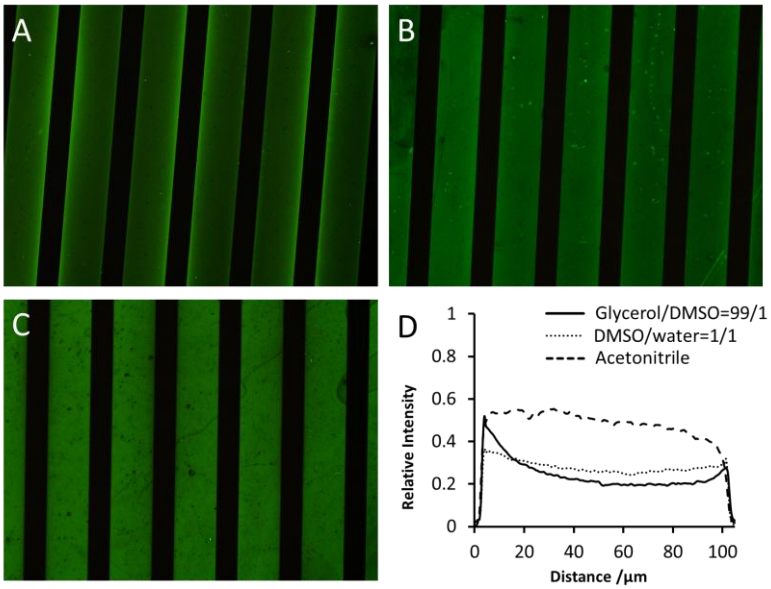
S6 Fluorescence microscopy images of surface chemical gradients of **1** obtained using 1mM **1** in DMSO, 0.2 mM $CuSO_4$ and TBTA and 0.8 mM Na_2SO_4, at the potential difference of 1.0 V for A) 4 min, B) 8 min, C) 16 min reaction time.



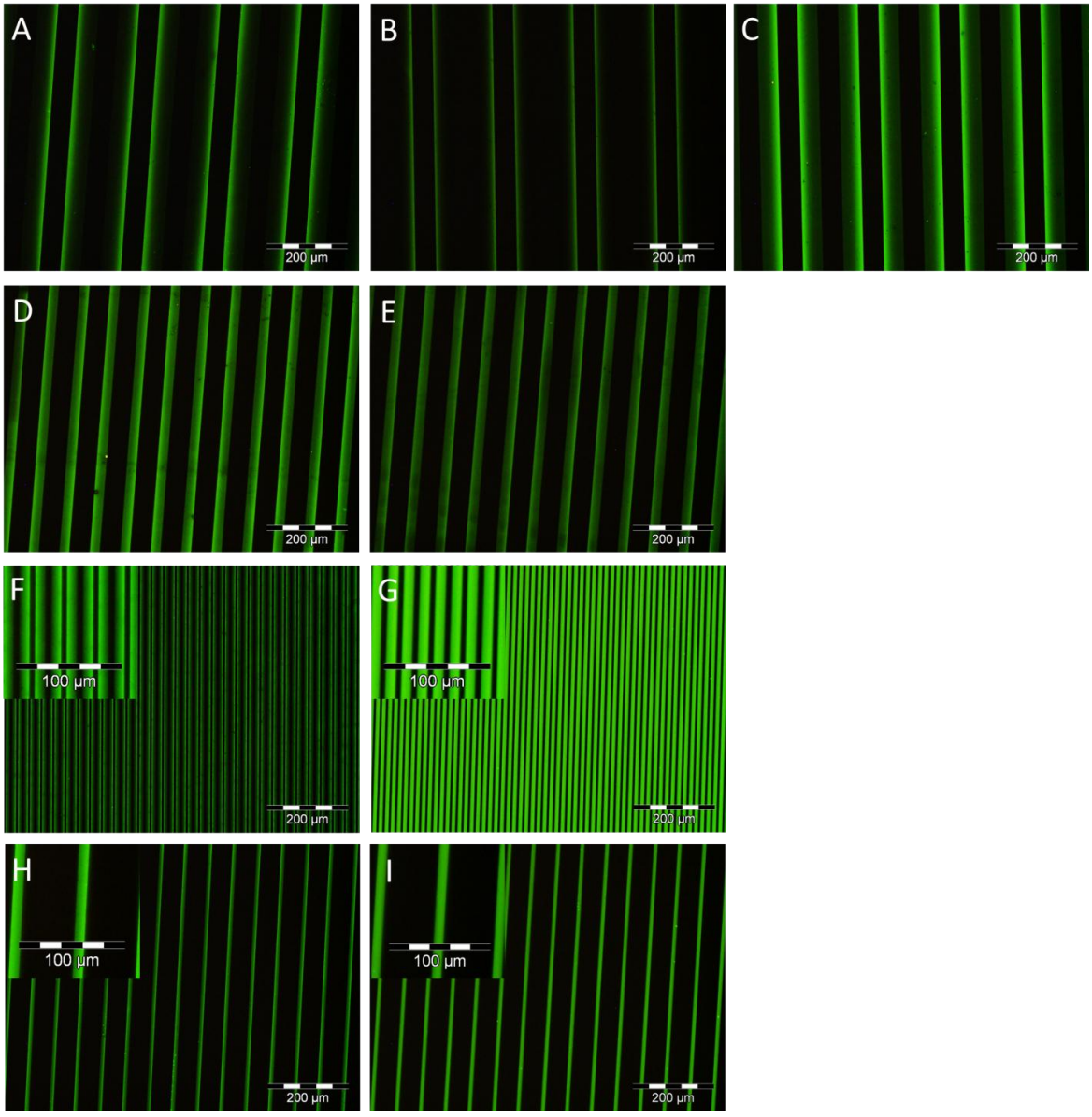
S7. Fluorescence microscopy images obtained reacting 1 mM of **2** in the presence of 1.0 mM $CuSO_4$ and 1.0 mM TBTA in DMSO at the potential difference of 1.0 V for various reaction time: A) 0 sec; B) 30 sec; C) 1 min; D) 2 min; E) 4 min; F) 8 min. Images were recorded at an excitation wavelength of 350 nm and an emission wavelength of 420 nm (long pass filter); exposure time: 1000 ms. G) Intensity profiles of the surface chemical gradients obtained reacting 1 mM of **2** in in the presence of 1 mM $CuSO_4$ and 1 mM TBTA in DMSO at the potential difference of 1.0 V upon various reaction time.



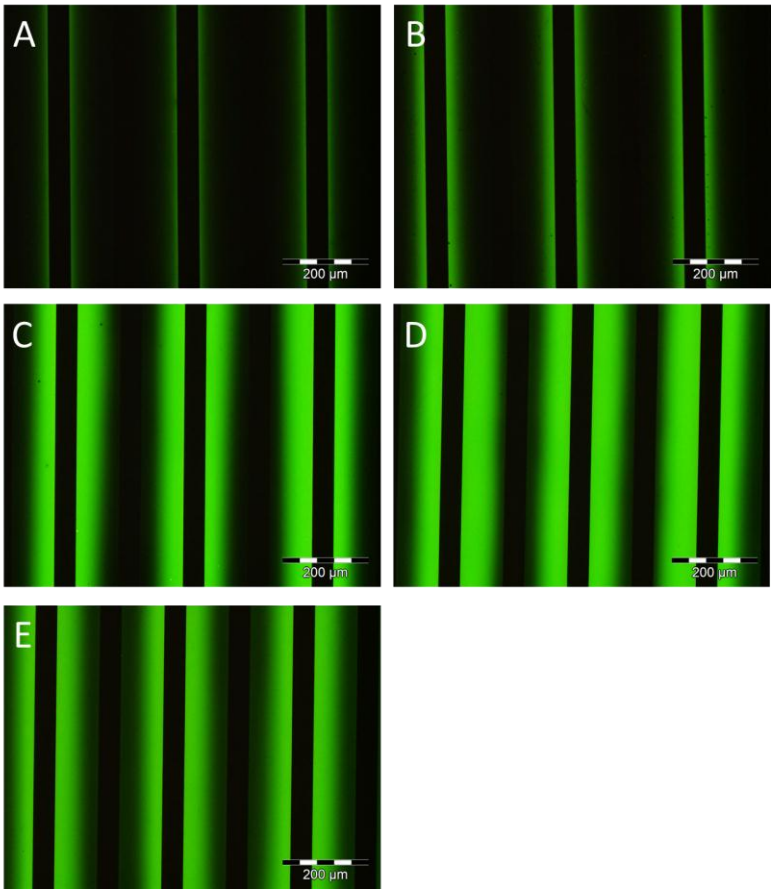
S8 Fluorescence microscopy image recorded after electrochemically activated CuAAC in the presence of 1mM **1** in DMSO (without $CuSO_4$) upon application of 1.0V for 4 min (λ_{ex}=460-490nm, λ_{em}=520nm, exposure time 400 ms)



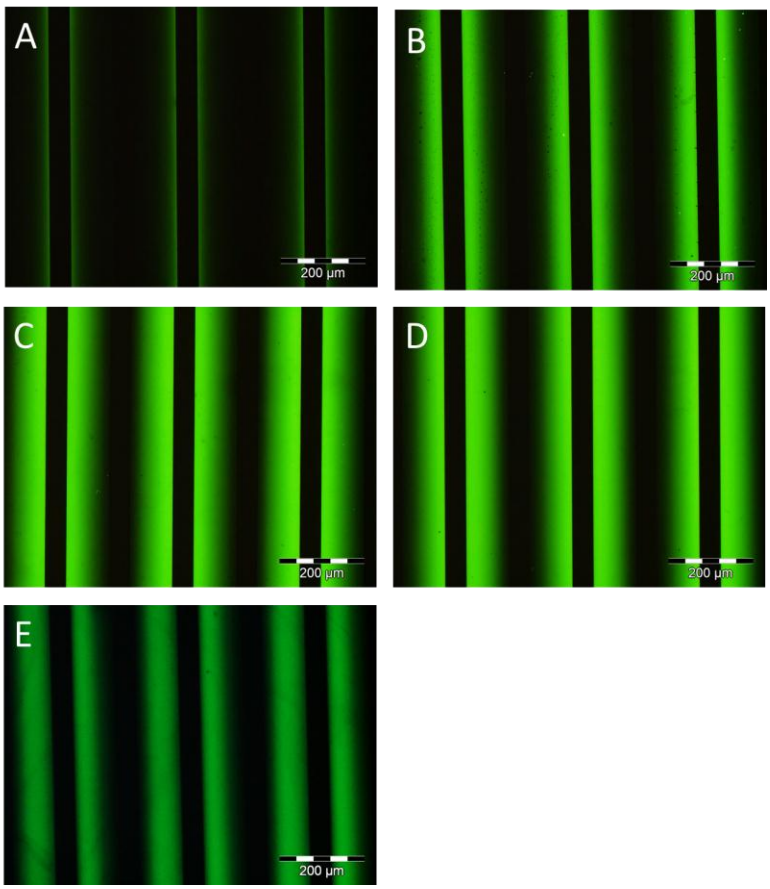
S9 Fluorescence microscopy images after reaction of 1 mM **1**, 1 mM $CuSO_4$, 1 mM TBTA, at the potential difference of 1.0 V for 4 min in A) glycerol/DMSO=99/1; B) DMSO/water=1/1; C) acetonitrile. D) Intensity profile of the previous images.



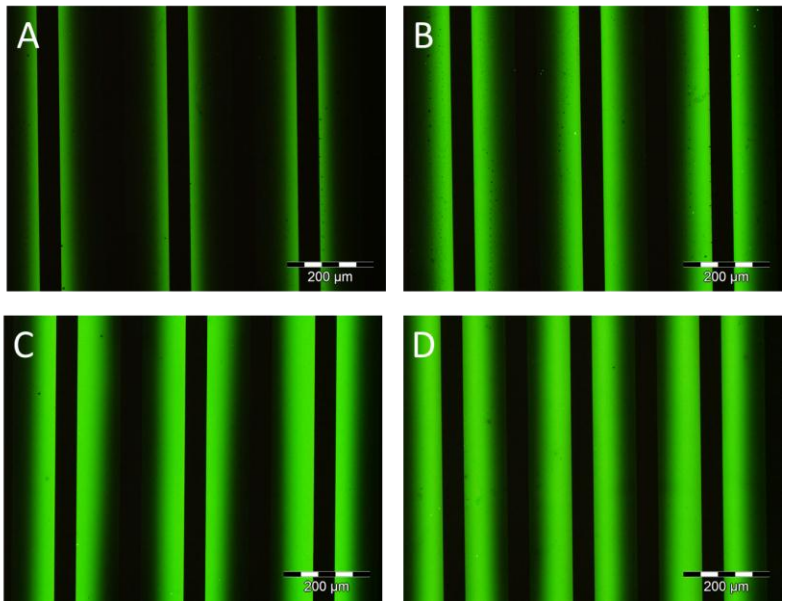
S10 Fluorescence microscopy images of surface chemical gradients of **1** obtained using 1mM of **1** in DMSO, and 1.0 V for 50 µm gap width at A) 1.0 mM $CuSO_4$/TBTA for 1 min; B) 0.2 mM $CuSO_4$/TBTA (0.8 mM Na_2SO_4) for 1 min; C) 0.2 mM $CuSO_4$/TBTA (0.8 mM Na_2SO_4) for 2 min; for 25 µm gap width at D) 0.2 mM $CuSO_4$/TBTA (0.8 mM Na_2SO_4) for 2 min; E) 0.2 mM $CuSO_4$/TBTA (0.8 mM Na_2SO_4) for 1 min; for 10 µm gap width (and 10 µm electrode width) at F) 0.2 mM $CuSO_4$/TBTA (0.8 mM Na_2SO_4) for 1 min; G) 1.0 mM $CuSO_4$/TBTA (0.8 mM Na_2SO_4) for 1 min; for 10 µm gap width (and 50 µm electrode width) at H) 0.2 mM $CuSO_4$/TBTA (0.8 mM Na_2SO_4) for 1 min; I) 1.0 mM $CuSO_4$/TBTA (0.8 mM Na_2SO_4) for 1 min;



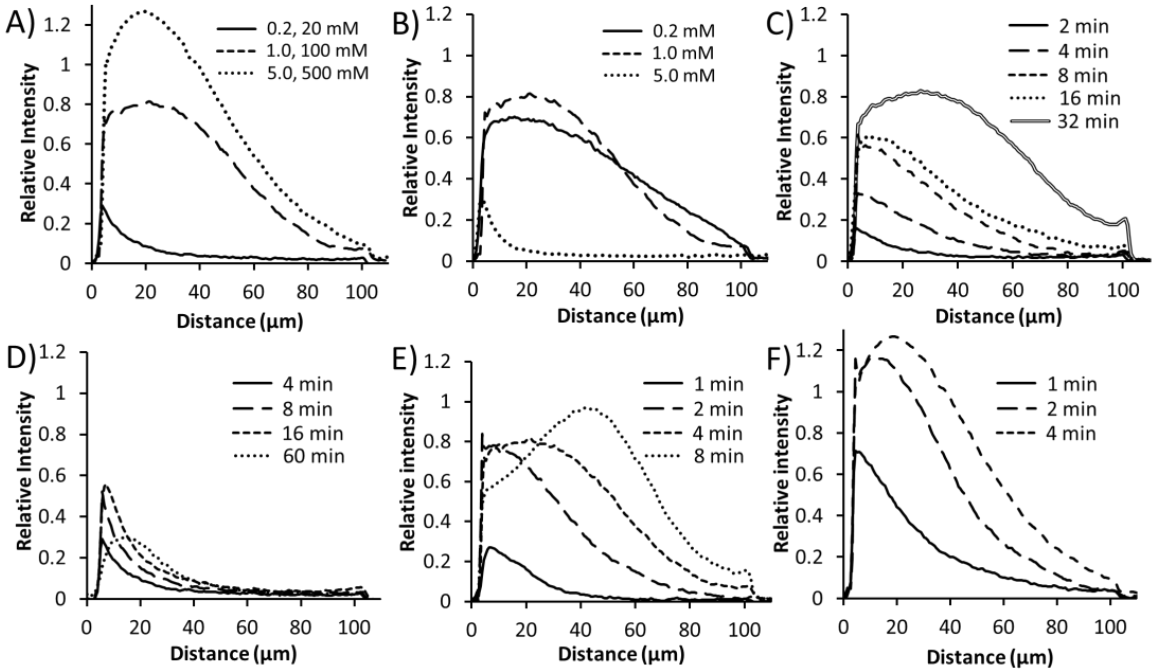
S11 Fluorescence microscopy images obtained reacting 1 mM of **1** in the presence of 1 mM $CuSO_4$ and 100 mM 2,6-lutidine in DMSO for 4 min reaction at potential difference: A) 0.4 V; B) 0.6 V; C) 0.8 V; D) 1.0 V; E) 1.2V.



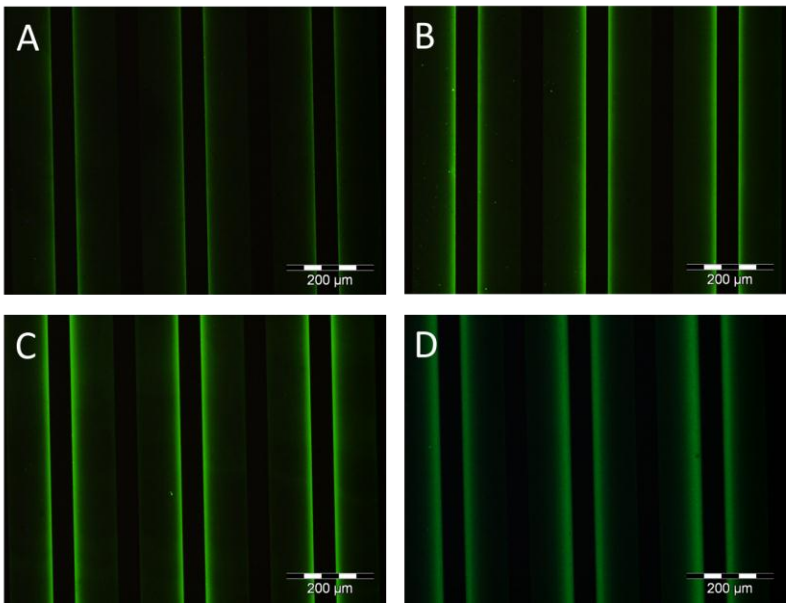
S12 Fluorescence microscopy images obtained reacting 1 mM of **1** in the presence of 1 mM $CuSO_4$ and 100 mM 2,6-lutidine in DMSO at the potential difference of 0.4 V for: A) 4 min; B) 4+ 8 min; C) 4+8+16 min; D) 28 min; E) 60 min.



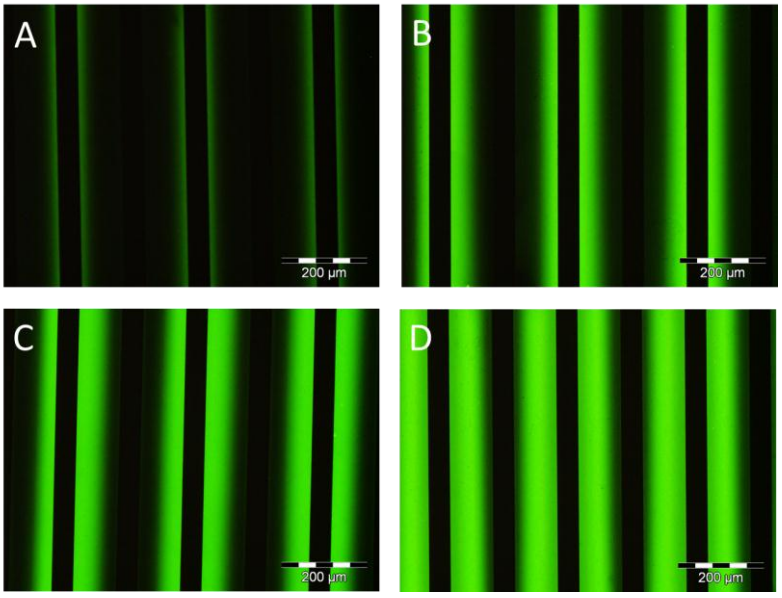
S13 Fluorescence microscopy images obtained reacting 1 mM of **1** in the presence of 1 mM $CuSO_4$ and 100 mM 2,6-lutidine in DMSO at the potential difference of 0.6 V for: A) 4 min; B) 4+ 8 min; and 0.8 V: C) 4 min; D) 4+8 min.



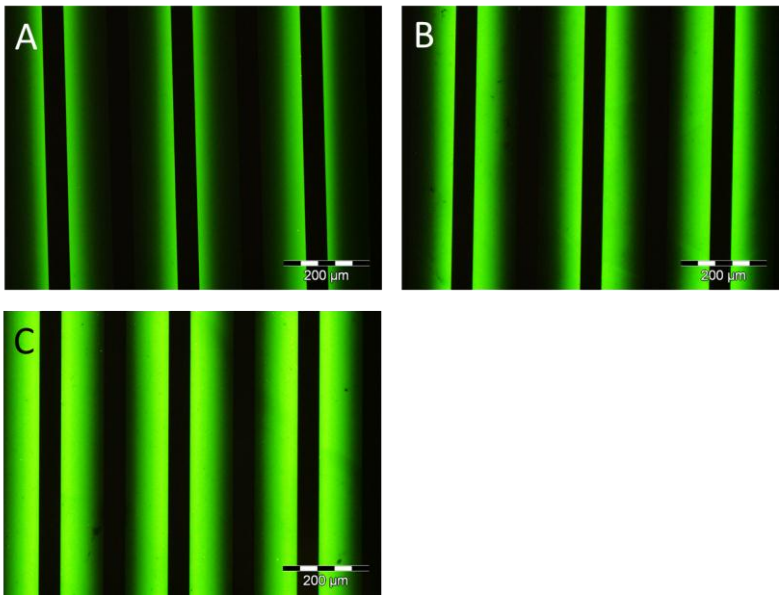
S14 Fluorescence intensity profiles of the surface chemical gradients obtained reacting **1** in DMSO at a potential difference of 1.0 V in the presence of A) different $CuSO_4$/2,6-lutidine concentrations for 4 min reaction; B) $CuSO_4$/2,6-lutidine at 1.0/100 mM for different concentrations of **1** for 4 min reaction. C) 1.0/100 mM and 100 mM of n-Bu_4NBF_4 at different reaction times; and for different reaction times in the presence of different $CuSO_4$/2,6-lutidine concentrations A) 0.2/20 mM; B) 1/100 mM; C) 5/500 mM. (see Figure S15-20, for the fluorescence images);



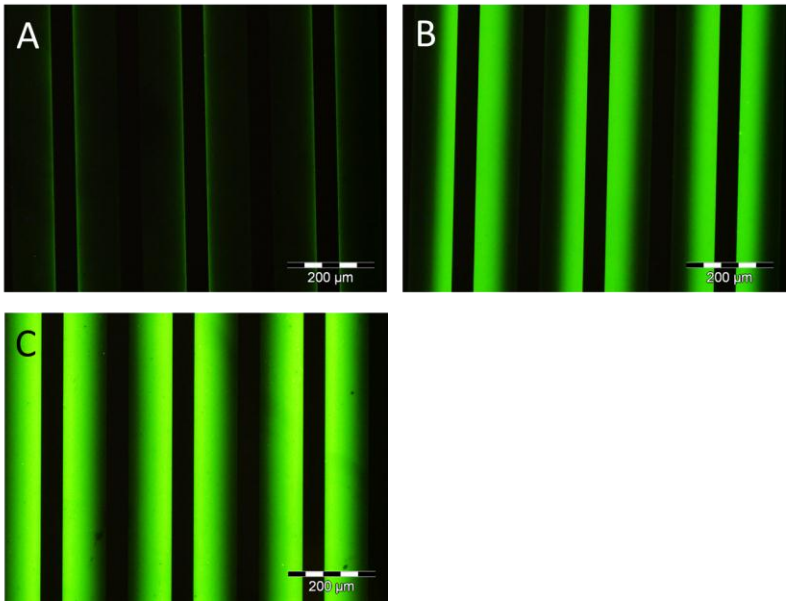
S15 Fluorescence microscopy images obtained reacting 1 mM of **1** in the presence of 0.2 mM $CuSO_4$, 0.8 mM Na_2SO_4 and 20 mM 2,6-lutidine in DMSO for various reaction time at the potential difference of 1.0 V: A) 4 min; B) 8 min; C) 16 min; D) 60 min.



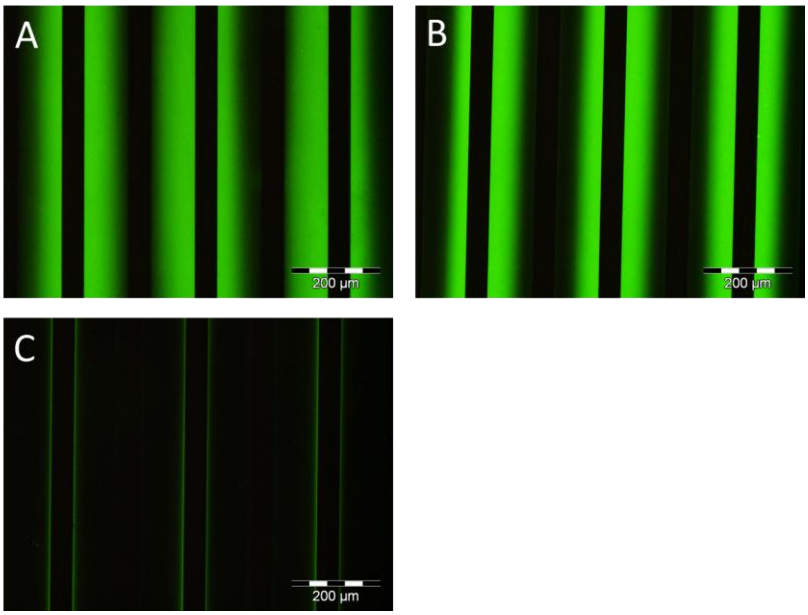
S16 Fluorescence microscopy images obtained reacting 1 mM of **1** in the presence of 1.0 mM $CuSO_4$ and 100 mM 2,6-lutidine in DMSO for various reaction time at the potential difference of 1.0 V: A) 1 min; B) 2 min; C) 4 min; D) 8 min.



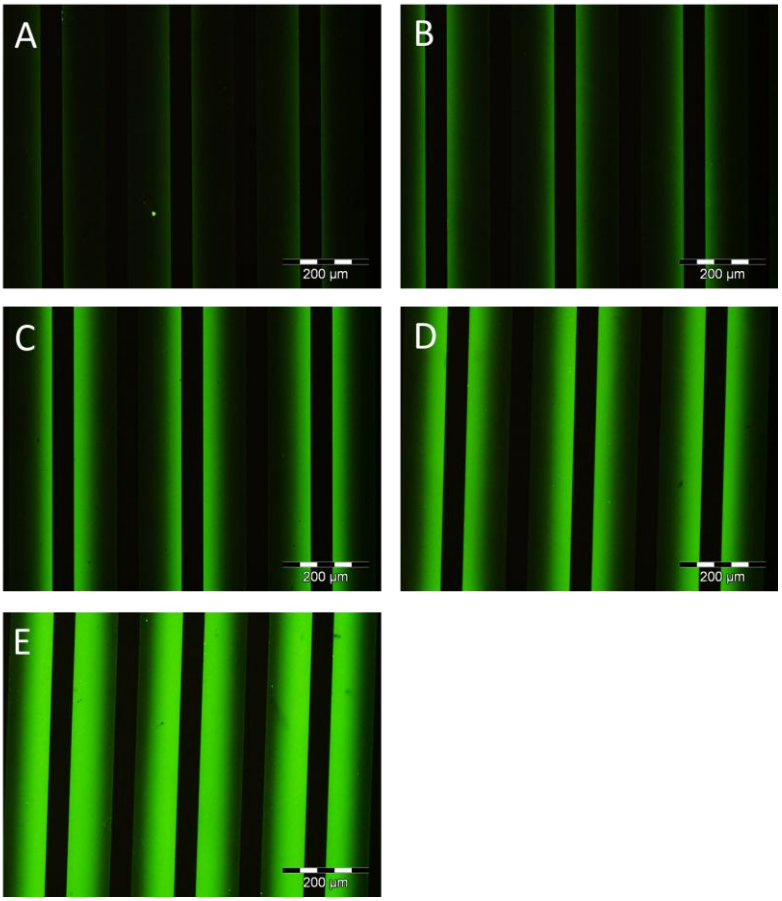
S17 Fluorescence microscopy images obtained reacting 1 mM of **1** in the presence of 5.0 mM $CuSO_4$ and 500 mM 2,6-lutidine in DMSO for various reaction time at the potential difference of 1.0 V: A) 1 min; B) 2 min; C) 4 min.



S18 Fluorescence microscopy images obtained reacting 1 mM of **1** in DMSO at the potential difference of 1.0 V for 4 min in the presence of A) 0.2 mM $CuSO_4$ and 20 mM 2,6-lutidine; B) 1.0 mM $CuSO_4$ and 100 mM 2,6-lutidine; C) 5.0 mM $CuSO_4$ and 500 mM 2,6-lutidine.



S19 Fluorescence microscopy images obtained reacting **1** in the presence of 1.0 mM $CuSO_4$ and 100 mM 2,6-lutidine in DMSO for various reaction time at the potential difference of 1.0 V for 4 min at different concentration of 1: A) 0.2 mM ; B) 1 mM; C) 5 mM.



S20 Fluorescence microscopy images obtained reacting 1 mM of **1** in the presence of 1.0 mM $CuSO_4$, 100 mM 2,6-lutidine and 100 mM n-Bu_4NBF_4 in DMSO at the potential difference of 1.0 V for various reaction time: A) 2 min; B) 4 min; C) 8 min; D) 16 min; E) 32 min.

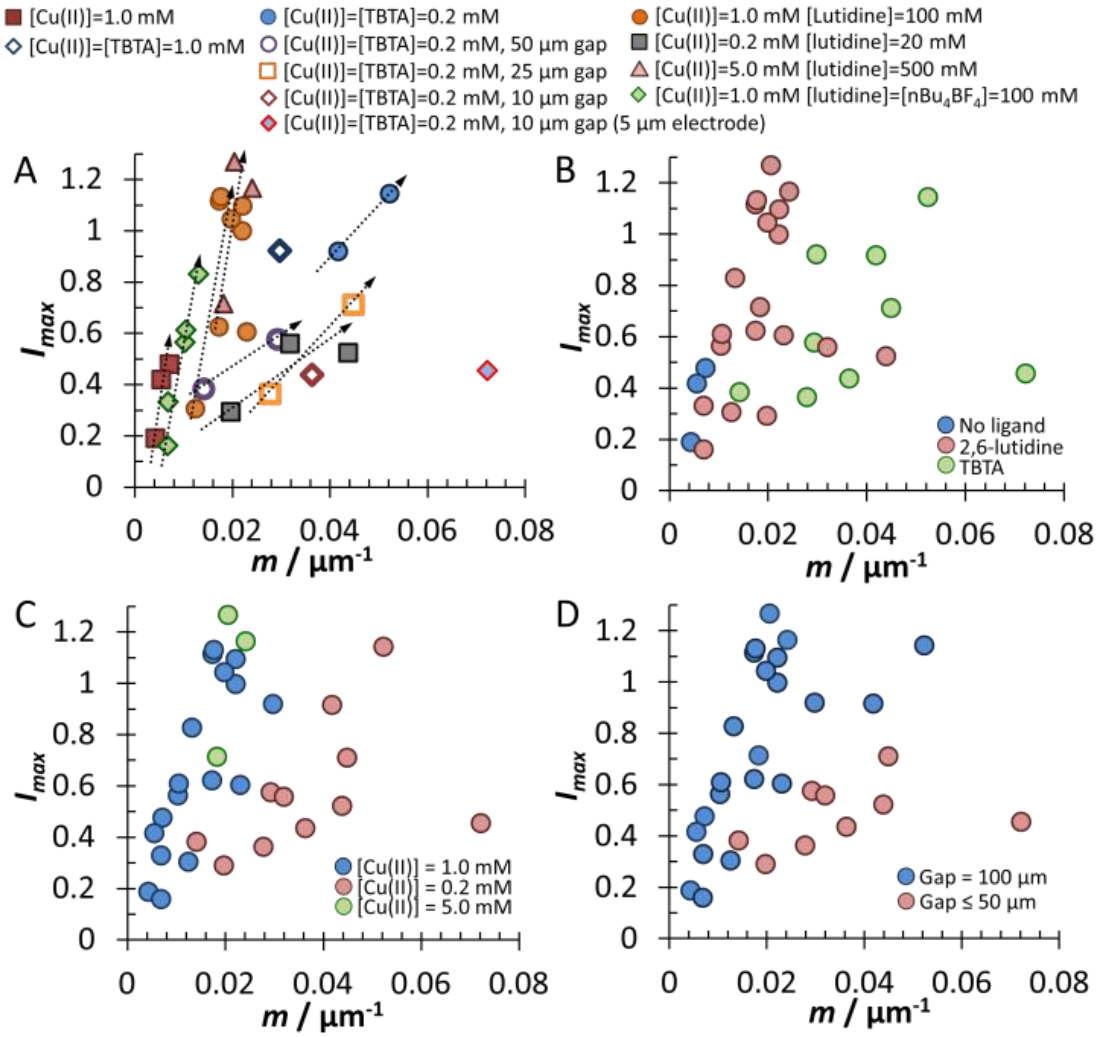
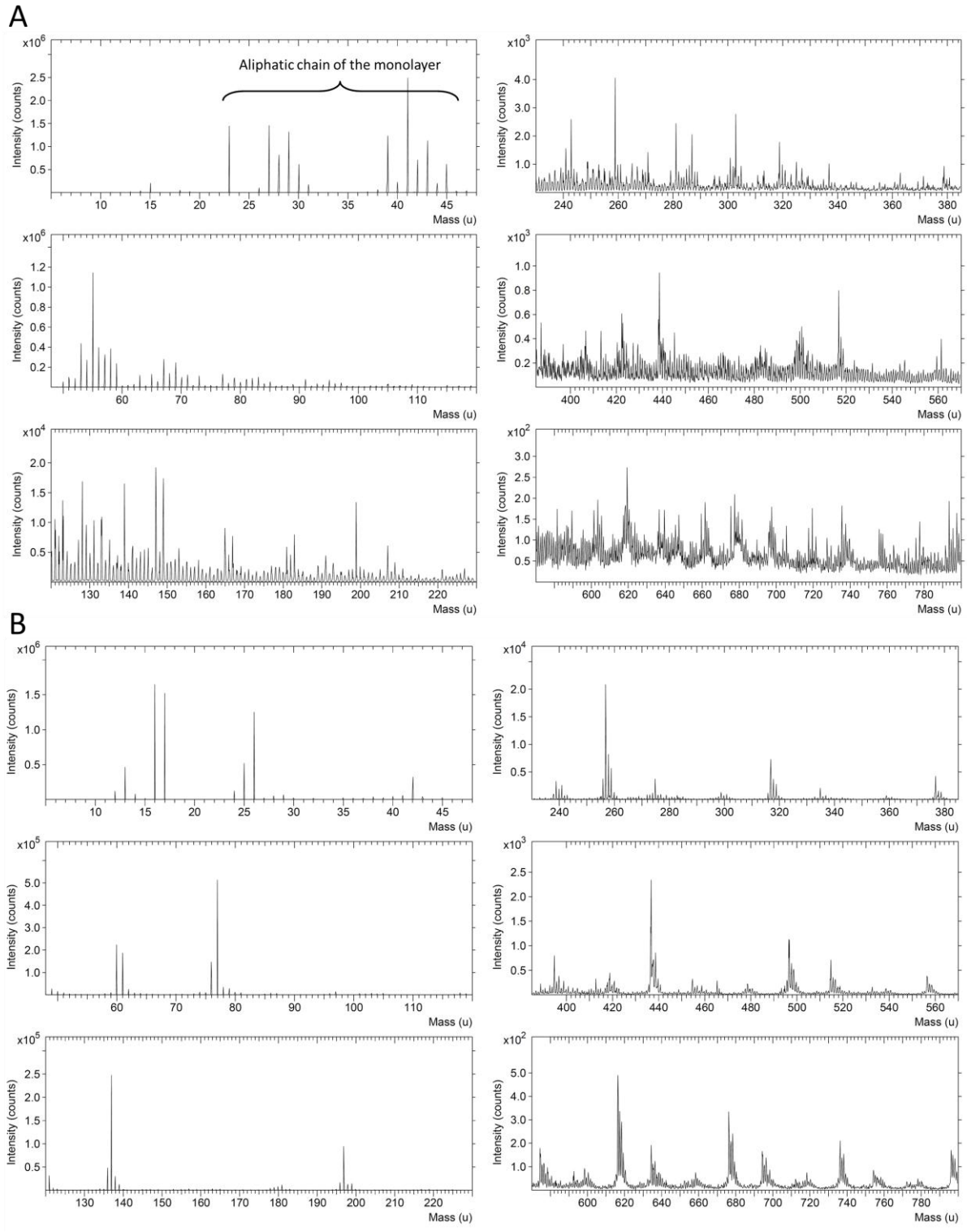
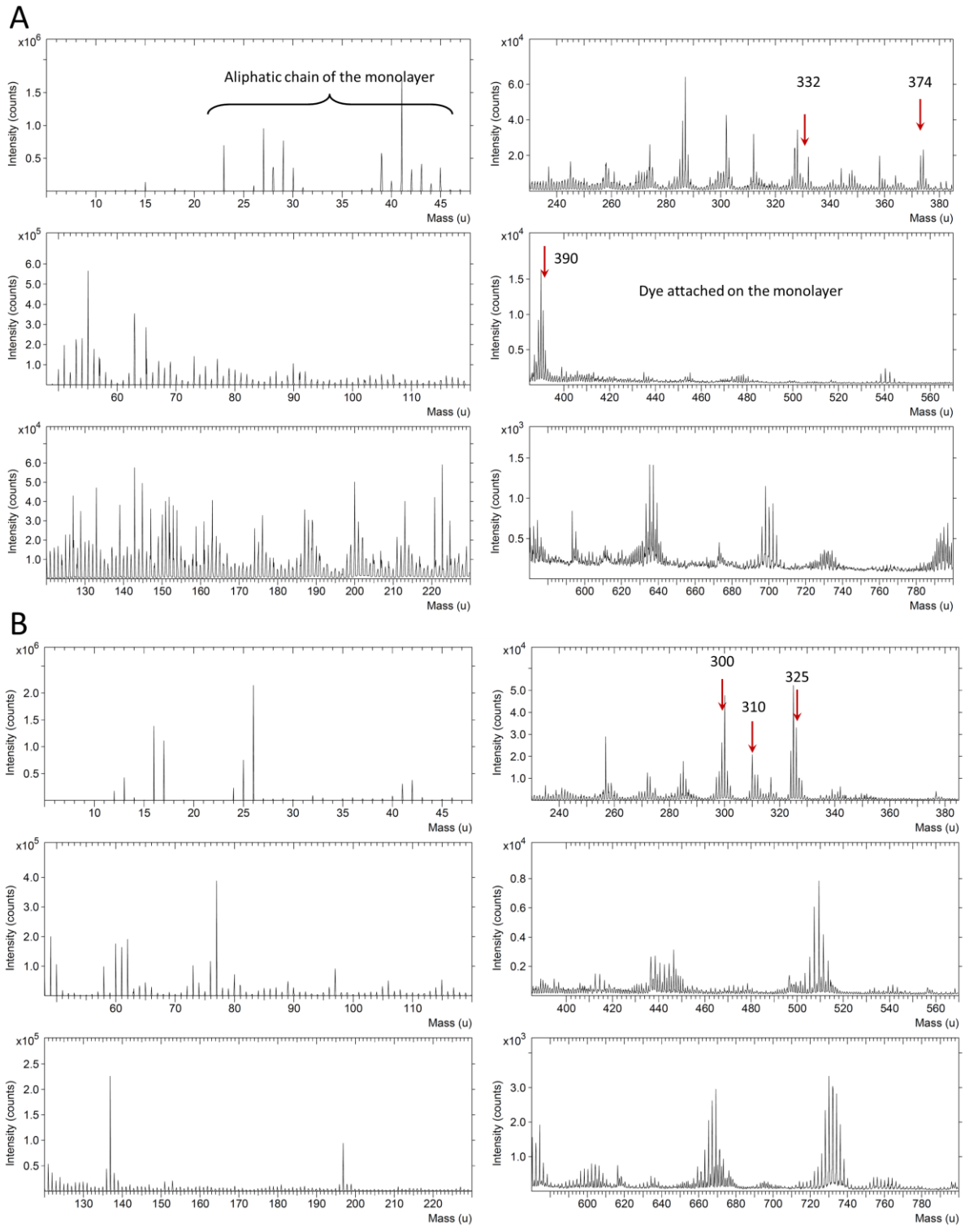


Fig. S21. A) Graph of the maximum fluorescence intensity, I_{max}, near the cathode and the steepness, m, under different working conditions. Graphs I_{max} vs. m highlighting the effects of B) Cu(I)-stabilizing ligand; C) Cu(II) concentration; and D) electrode gap under different reaction conditions.



S22 Surface analysis by means of Tof-SIMS of an azide monolayer on glass, in (A) positive and (B) negative mode. The most intense signals were recorded in the region with mass below 60 u, belonging to $(CH_2)_xN_x$ fragments, typical of the azide monolayer ($Si(CH_2)_{11}N_3$).



S23 Surface analysis by means of Tof-SIMS of an azide monolayer on glass after functionalization with **1** (1 mM **1**, 10uM $CuSO_4$ and 1mM ascorbic acid in tert-butanol/water=1/2 for 24 h), in (A) positive and (B) negative mode. The typical peaks for the monolayer of **1** in positive mode are: 332 ($C_{20}H_{12}0_5^+$), 374 ($C_{21}H_{12}0_4NS^+$) and 390 ($C_{21}H_{12}O_5NS^+$) Dalton; and in negative mode are 300, 310 and 325.