Electronic Supplementary Information (ESI)

Lophine derivatives as activators in peroxyoxalate chemiluminescence

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[1] (mmol L^{-1})	**I_{max} (E s^{-1}) × 10^{12}**	**k_1 (s^{-1}) × 10^3**	**k_2 (s^{-1}) × 10^1**	**Φ_{CL} (E mol^{-1}) × 10^3**	**Φ_S (E mol^{-1}) × 10^2**
1.00	0.88 ± 0.02	3.79 ± 0.09	3.5 ± 0.3	0.757 ± 0.009	0.168 ± 0.002
0.75	0.77 ± 0.01	3.70 ± 0.02	3.4 ± 0.7	0.676 ± 0.005	0.150 ± 0.001
0.50	0.65 ± 0.01	3.75 ± 0.03	3.5 ± 0.6	0.561 ± 0.005	0.125 ± 0.001
0.25	0.44 ± 0.01	3.72 ± 0.07	3.2 ± 0.1	0.383 ± 0.003	0.085 ± 0.001
0.10	0.23 ± 0.01	3.74 ± 0.04	2.9 ± 0.3	0.201 ± 0.001	0.045 ± 0.001
[2] (mmol L^{-1})	**I_{max} (E s^{-1}) × 10^{12}**	**k_1 (s^{-1}) × 10^3**	**k_2 (s^{-1}) × 10^1**	**Φ_{CL} (E mol^{-1}) × 10^3**	**Φ_S (E mol^{-1}) × 10^2**
1.00	0.92 ± 0.01	3.28 ± 0.03	4.1 ± 0.8	0.91 ± 0.01	0.234 ± 0.001
0.75	0.87 ± 0.02	3.22 ± 0.06	2.2 ± 0.6	0.88 ± 0.01	0.224 ± 0.001
0.50	0.86 ± 0.01	3.31 ± 0.02	3.5 ±0.6	0.84 ± 0.01	0.215 ± 0.001
0.25	0.67 ± 0.01	3.25 ± 0.03	1.9 ± 0.1	0.67 ± 0.01	0.171 ± 0.003
0.10	0.45 ± 0.01	3.27 ± 0.02	2.2 ± 0.3	0.44 ± 0.01	0.114 ± 0.001
[3] (mmol L^{-1})	**I_{max} (E s^{-1}) × 10^{12}**	**k_1 (s^{-1}) × 10^3**	**k_2 (s^{-1}) × 10^1**	**Φ_{CL} (E mol^{-1}) × 10^3**	**Φ_S (E mol^{-1}) × 10^2**
10.0	1.37 ± 0.02	3.84 ± 0.03	1.7 ± 0.1	1.13 ± 0.01	0.305 ± 0.004
7.5	1.32 ± 0.06	3.7 ± 0.1	1.9 ± 0.2	1.14 ± 0.03	0.309 ± 0.007
5.0	1.30 ± 0.03	3.69 ± 0.04	2.1 ± 0.3	1.13 ± 0.03	0.305 ± 0.007
2.5	1.24 ± 0.03	3.72 ± 0.06	2.1 ± 0.3	1.07 ± 0.01	0.290 ± 0.003
1.0	1.14 ± 0.01	3.81 ± 0.06	1.9 ± 0.1	0.961 ± 0.007	0.260 ± 0.002
0.5	1.966 ± 0.003	3.94 ± 0.03	2.2 ± 0.6	0.789 ± 0.004	0.213 ± 0.001
0.1	0.467 ± 0.004	3.90 ± 0.05	3.5 ± 0.4	0.388 ± 0.007	0.105 ± 0.002
[4] (mmol L^{-1})	**I_{max} (E s^{-1}) × 10^{12}**	**k_1 (s^{-1}) × 10^3**	**k_2 (s^{-1}) × 10^1**	**Φ_{CL} (E mol^{-1}) × 10^3**	**Φ_S (E mol^{-1}) × 10^2**
1.00	0.184 ± 0.004	3.8 ± 0.1	3.2 ± 0.7	0.156 ± 0.001	0.195 ± 0.002
0.75	0.157 ± 0.002	3.7 ± 0.1	3.2 ± 0.6	0.138 ± 0.001	0.172 ± 0.001
0.50	0.136 ± 0.001	3.8 ± 0.1	3.5 ± 0.3	0.116 ± 0.001	0.145 ± 0.001
0.25	0.091 ± 0.003	3.8 ± 0.1	3.3 ± 0.1	0.077 ± 0.001	0.097 ± 0.001
0.10	0.048 ± 0.001	3.8 ± 0.1	3.1 ± 0.4	0.042 ± 0.001	0.052 ± 0.001
[5] (mmol L^{-1})	**I_{max} (E s^{-1}) × 10^{12}**	**k_1 (s^{-1}) × 10^3**	**k_2 (s^{-1}) × 10^1**	**Φ_{CL} (E mol^{-1}) × 10^3**	**Φ_S (E mol^{-1}) × 10^2**
1.00	15.1 ± 0.3	4.21 ± 0.07	4.7 ± 0.4	11.68 ± 0.09	2.60 ± 0.02
0.75	12.3 ± 0.1	4.19 ± 0.04	4.6 ± 0.8	9.51 ± 0.07	2.11 ± 0.02
0.50	9.2 ± 0.1	4.25 ± 0.04	5 ± 1	7.00 ± 0.02	1.56 ± 0.01
0.25	5.2 ± 0.1	4.21 ± 0.03	5 ± 1	4.02 ± 0.02	0.89 ± 0.01
0.10	2.4 ± 0.1	4.25 ± 0.05	5 ± 1	1.82 ± 0.01	0.41 ± 0.01
Mean value	–	3.7 ± 0.3	3 ± 1	–	–

Table S2. Observed fall (k_1) and rise (k_2) rate constants, and relative chemiluminescence emission yields (Q_{rel}) for the peroxyoxalate reaction with **1** (1.0 mmol L^{-1}) as activator, varying the concentration of IMI-H. In EtOAc, at 25 °C, [TCPO] = 0.1 mmol L^{-1}, [H_2O_2] = 0.1 mmol L^{-1}.

[IMI-H] (mmol L^{-1})	**k_1 (s^{-1})**	**k_2 (s^{-1})**	**Q_{rel}**
20.0	0.410 ± 0.004	—*	0.01
10.0	0.114 ± 0.001	—*	0.12
8.0	0.077 ± 0.001	—*	0.18
6.0	0.047 ± 0,001	—*	0.26
4.0	0.026 ± 0.002	—*	0.37
2.0	0.0078 ± 0.0001	2.19 ± 0,01	0.61
0.9	0.0030 ± 0.0001	0.72 ± 0,01	0.81
0.7	0.00230 ± 0.00002	0.440 ± 0,007	0.86
0.5	0.00150 ± 0.00002	0.31 ± 0,03	0.93
0.2	0.00062 ± 0.00004	0.100 ± 0,009	1.00

*not measurable

Table S3. Observed fall (k_1) and rise (k_2) rate constants, and relative chemiluminescence emission yields (Q_{rel}) for the peroxyoxalate reaction with **1** (1.0 mmol L^{-1}) as activator, varying the concentration of H_2O_2. In EtOAc, at 25 °C, [TCPO] = 0.1 mmol L^{-1}, [IMI-H] = 1.0 mmol L^{-1}.

[H_2O_2] (mmol L^{-1})	**k_1 (s^{-1})**	**k_2 (s^{-1})**	**Q_{rel}**
10.0	0.00300 ± 0.00005	0.42 ± 0.01	0.89
5.0	0.00200 ± 0.00003	0.237 ± 0.001	0.93
2.5	0.00170 ± 0.00002	0.13 ± 0.01	0.97
1.0	0.00140 ± 0.00002	0.053 ± 0.005	0.98
0.50	0.00130 ± 0.00002	0.026 ± 0.001	0.99
0.25	0.00120 ± 0.00004	0.0190 ± 0.0006	1.00

Table S4. Chemiluminescence (Φ_{CL}) and singlet excited state formation (Φ_S) quantum yields for the peroxyoxalate reaction at high concentrations of the activators. In EtOAc, at 25 °C, [TCPO] = 0.1 mmol L^{-1}, [IMI-H] = 1.0 mmol L^{-1}, [H_2O_2] = 10.0 mmol L^{-1}.

ACT	**[ACT] (mmol L^{-1})**	**Φ_{CL} (E mol^{-1}) × 10^3**	**Φ_S (E mol^{-1}) × 10^3**
1	10.0	1.04 ±0.01	2.30 ± 0.02
2	2.0*	1.06 ± 0.01	2.72 ± 0.03
3	10.0	1.15 ± 0.01	3.10 ± 0.03
4	10.0	0.229 ± 0.003	2.86 ± 0.03
5	10.0	21.6 ± 0.4	48 ± 1

*Insoluble in EtOAc at concentrations above 2.0 mmol L^{-1}.

Figures Section

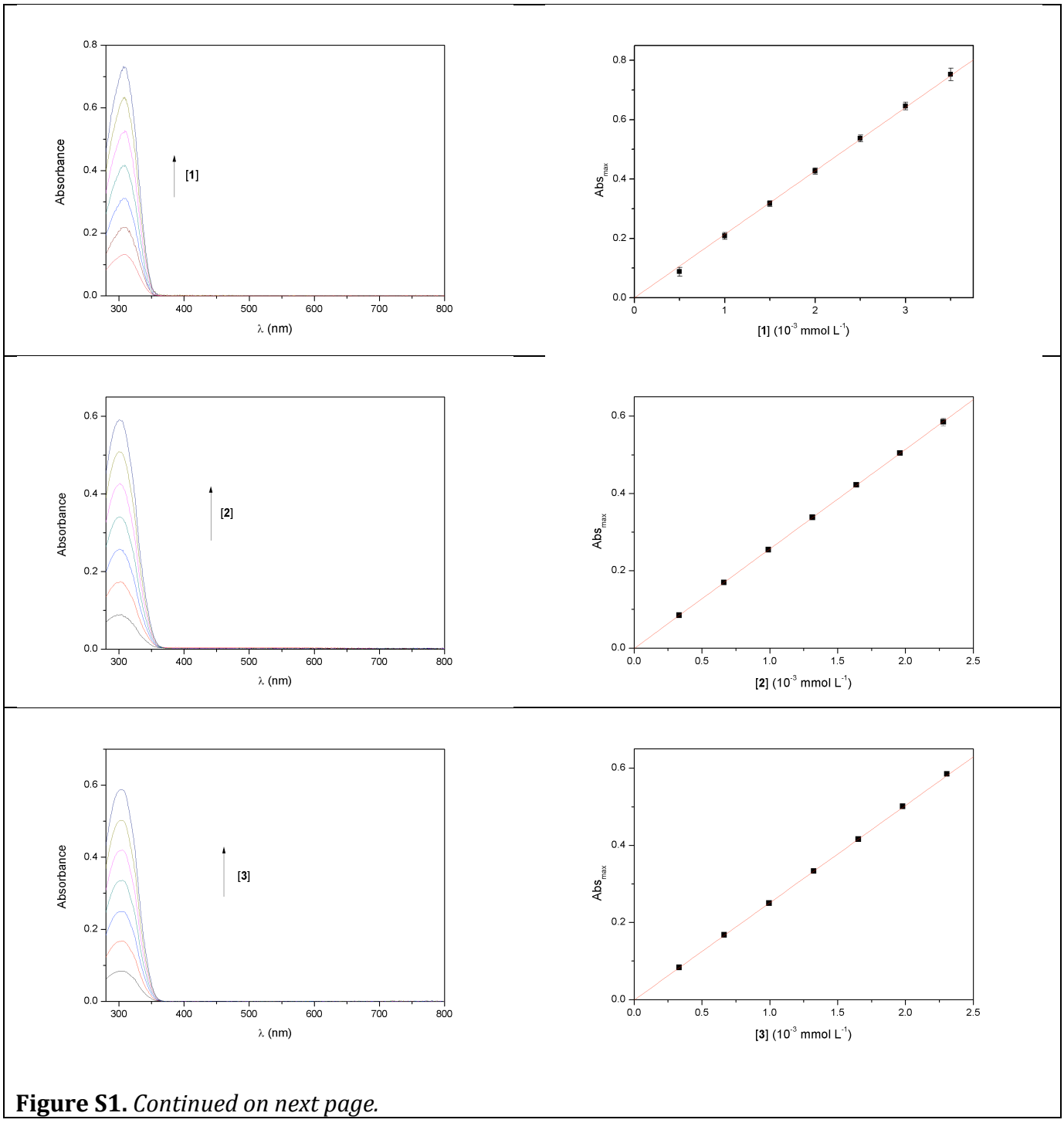

Figure S1. *Continued on next page.*

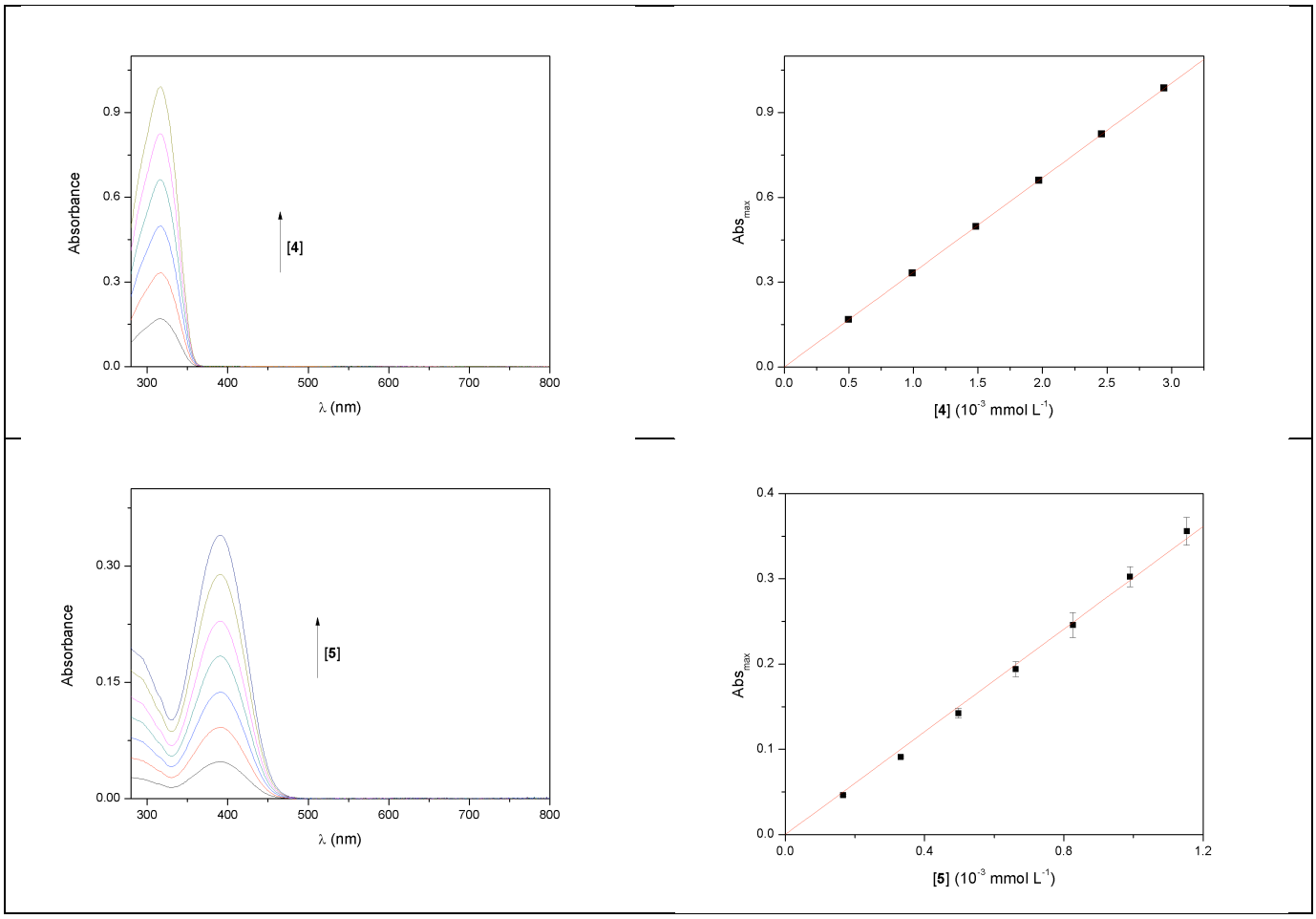

Figure S1. Photometric assays (left) for the determination of the molar extinction coefficient (ε) of lophine derivatives **1**–**5**, determined as the angular coefficient of the linear plots setting the linear coefficient as zero (right); r > 0.9999 in all cases.

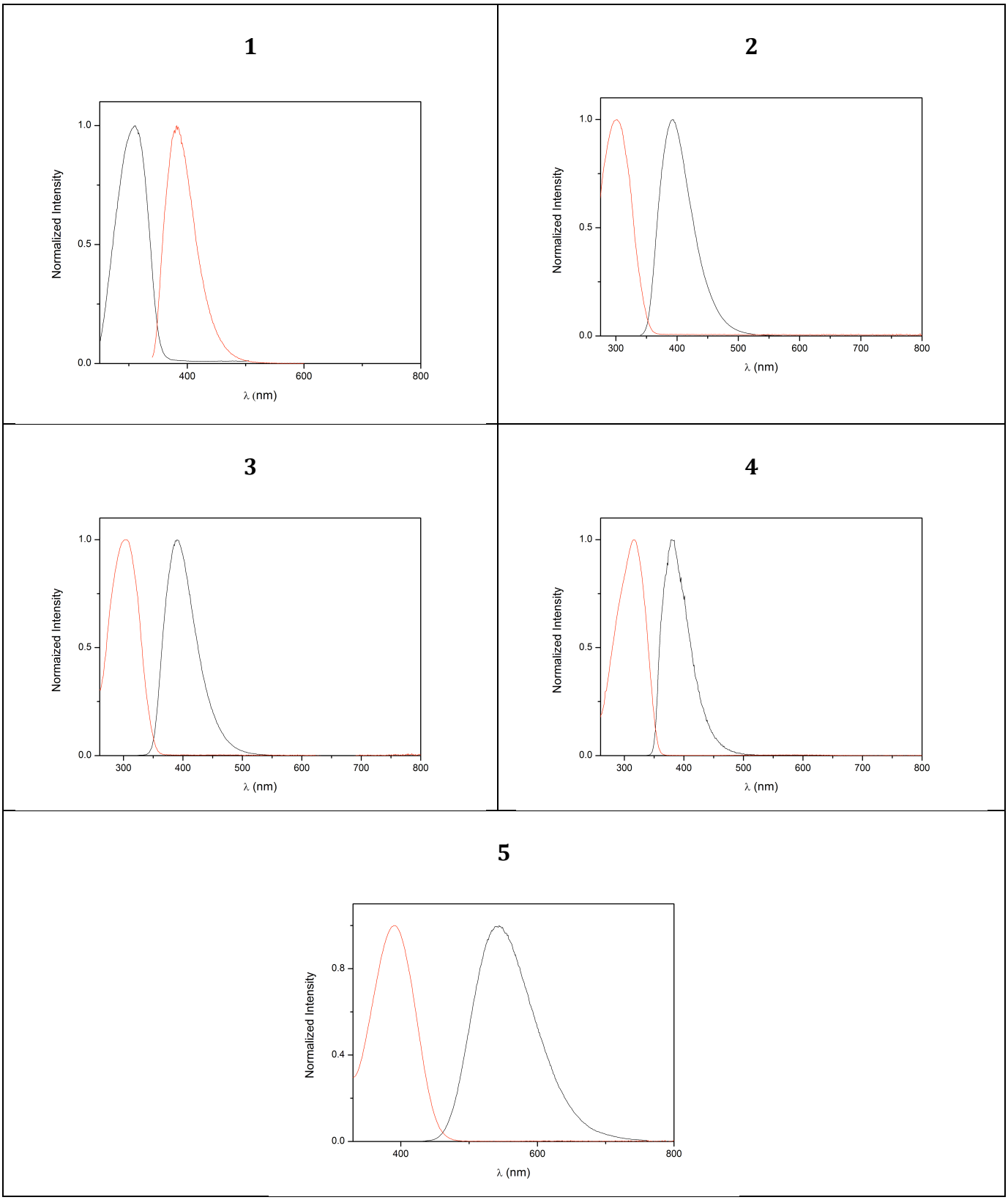

Figure S2. Absorption and emission spectra for the lophine derivatives **1**–**5** (in EtOAc, at 25 °C).

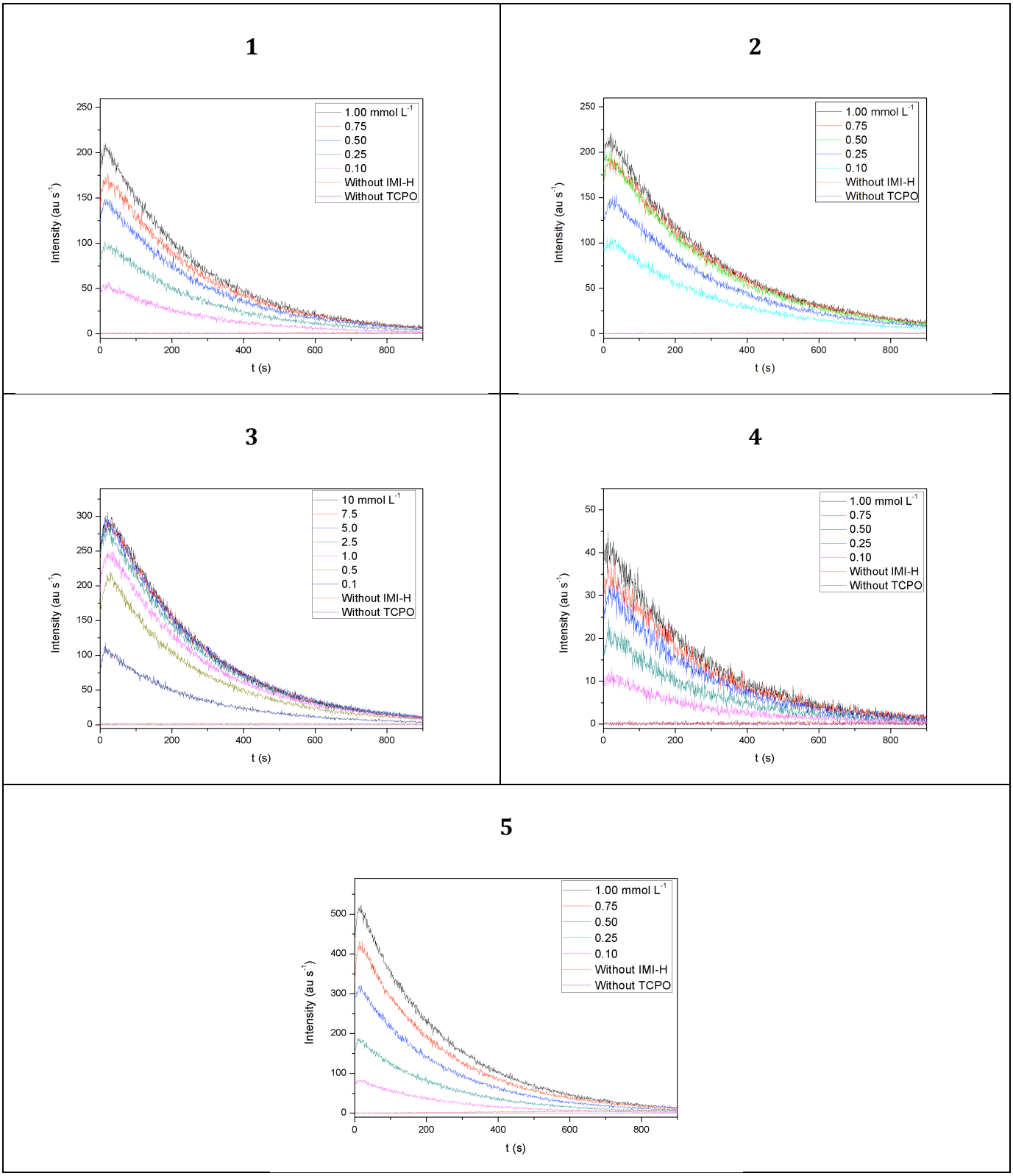

Figure S3. Chemiluminescence emission time-profiles for the peroxyoxalate reaction using lophine derivatives **1**–**5** as activators. In EtOAc, at 25 °C, [TCPO] = 0.1 mmol L^{-1}, [IMI-H] = 1.0 mmol L^{-1}, [H_2O_2] = 10.0 mmol L^{-1}; intensity in arbitrary units; experiments for each concentration were conducted at least three times. Assays without IMI-H or TCPO were conducted at the highest ACT concentration.

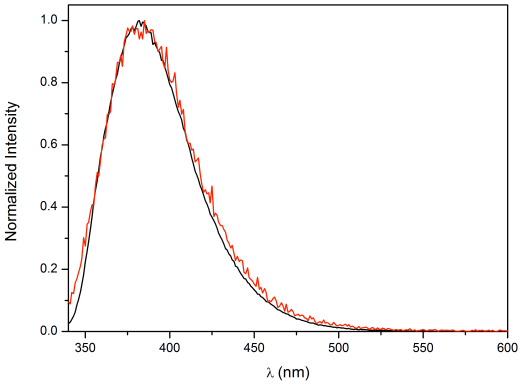

Figure S4. Spectra for lophine (1.0 mmol L^{-1}) fluorescence (black line) and for the peroxyoxalate reaction chemiluminescence emission (red line, in EtOAc, at 25 °C, [TCPO] = 0.1 mmol L^{-1}, [IMI-H] = 1.0 mmol L^{-1}, [H_2O_2] = 10.0 mmol L^{-1}).