

Table 1S. Information for the Photochemical Experiments (25° C, ionic strength = 0.10 M NaCl): Solution Composition, Calculated Equilibrium Speciation of Cu(II) (f_i) and of the Free Dicarboxylate Species ($[H_2L(aq)]$, $[HL^-]$, and $[L^{2-}]$), and a Comparison of Experimental Results (Measured) with the Best-Fit of the Photochemical Kinetic Model (Eq. 9).

[Cu(II)] _T μM	[L] _T μM	pH	f_{CuL}	f_{CuL2}	$f_{Cu(HL)}$	f_{in}	[H ₂ L(aq)] μM	[HL ⁻] μM	[L ²⁻] μM	Measured	Best Fit of Model
Cu(II)/Malonate											
50	400	7.00	0.812	0.157	—	0.031	0.00045	8.4	336	1.596	1.793
50	500	7.00	0.782	0.194	—	0.024	0.00058	10.5	431	1.898	1.616
50	600	7.00	0.753	0.228	—	0.019	0.00071	12.6	527	1.439	1.462
50	800	7.00	0.699	0.289	—	0.012	0.00097	17.6	718	1.421	1.187
50	1000	7.00	0.650	0.341	—	0.009	0.00122	22	911	0.930	0.995
50	1200	7.00	0.607	0.386	—	0.007	0.00148	27.6	1,104	0.881	0.826
50	1400	7.00	0.569	0.425	—	0.006	0.00174	32.2	1,298	0.709	0.710
50	2000	7.00	0.479	0.518	—	0.003	0.00252	46	1,878	0.474	0.481
50	5000	7.00	0.266	0.733	—	0.001	0.00644	115	4,795	0.150	0.140
50	500	5.00	0.866	0.065	—	0.069	1.747	319	130	0.174	0.166
50	500	5.50	0.843	0.122	—	0.035	0.337	194	251	0.191	0.255
50	500	6.00	0.810	0.166	—	0.024	0.0478	87	356	0.457	0.489
50	500	6.50	0.792	0.187	—	0.021	0.00551	31.5	410	1.154	0.983
50	25	6.00	0.355	—	—	0.645	0.00077	1.4	5.75	1.020	1.020
50	2000	6.00	0.527	0.469	—	0.004	0.208	378	1,548	0.080	0.088
60	500	7.00	0.786	0.190	—	0.024	0.00056	10.5	420	1.658	1.623
60	2000	7.00	0.481	0.516	—	0.003	0.00250	46	1,864	0.414	0.483

A blank entry (—) in the table indicates that $f_i < 0.0010$ or that the concentration ($[H_2L(aq)]$, $[HL^-]$, and $[L^{2-}]$) is < 0.0010 μM.

$$^a \Phi_{Cu(II)}\epsilon_{Cu(II)} - \Phi_{Cu(II),in}\epsilon_{in}f_{in} = (R_{Cu(II)}^0 - R_{Cu(II),in}^0) / \{\ln(10)I_0D[Cu(II)]_T\}$$

Table 2S. Information for the Determination of Molar Absorptivities at 313 nm [25° C, ionic strength = 0.10 M (NaCl, almost always 0.10 M), air saturated]: Solution Composition, Calculated Equilibrium Speciation of Cu(II) (f_i) and of the Free Dicarboxylate Species ($[\text{H}_2\text{L}(\text{aq})]$, $[\text{HL}^-]$, and $[\text{L}^{2-}]$), and a Comparison of Experimental Results (Measured) with the Best-Fit to the Model.

$[\text{Cu(II)}]_{\text{T}}$ μM	$[\text{L}]_{\text{T}}$ μM	pH	f_{CuL}	f_{CuL2}	$f_{\text{Cu(HL)}}$	f_{in}	$[\text{H}_2\text{L}(\text{aq})]$ μM	$[\text{HL}^-]$ μM	$[\text{L}^{2-}]$ μM	Measured	Best Fit of Model
$\epsilon_{\text{Cu(II)}} - \epsilon_{\text{in}} f_{\text{in}}$ $\text{M}^{-1} \text{cm}^{-1}$											
Cu(II)/Malonate											
50	5000	4.00	0.842	0.089	0.023	0.046	250	4515	185	18.366	20.325
50	5000	4.25	0.811	0.152	0.012	0.025	140	4480	325	20.468	21.329
50	5000	4.50	0.742	0.238	—	0.020	75	4305	555	21.690	22.215
50	5000	4.75	0.648	0.341	—	0.011	39	3980	915	21.937	23.337
50	5000	5.00	0.547	0.448	—	0.005	19	3485	1425	20.770	24.435
50	5000	5.25	0.455	0.542	—	0.003	9	2845	2070	21.983	25.333
50	5000	5.50	0.385	0.614	—	0.001	4	2145	2770	23.995	26.030
50	5000	5.75	0.336	0.663	—	0.001	1	1490	3425	25.794	26.477
50	5000	6.00	0.305	0.694	—	0.001	0.5	965	3950	27.393	26.759
50	5000	6.50	0.276	0.724	—	—	0.06	355	4560	28.2	27.053
50	5000	7.00	0.266	0.733	—	0.001	0.006	115	4795	29.430	27.115

A blank entry (—) in the table indicates that $f_i < 0.0010$ or that the concentration ($[\text{H}_2\text{L}(\text{aq})]$, $[\text{HL}^-]$, and $[\text{L}^{2-}]$) is $< 0.0010 \mu\text{M}$.

Table 2S (continued). Information for the Determination of Molar Absorptivities at 313 nm [25° C, ionic strength = 0.10 M (NaCl, almost always 0.10 M), air saturated]: Solution Composition, Calculated Equilibrium Speciation of Cu(II) (f_i) and of the Free Dicarboxylate Species ($[\text{H}_2\text{L}(\text{aq})]$, $[\text{HL}^-]$, and $[\text{L}^{2-}]$), and a Comparison of Experimental Results (Measured) with the Best-Fit to the Model.

[Cu(II)] _T μM	[L] _T μM	pH	f_{CuL}	f_{CuL_2}	$f_{\text{Cu(HL)}}$	f_{in}	$[\text{H}_2\text{L}(\text{aq})]$ μM	$[\text{HL}^-]$ μM	$[\text{L}^{2-}]$ μM	Measured	Best Fit of Model
$\frac{\epsilon_{\text{Cu(II)}} - \epsilon_{\text{in}} f_{\text{in}}}{M^{-1} \text{ cm}^{-1}}$											
Cu(II)/Malonate											
50	5000	4.00	0.842	0.089	0.023	0.046	250	4515	185	21.984	20.305
50	5000	4.25	0.811	0.152	0.012	0.025	140	4480	325	23.686	21.329
50	5000	4.50	0.742	0.238	—	0.020	75	4305	555	24.308	22.215
50	5000	4.75	0.648	0.341	—	0.011	39	3980	915	24.955	23.337
50	5000	5.00	0.547	0.448	—	0.005	19	3485	1425	25.388	24.435
50	5000	5.25	0.455	0.542	—	0.003	9	2845	2070	26.001	25.333
50	5000	5.50	0.385	0.614	—	0.001	4	2145	2770	26.213	26.030
50	5000	5.75	0.336	0.663	—	0.001	1	1490	3425	26.612	26.477
50	5000	6.00	0.305	0.694	—	0.001	0.5	965	3950	26.611	26.759
50	5000	6.50	0.276	0.724	—	—	0.06	355	4560	27.418	27.053
50	5000	7.00	0.266	0.733	—	0.001	0.006	115	4795	27.648	27.115

A blank entry (—) in the table indicates that $f_i < 0.0010$ or that the concentration ($[\text{H}_2\text{L}(\text{aq})]$, $[\text{HL}^-]$, and $[\text{L}^{2-}]$) is < 0.0010 μM.

Table 3S. Information for the Photochemical Experiments at 313 nm [25° C, I = 0.1 M (NaCl, almost always 0.1 M), N₂ purged]: Solution Composition, Calculated Equilibrium Speciation of Cu(II) (f_i) and of the Free Dicarboxylate Species ([H₂L(aq)], [HL⁻], [L²⁻]), and a Comparison of Experimental Results (Measured) with the Best-Fit to the Photochemical Model (Eq. 8).

[Cu(II)] _T μM	[L] _T μM	pH	f _{CuL}	f _{in}	[H ₂ L(aq)] μM	[HL ⁻] μM	[L ²⁻] μM	Measured L einstein ⁻¹ cm ⁻¹	Best Fit of Model
Cu(II)/Glutarate									
50	5340	6.00	0.476	0.524	10	603	4699	0.917	1.1686
50	7030	6.00	0.541	0.459	14	794	6200	1.472	1.3282
50	10,550	6.00	0.631	0.369	20	1171	9326	1.612	1.5492
50	15,360	6.00	0.705	0.295	29	1690	13609	1.765	1.7309
50	20,130	6.00	0.751	0.249	37	2174	17875	1.909	1.8440
50	30,040	6.00	0.807	0.193	53	3184	26766	1.895	1.9813
Cu(II)/Adipate									
50	7090	6.00	0.519	0.781	20	851	6190	1.164	1.073
50	11700	6.00	0.614	0.386	32	1357	10284	1.372	1.269
50	15,220	6.00	0.668	0.332	41	1735	13409	1.441	1.3809
50	21,120	6.00	0.727	0.273	55	2387	18649	1.443	1.5028
50	29,870	6.00	0.779	0.221	75	3286	26465	1.465	1.6103
50	35,120	6.00	0.800	0.200	87	3828	31187	1.619	1.6537
Cu(II)/Pimelate									
50	3000	6.00	0.268	0.645	10	399	2577	0.774	0.627
50	6000	6.00	0.422	0.509	21	798	5154	0.848	0.988
50	21,000	6.00	0.720	0.247	73	2793	18039	1.619	1.686
50	21,000	6.00	0.720	0.247	73	2793	18039	1.780	1.686

Table 4S. Information for the Determination of Molar Absorptivities at 313 nm [25° C, I = 0.1 M (NaCl, almost always 0.1 M), air saturated]: Solution Composition, Calculated Equilibrium Speciation of Cu(II) (f_i) and of the Free Dicarboxylate Species ($[H_2L(aq)]$, $[HL^-]$, $[L^{2-}]$), and a Comparison of Experimental Results (Measured) with the Best-Fit to the Model.

[Cu(II)] _T μM	[L] _T μM	pH	f_{CuL}	f_{in}	[H ₂ L(aq)] μM	[HL ⁻ (aq)] μM	[L ²⁻ (aq)] μM	$\epsilon_{Cu(II)} - \epsilon_{in} f_{in}$ M ⁻¹ cm ⁻¹	
								Measured	Best Fit of Model
Cu(II)/Glutarate									
50	50,000	4.25	0.481	0.519	24000	23250	2750	23.65	21.90
50	50,000	4.50	0.651	0.349	16000	27900	6050	29.88	29.64
50	50,000	4.75	0.764	0.236	9250	29100	11650	35.25	34.79
50	50,000	5.00	0.828	0.172	4600	26050	19300	36.58	37.70
50	50,000	5.25	0.862	0.138	2000	20300	27700	39.83	39.25
50	50,000	5.50	0.880	0.120	750	14100	35100	41.96	40.07
50	50,000	5.75	0.889	0.111	273	9050	40650	43.17	40.48
50	50,000	4.25	0.481	0.519	24000	23250	2750	22.45	21.90
50	50,000	4.50	0.651	0.349	16000	27900	6050	27.48	29.64
50	50,000	4.75	0.764	0.236	9250	29100	11650	32.65	34.79
50	50,000	5.00	0.828	0.172	4600	26050	19300	34.98	37.70
50	50,000	5.25	0.862	0.138	2000	20300	27700	38.63	39.25
50	50,000	5.50	0.880	0.120	750	14100	35100	40.56	40.07
50	50,000	6.00	0.894	0.106	93	5500	44350	40.86	40.71
Cu(II)/Adipate									
50	50,000	4.50	0.581	0.419	19900	25000	5100	34.10	28.71
50	50,000	4.75	0.716	0.284	12100	27500	10400	36.58	35.39
50	50,000	5.00	0.796	0.204	6250	25700	18050	40.39	39.34
50	50,000	5.25	0.838	0.162	2750	20550	26650	44.29	41.41
50	50,000	5.50	0.860	0.140	1100	14500	34350	45.46	42.50
50	50,000	5.75	0.872	0.128	500	9350	40200	45.87	43.09

Table 4S (continued). Information for the Determination of Molar Absorptivities at 313 nm [25° C, I = 0.1 M (NaCl, almost always 0.1 M), air saturated]: Solution Composition, Calculated Equilibrium Speciation of Cu(II) (f_i) and of the Free Dicarboxylate Species ($[H_2L(aq)]$, $[HL^-]$, $[L^{2-}]$), and a Comparison of Experimental Results (Measured) with the Best-Fit to the Model.

[Cu(II)] _r μM	[L] _r μM	pH	f_{cal}	f_{in}	[H ₂ L(aq)] μM	[HL ⁻ (aq)] μM	[L ²⁻ (aq)] μM	Measured	Best Fit of Model
$\epsilon_{Cu(II)} - \epsilon_{in} f_{in}$ M ⁻¹ cm ⁻¹									

Cu(II)/Adipate									
50	50,000	6.00	0.877	0.123	125	5700	44100	46.55	43.34
50	50,000	4.50	0.581	0.419	19900	25000	5100	27.90	28.71
50	50,000	4.75	0.716	0.284	12100	27500	10400	33.58	35.39
50	50,000	5.00	0.796	0.204	6250	25700	18050	34.99	39.34
50	50,000	5.25	0.838	0.162	2750	20550	26650	37.69	41.41
50	50,000	5.50	0.860	0.140	1100	14500	34350	39.66	42.50
50	50,000	5.75	0.872	0.128	500	9350	40200	40.27	43.09
50	50,000	6.00	0.877	0.123	125	5700	44100	41.35	43.34
Cu(II)/Pimelate									
50	3000	4.00	0.000	1.000	2106	843	66	2.12	0
50	3000	4.25	0.019	0.981	1680	1188	144	2.41	0.97
50	3000	4.50	0.042	0.958	1170	1488	345	3.73	2.14
50	3000	4.75	0.080	0.920	732	1626	642	5.95	4.08
50	3000	5.00	0.129	0.871	399	1560	1047	7.84	6.58
50	3000	5.25	0.179	0.821	189	1299	1500	9.39	9.13
50	3000	5.50	0.221	0.779	78	966	1944	10.87	11.28
50	3000	5.75	0.250	0.750	27	657	2298	12.55	12.76
50	3000	6.00	0.268	0.732	9	417	2568	12.52	13.67