

## Supporting Information

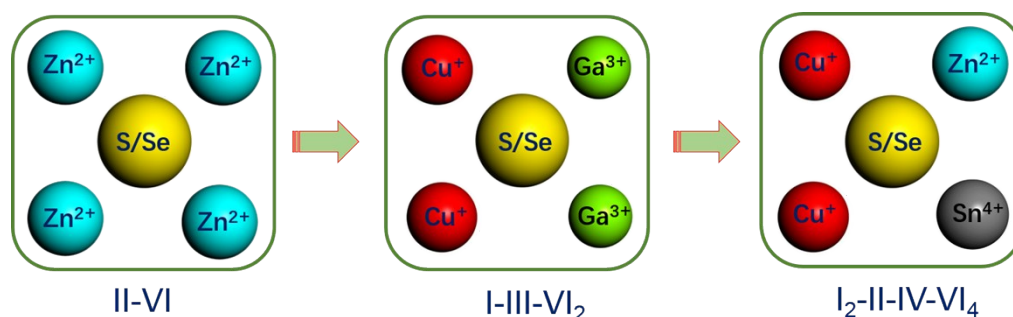
### Heterovalent Ga<sup>3+</sup> Doping in Solution-Processed Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub> Solar Cells for Better Optoelectronic Performance

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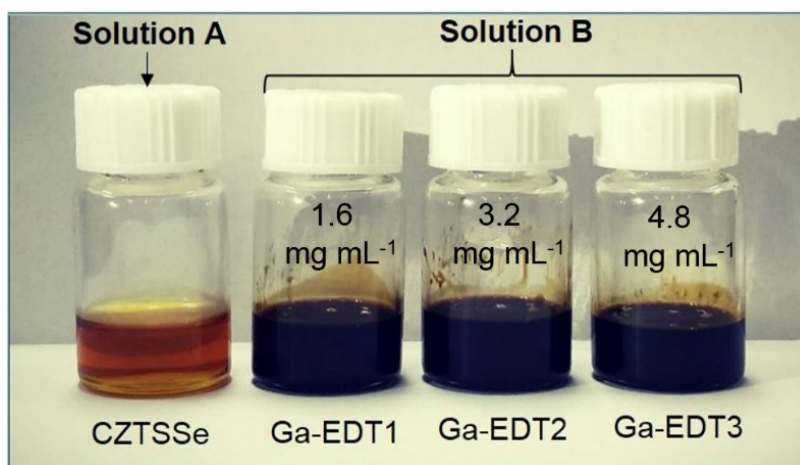
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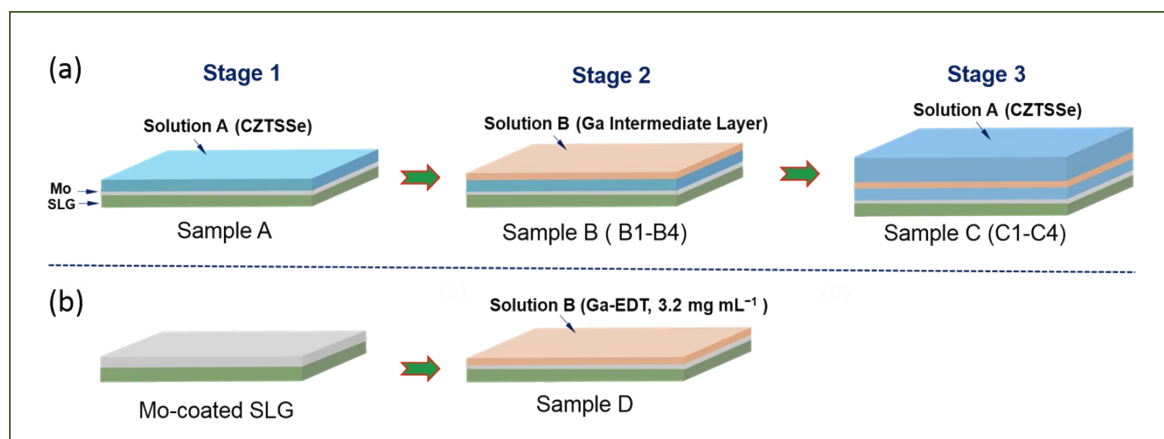
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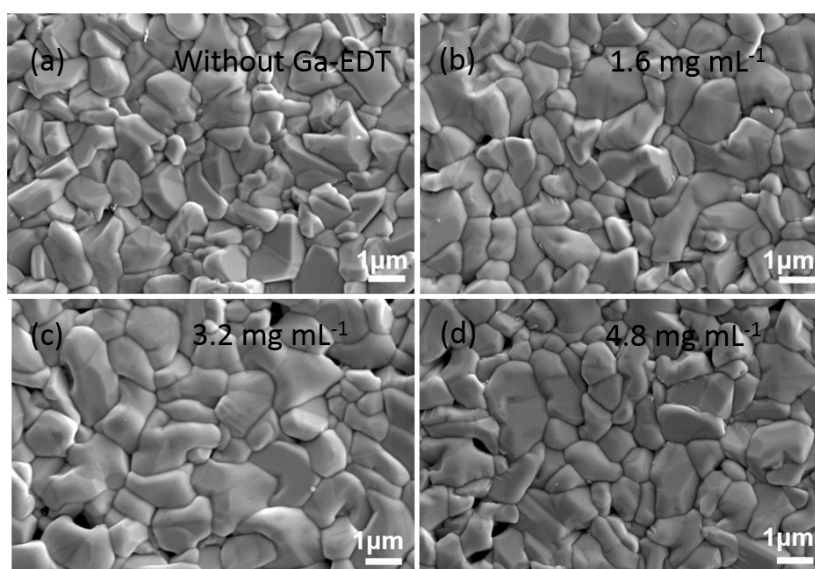
**Figure S1.** Schematic of the derivation of I<sub>2</sub>-II-IV-VI<sub>4</sub> semiconductors from binary II-VI and ternary I-III-VI<sub>2</sub> parent compounds.



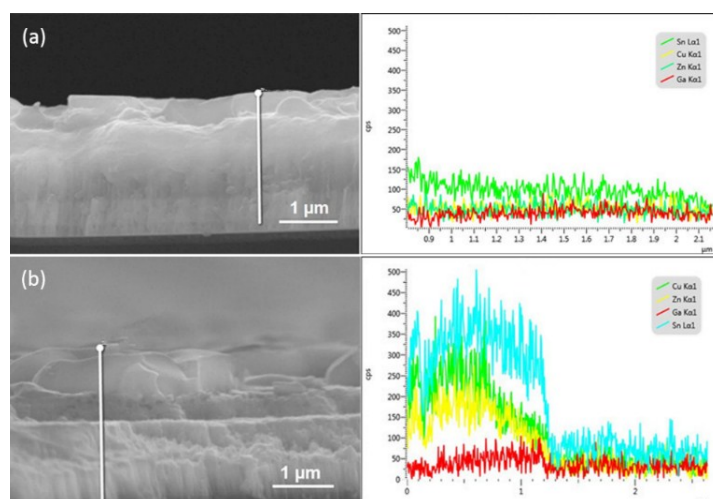
**Figure S2.** Digital photographs of the CZTSSe precursor solution and the three Ga-EDT precursor solutions with different Ga concentrations.



**Figure S3.** Schematic illustration of the fabrication procedures of Sample A-D.



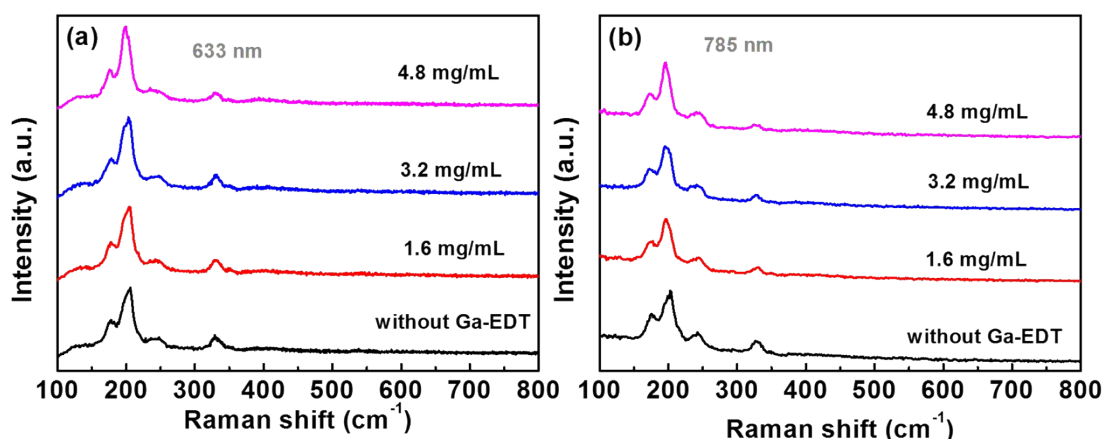
**Figure S4.** Top-view SEM images of the completed Ga doping  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  thin films with different doping level, (a)  $x = 0 \text{ mg mL}^{-1}$ , (b)  $x = 1.6 \text{ mg mL}^{-1}$ , (c)  $x = 3.2 \text{ mg mL}^{-1}$ , (d)  $x = 4.8 \text{ mg mL}^{-1}$ .



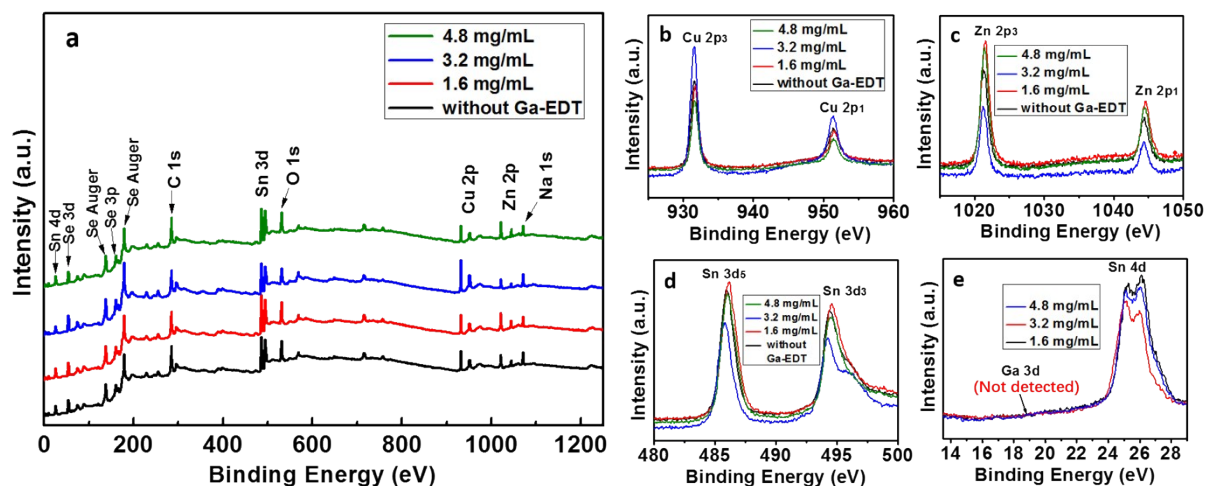
**Figure S5.** EDS line scan of the as-prepared film (a) and selenized film (b), [Sample B, Ga-EDT,  $x=3.2$  mg/mL].

**Table S1.** The ICP-OES measurements for the completed selenized  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  thin films with different contents of Ga-EDT ( $x=0, 1.6, 3.2,$  and  $4.8$  mg  $\text{mL}^{-1}$ )

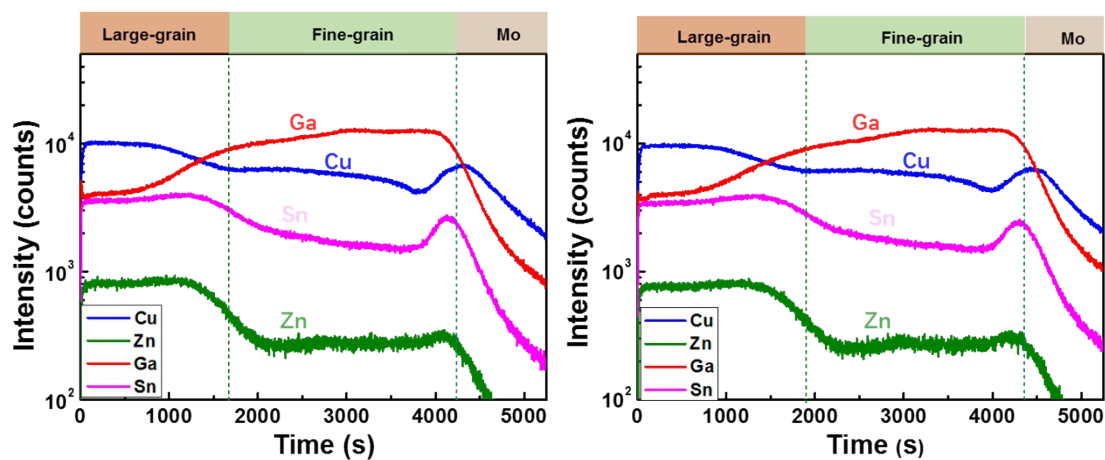
ICP-OES	Cu/(Zn+Sn+Ga)	Ga/(Zn+Sn) [%]	[Cu] [%]	[Zn] [%]	[Sn] [%]	[Ga] [%]
<b>Without Ga-EDT</b>	0.700	0	41.17	32.11	26.72	0
<b>1.6 mg/mL</b>	0.689	2.65	40.78	31.78	25.91	1.53
<b>3.2 mg/mL</b>	0.704	5.41	41.31	31.23	24.45	3.01
<b>4.8 mg/mL</b>	0.698	7.80	41.09	30.67	23.98	4.26



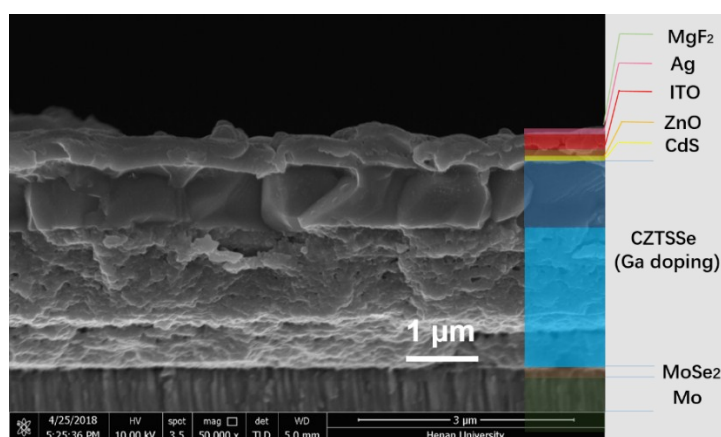
**Figure S6.** Raman spectra for the selenized CZTSSe thin films at different excitation wavelength: (a) 633 nm, (b) 785 nm.



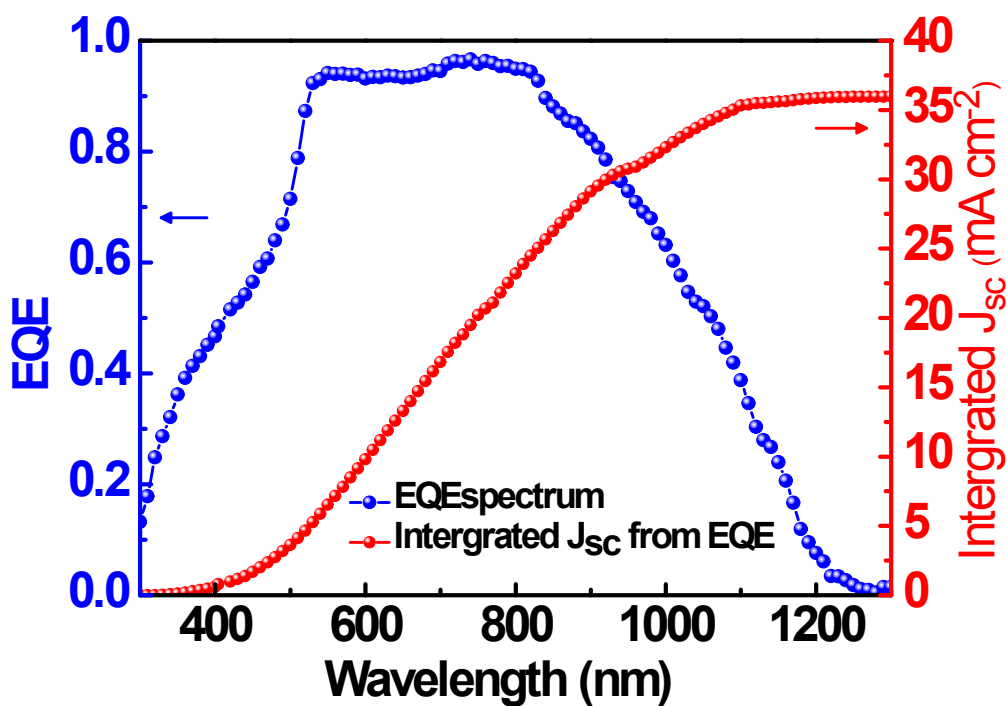
**Figure S7.** (a) Wide-scan X-ray photoelectron spectroscopy of the selenized  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  films with different Ga doping level. High-resolution XPS data (b) Cu 2p region, (c) Zn 2p region, (d) Sn 3d region, and (e) Ga 3d region (not detected).



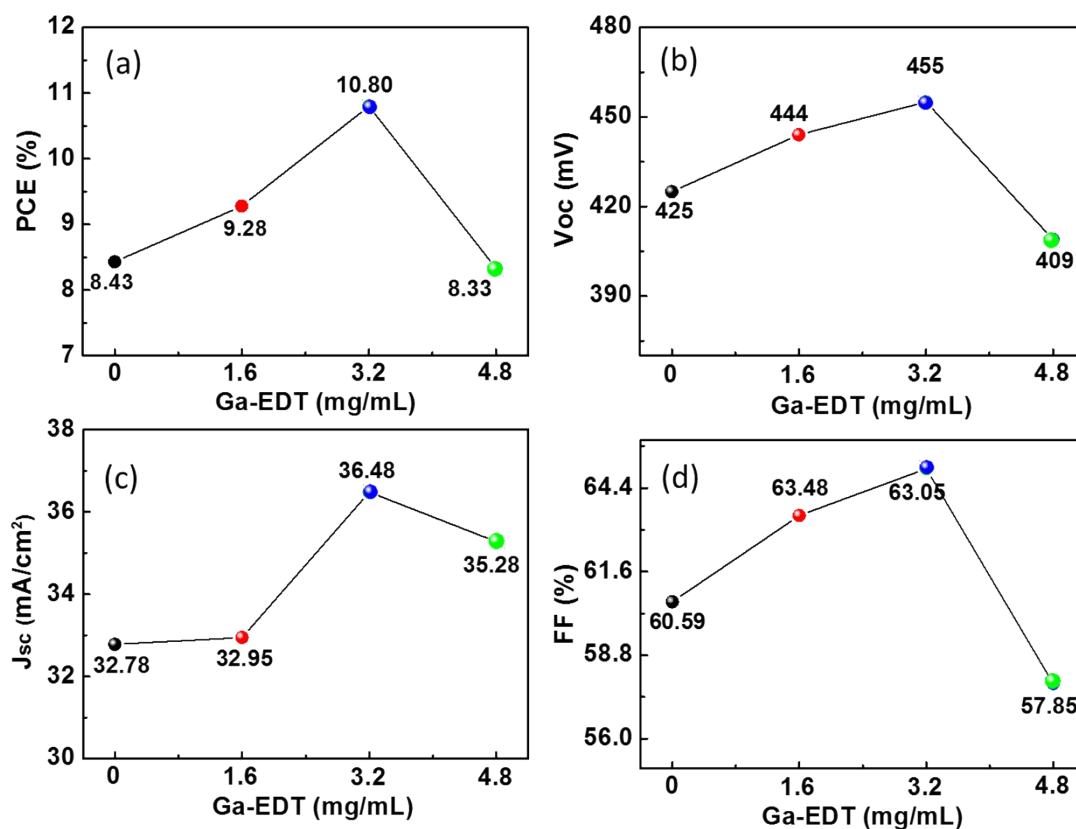
**Figure S8.** SIMS elemental depth profiles of the representative selenized  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  films ( $x= 3.2 \text{ mg mL}^{-1}$ )



**Figure S9.** Cross-section SEM image of the Ga doped  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  solar cells ( $x= 3.2 \text{ mg/mL}$ ).



**Figure S10.** EQE spectrum and the intergrated  $J_{sc}$  of the champion Ga doped  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  ( $x = 3.2 \text{ mg mL}^{-1}$ ) solar cells.



**Figure S11.** Variation of typical parameters of Ga doped  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  solar cells with different Ga doping level: (a) PCE, (b)  $V_{oc}$ , (c)  $J_{sc}$ , and (d) FF.

**Table S2.** The detailed photovoltaic parameters of Ga doped  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  devices with different doping level, in which each sample contained 30 solar cells.

<b>Ga-EDT</b> <b>[without]</b>	<b>Efficiency</b> <b>[%]</b>	<b>Voc</b> <b>[mV]</b>	<b>Jsc</b> <b>[mA/cm<sup>2</sup>]</b>	<b>FF</b> <b>[%]</b>
C1	8.12	420	36.38	53.11
C2	8.16	387	35.24	59.87
C3	7.08	391	34.39	52.61
C4	8.14	390	34.09	61.19
C5	7.21	376	32.68	58.73
C6	7.83	370	35.04	60.44
C7	6.97	371	31.82	59.06
C8	7.72	365	35.58	59.42
C9	8.25	402	33.45	61.38
C10	7.49	393	32.98	57.81
C11	7.19	389	31.56	58.49
C12	7.56	406	36.06	51.66
C13	7.26	403	30.44	59.19
C14	8.02	418	33.47	57.32
C15	8.43	425	32.78	60.59
C16	7.72	406	34.02	55.93
C17	8.19	413	32.84	60.49
C18	8.31	415	32.82	61.08
C19	7.70	388	31.80	62.46
C20	7.17	383	30.67	61.08
C21	6.95	377	30.47	60.40
C22	7.38	398	33.20	55.83
C23	6.80	373	30.29	60.11
C24	7.99	382	36.78	56.86
C25	7.59	394	35.37	54.41
C26	6.72	391	30.26	56.73
C27	8.18	383	36.44	58.58
C28	7.56	378	35.57	56.19
C29	7.68	374	37.15	55.32
C30	7.00	372	33.06	56.92
<b>Average</b>	<b>7.61</b>	<b>391</b>	<b>33.56</b>	<b>58.11</b>

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<b>Ga-EDT</b> <b>[1.6 mg/mL]</b>	<b>Efficiency</b> <b>[%]</b>	<b>Voc</b> <b>[mV]</b>	<b>Jsc</b> <b>[mA/cm<sup>2</sup>]</b>	<b>FF</b> <b>[%]</b>
C1	7.20	418	29.81	57.79
C2	7.93	405	33.93	57.66
C3	7.14	409	29.96	58.30
C4	6.93	421	28.44	57.85
C5	7.07	394	30.63	58.55
C6	8.38	424	31.55	62.68
C7	7.87	425	29.55	62.72
C8	8.15	411	31.96	62.10
C9	7.77	418	30.57	60.83
C10	7.09	421	27.19	61.93
C11	7.07	403	28.08	62.43
C12	8.66	429	32.82	61.56
C13	7.34	391	32.49	57.85
C14	8.36	415	32.23	62.41
C15	8.97	425	33.33	63.35
C16	6.89	384	30.95	57.99
C17	7.91	420	30.88	61.06
C18	9.28	444	32.95	63.48
C19	9.29	443	32.81	63.89
C20	9.09	439	32.49	63.71
C21	8.12	435	31.81	58.72
C22	9.03	442	31.92	63.99
C23	7.49	401	31.70	58.92
C24	7.84	435	30.40	59.23
C25	8.52	418	34.10	59.7
C26	8.15	430	32.45	58.45
C27	8.32	423	32.37	60.86
C28	7.22	422	28.75	59.49
C29	8.04	401	32.30	62.04
C30	7.77	410	33.02	57.36
<b>Average</b>	<b>7.96</b>	<b>419</b>	<b>31.38</b>	<b>60.56</b>

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<b>Ga-EDT</b> <b>[3.2 mg/mL]</b>	<b>Efficiency</b> <b>[%]</b>	<b>Voc</b> <b>[mV]</b>	<b>Jsc</b> <b>[mA/cm<sup>2</sup>]</b>	<b>FF</b> <b>[%]</b>
C1	9.25	411	35.20	63.93
C2	9.13	420	34.77	62.49
C3	9.80	436	34.96	64.36
C4	9.05	420	34.44	62.59
C5	8.92	431	34.21	60.56
C6	9.21	401	36.07	63.68
C7	8.79	412	34.32	62.08
C8	9.00	430	35.41	59.18
C9	9.01	420	35.42	60.54
C10	8.64	415	34.42	60.49
C11	9.04	425	34.39	61.78
C12	8.69	423	33.28	61.74
C13	9.21	433	34.67	61.35
C14	8.92	403	37.25	59.45
C15	8.97	437	33.11	61.95
C16	9.60	453	35.06	60.49
C17	9.60	450	35.62	59.88
C18	8.96	436	34.06	60.27
C19	9.05	419	36.56	59.15
C20	9.55	415	36.94	62.20
C21	9.15	420	34.19	63.67
C22	8.92	421	35.13	60.40
C23	10.80	455	36.48	65.05
C24	9.91	436	37.05	61.31
C25	10.02	437	37.10	61.73
C26	10.03	439	37.41	61.13
C27	10.04	445	36.85	61.24
C28	9.82	441	36.88	60.35
C29	9.15	443	34.19	60.41
C30	9.11	448	34.00	59.82
<b>Average</b>	<b>9.31</b>	<b>429</b>	<b>35.36</b>	<b>61.37</b>

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<b>Ga-EDT</b> <b>[4.8 mg/mL]</b>	<b>Efficiency</b> <b>[%]</b>	<b>Voc</b> <b>[mV]</b>	<b>Jsc</b> <b>[mA/cm<sup>2</sup>]</b>	<b>FF</b> <b>[%]</b>
C1	7.71	382	34.84	57.99
C2	7.07	409	29.40	58.72
C3	6.88	397	31.87	54.44
C4	6.40	404	28.62	55.32
C5	7.13	400	32.11	55.57
C6	7.56	412	30.63	59.94
C7	8.28	423	32.62	60.04
C8	8.30	425	32.68	59.70
C9	8.01	411	33.27	58.61
C10	7.61	415	29.88	61.33
C11	7.06	386	32.64	56.07
C12	6.74	408	29.24	56.59
C13	6.68	399	29.23	57.26
C14	6.81	398	31.42	54.55
C15	6.89	406	29.97	56.70
C16	6.44	394	30.46	53.65
C17	6.97	423	26.97	61.03
C18	7.46	411	29.97	60.62
C19	7.55	427	31.31	56.51
C20	8.34	429	32.93	59.02
C21	7.13	385	35.59	52.00
C22	8.34	409	35.28	57.85
C23	6.48	415	28.07	55.70
C24	7.37	418	30.47	57.87
C25	7.70	402	33.75	56.77
C26	6.70	391	31.78	53.92
C27	7.00	403	30.08	57.70
C28	6.58	413	26.12	61.07
C29	7.02	405	29.60	58.57
C30	7.08	404	30.27	57.88
<b>Average</b>	<b>7.24</b>	<b>407</b>	<b>31.04</b>	<b>57.43</b>

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