ESI to accompany:

Positional isomerism makes a difference: phosphonic acid anchoring ligands with thienyl spacers in copper(I)-based dye-sensitized solar cells

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Synthetic details of precursors:

(1*E*,5*E*)-1,6-Bis(5-bromothiophen-2-yl)hexa-1,5-diene-3,4-dione. 2,3-Butanedione (3.68 g, 42.1 mmol), 5-bromo-2-thiophenecarboxaldehyde (16.1 g, 84.2 mmol) and piperidine (0.72 g, 8.4 mmol) were dissolved in MeOH (200 mL) and the reaction mixture was heated at reflux for 2h. A precipitate started to form after 30 min. The reaction mixture was cooled at −19 °C (refrigerator) overnight. The resulting precipitate was removed by filtration, and washed with cold MeOH (2 × 10 mL). The product was isolated as a brown powder (3.80 g, 8.79 mmol, 20.9%). Decomp. >155 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ/ppm 7.84 (d, J = 15.8, 2H, H^{a}), 7.16 (overlapping d, J = 15.7 Hz and J = 3.9 Hz, 4H, H^{b+B3}), 7.08 (d, J = 3.9 Hz, 2H, H^{B4}). ^{13}C NMR (126 MHz, CD_2Cl_2) δ/ppm 187.5 ($C^{C=O}$), 141.8 (C^{B2}), 138.7 (C^{a}), 133.5 (C^{B3}), 131.6 (C^{B4}), 118.5 (C^{B5}), 118.3 (C^{b}).

(1*E*,5*E*)-1,6-Bis(4-bromothiophen-2-yl)hexa-1,5-diene-3,4-dione. The method was as for (1*E*,5*E*)-1,6-Bis(5-bromothiophen-2-yl)hexa-1,5-diene-3,4-dione but starting with 2,3-butanedione (2.37 g, 27.5 mmol), 4-bromothiophene-2-carboxaldehyde (10.5 g, 55.0 mmol) and piperidine (0.47 g, 5.5 mmol) in MeOH (150 mL). The product was isolated as a yellow powder (1.60 g, 3.7 mmol, 13.5%). Decomp. >208 °C. ^{1}H NMR (500 MHz, CD_2Cl_2) δ/ppm 7.87 (d, J = 15.8 Hz, 2H, H^{a}), 7.37 (m, 2H, H^{B5}), 7.32 (m, 2H, H^{B3}), 7.29 (d, J = 15.8 Hz, 2H, H^{b}). ^{13}C NMR (126 MHz, CD_2Cl_2) δ/ppm 187.2 ($C^{C=O}$), 141.0 (C^{B2}), 138.4 (C^{a}), 134.6 (C^{B3}), 127.3 (C^{B5}), 119.1 (C^{b}), 111.7 (C^{B4}).

4,4'-Bis(5-bromothiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine. (1*E*,5*E*)-1,6-Bis(5-bromothiophen-2-yl)hexa-1,5-diene-3,4-dione (2.00 g, 4.63 mmol), 1-(2-oxopropyl)pyridin-1-ium chloride (1.99 g, 11.6 mmol) and NH_4OAc (5.00 g, 64.8 mmol) were dissolved in EtOH (100 mL) and the reaction mixture was heated at reflux for 4h. The reaction mixture was concentrated by solvent removal in vacuo and cooled at −19 °C (refrigerator) until a preciptate formed. The precipitate was removed by filtration and was washed with cold MeOH (2 × 15 mL). 4,4'-Bis(5-

bromothiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine was isolated as an off-white powder (0.91 g, 1.8 mmol, 39%). M.p. 233 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 8.35 (d, J = 1.6 Hz, 2H, H^{A3}), 7.37 (d, J = 3.9 Hz, 2H, H^{B3}), 7.26 (m, 2H, H^{A5}), 7.10 (d, J = 3.9 Hz, 2H, H^{B4}), 2.67 (s, 6H, H^{Me}). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ppm 159.0 (C^{A6}), 156.5 (C^{A2}), 143.4 (C$^{A4/B2}$), 141.8 (C$^{A4/B2}$), 131.3 (C^{B4}), 125.8 (C^{B3}), 119.2 (C^{A5}), 114.6 (C^{A3}), 114.1 (C^{B5}), 24.8 (C^{Me}). ESI MS m/z 506.7 $[M+H]^+$ (calc. 506.9).

4,4'-Bis(4-bromothiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine. The method was as for 4,4'-bis(5-bromothiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine, but starting with (1*E*,5*E*)-1,6-bis(4-bromothiophen-2-yl)hexa-1,5-diene-3,4-dione (0.99 g, 2.29 mmol), 1-(2-oxopropyl)pyridin-1-ium chloride (0.98 g, 5.73 mmol) and NH_4OAc (2.65 g, 34.4 mmol) in EtOH (70 mL). 4,4'-Bis(4-bromothiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine was isolated as an off-white powder (0.24 g, 0.47 mmol, 21%). M.p. 228 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 8.40 (d, J = 1.6 Hz, 2H, H^{A3}), 7.52 (d, J = 1.4 Hz, 2H, H^{B3}), 7.32 (d, J = 1.7 Hz, 2H, H^{A5}), 7.31 (d, J = 1.4 Hz, 2H, H^{B5}), 2.69 (s, 6H, H^{Me}). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ/ppm 159.1 (C^{A6}), 156.5 (C^{A2}), 143.0 (C$^{A4/B2}$), 141.4 (C$^{A4/B2}$), 128.0 (C^{B3}), 124.0 (C^{B5}), 119.4 (C^{A5}), 114.8 (C^{A3}), 111.2 (C^{B4}), 24.8 (C^{Me}). ESI MS m/z 506.9 $[M+H]^+$ (calc. 506.9).

DSC preparation. Working electrodes were either commercial (Solaronix Test Cell Titania Electrodes) or were made by screen-printing TiO_2 paste on FTO glass as previously detailed[1] using a post-treatment with $TiCl_4$ (40 mM aqueous solution). The electrodes were washed with milliQ water and EtOH and sintered at 450 °C for 30 min, then cooled to ≈80 °C and immersed in a DMSO solution of **1**, **2** or **3** (1.0 mM) for 24 h at room temperature. The colourless electrodes were removed from the solution, washed with DMSO and EtOH and dried using a heat gun (100 °C). Each electrode was then immersed for 3 days in an acetone solution of [Cu(**4**)$_2$][PF_6], [Cu(**5**)$_2$][PF_6], [Cu(**6**)$_2$][PF_6] or [Cu(**7**)$_2$][PF_6] (0.1 mM); during this period, the electrodes turned red-orange. They were removed from the dye-bath, washed with acetone and dried with a heat gun (80 °C). An N719 reference electrode was made by immersing a Solaronix Test Cell

Titania Electrode in a 0.3 mM EtOH solution of N719 (Solaronix) for 3 days. The electrode was then removed, washed with EtOH and dried with a heat gun (80 °C). For the counter electrodes, Solaronix Test Cell Platinum Electrodes were used, and volatile organic impurities were removed by heating on a heating plate (450 ^{o}C, 30 min).

The dye-covered TiO_2 electrode and Pt counter-electrode were combined using thermoplast hot-melt sealing foil (Solaronix Test Cell Gaskets) by heating while pressing them together. The electrolyte (LiI (0.1 M), I_2 (0.05 M), 1-methylbenzimidazole (0.5 M), 1-butyl-3-methylimidazolinium iodide (0.6 M) in 3-methoxypropionitrile) was introduced into the DSC by vacuum backfilling. The hole in the counter electrode was sealed with hot-melt sealing foil (Solaronix Test Cell Sealings) and a cover glass (Solaronix Test Cell Caps).

Measurements were made by irradiating from behind using a light source LOT Quantum Design LS0811 (100 mW cm^{-2} = 1 sun). The power of the simulated light was calibrated using a reference Si cell. All DSCs were completely masked before measurements were made.

For solid-state absorption spectra of adsorbed dyes, Solaronix Test Cell Titania Electrodes Transparent were used and the dye assembly used the same soaking regime as described above

External quantum efficiencies. External quantum efficiency (EQE) measurements were made using a Spe-Quest quantum efficiency instrument from Rera Systems (Netherlands) with a 100 W halogen lamp (QTH) and a lambda 300 grating monochromator (Lot Oriel). The monochromatic light was modulated to 3Hz using a chopper wheel (ThorLabs). The cell response was amplified with a large dynamic range IV converter (CVI Melles Griot) and measured with a SR830 DSP Lock-In amplifier (Stanford Research).

Electrochemical impedance spectroscopy. Electrochemical impedance spectroscopy (EIS) measurements were carried out on a ModuLab® XM PhotoEchem photoelectrochemical measurement system from Solartron Analytical. The impedance was measured around the open-circuit potential of the cell at different light intensities (590 nm) in the frequency range

0.05 Hz to 400 kHz using an amplitude of 10 mV. The impedance data was analysed using ZView® software from Scribner Associates Inc.

References

1. B. Bozic-Weber, E. C. Constable, S. O. Fürer, C. E. Housecroft, L. J. Troxler and J. A. Zampese, *Chem*. *Commun*., 2013, **49**, 7222.

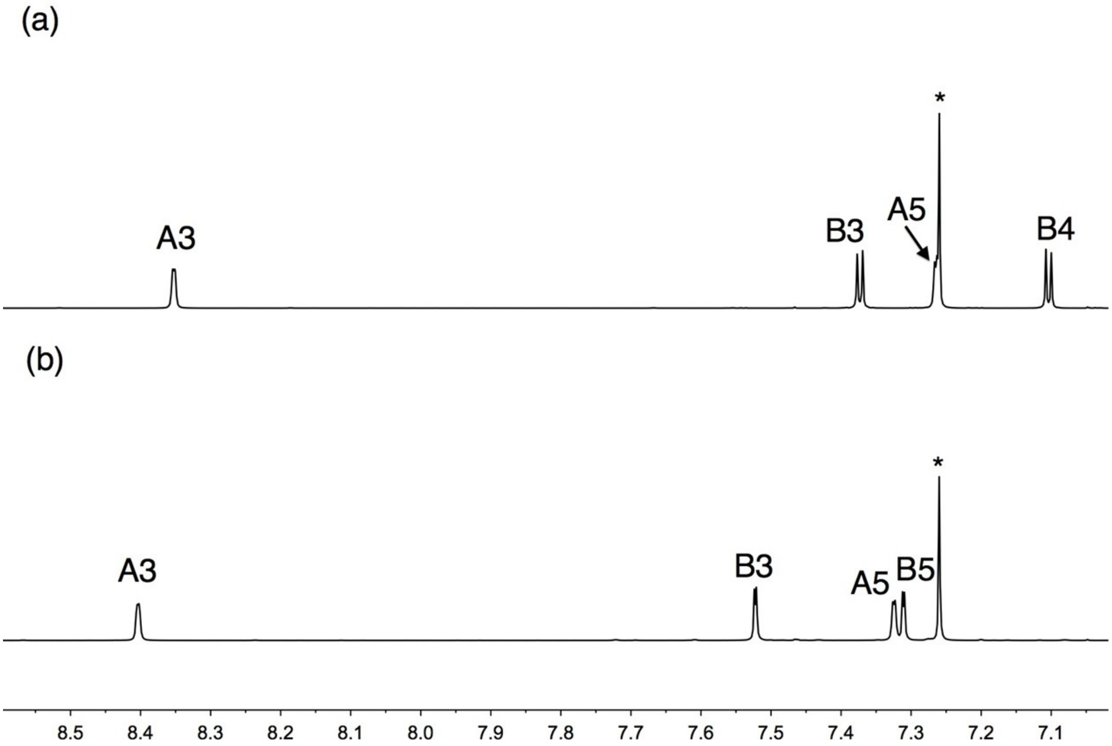
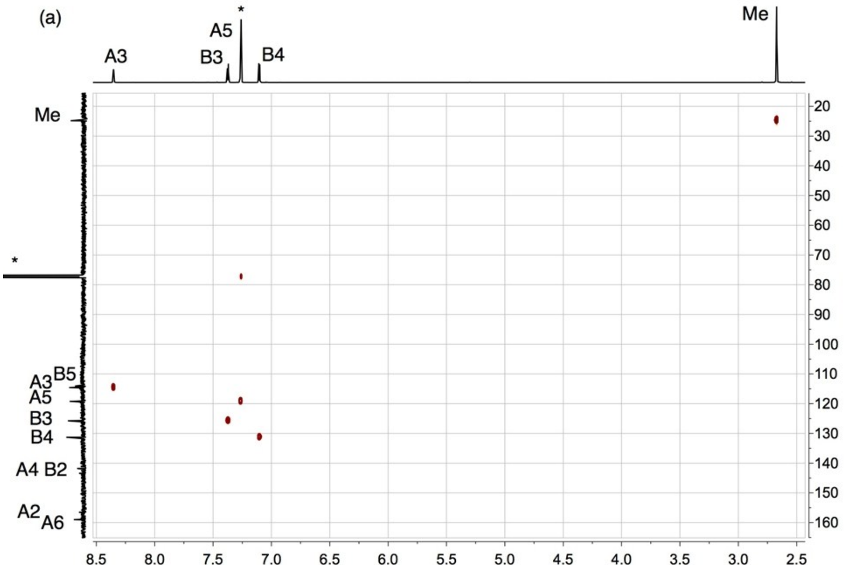


Fig. S1. Aromatic regions of the 500 MHz ^{1}H NMR spectra of (a) 4,4'-bis(5-bromothiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine and (b) 4,4'-bis(4-bromothiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine. * = residual $CHCl_3$ in $CDCl_3$ solvent. Chemical shifts in δ/ppm.



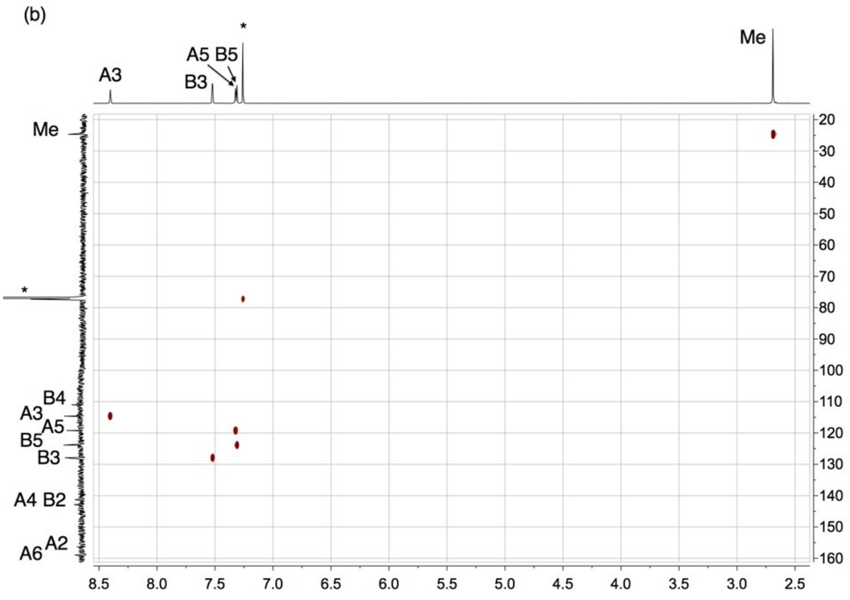
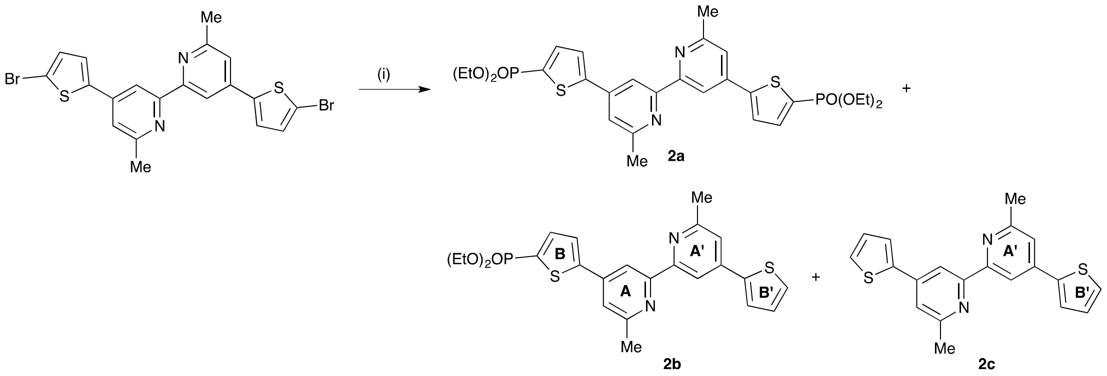


Fig. S2. HMBC spectra (^{1}H, 500 MHz; ^{13}C, 126 MHz) of (a) 4,4'-bis(5-bromothiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine and (b) 4,4'-bis(4-bromothiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine. * = residual $CHCl_3$/$CDCl_3$ solvent. Chemical shifts in δ/ppm.

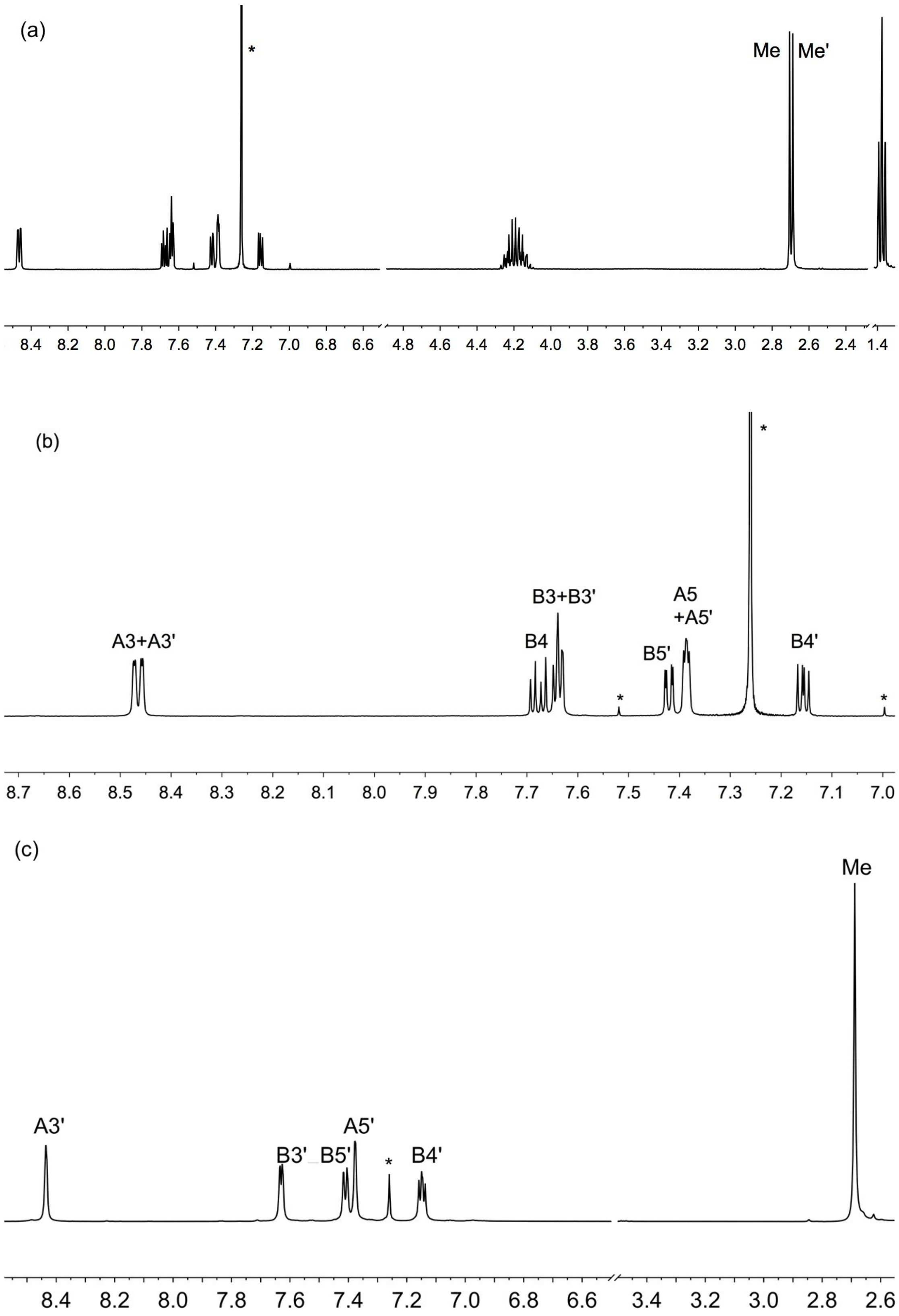


Scheme S1. Competing reactions in the conversion of 4,4'-bis(5-bromothiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine to **2a**; analogous reactions occur during the conversion of 4,4'-bis(5-bromothiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine to **3a**. Cs_2CO_3, $[Pd(PPh_3)_4]$, $HPO(OEt)_2$ in THF, microwave reactor, 90 °C, 2h.

Characterization data for 2b and 2c

2b: M.p. 198 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 8.47 (d, J = 1.6 Hz, 1H, $H^{A3/A3'}$), 8.45 (d, J = 1.6 Hz, 1H, $H^{A3/A3'}$), 7.68 (dd, J_{PH} = 8.2 Hz, J_{HH} = 3.8 Hz, 1H, H^{B4}), 7.63 (m, 1H, $H^{B3+B3'/B5'}$), 7.63 (m, 1H, $H^{B3+B3'}$), 7.42 (dd, J = 5.0, 1.1 Hz, 1H, $H^{B5'}$), (overlapping d, 2H, $H^{A5+A5'}$), 7.15 (dd, J = 5.1, 3.6 Hz, 1H, $H^{B4'}$), 4.27–4.11 (m, 4H, H$^{\text{Et-CH}_2}$), 2.73 (s, 3H, H$^{\text{Me/Me'}}$), 2.69 (s, 3H, H$^{\text{Me/Me'}}$), 1.37 (m, 6H, H$^{\text{Et-CH}_3}$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ/ppm 159.1 (C$^{\text{A6/A6'}}$), 158.8 (C$^{\text{A6/A6'}}$), 156.9 (C$^{\text{A2/A2'}}$), 156.2 (C$^{\text{A2/A2'}}$), 150.0 (C$^{\text{B2}}$), 142.7 (C$^{\text{A4/A4'}}$), 142.0 (C$^{\text{B2'}}$), 141.4 (C$^{\text{A4/A4'}}$), 137.7 (d, J_{PC} = 11 Hz, C$^{\text{B4}}$), 129.0 (d, J_{PC} = 209 Hz, C$^{\text{B5}}$), 128.5 (C$^{\text{B4'}}$), 127.0 (C$^{\text{B5'}}$), 126.1 (d, J_{PC} = 17 Hz, C$^{\text{B3}}$), 125.6 (C$^{\text{B3'}}$), 119.8 (C$^{\text{A5+A5'}}$), 115.3 (C$^{\text{A3/A3'}}$), 115.1 (C$^{\text{A3/A3'}}$), 63.0 (d, J_{PC} = 5.3 Hz, C$^{\text{Et-CH}_2}$), 24.85 (C$^{\text{Me/Me'}}$), 24.8 (C$^{\text{Me/Me'}}$), 16.5 (d, J_{PC} = 6.6 Hz, C$^{\text{Et-CH}_3}$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ/ppm +10.9. ESI-MS *m/z* 485.1 [M+H] (calc. 485.1). Found C 59.63, H 5.14, N 5.44%; $C_{24}H_{25}N_2O_3PS_2$ requires C 59.49, H 5.20, N 5.78%.

2c: Decomp. >210 ^{o}C. ^{1}H NMR (500 MHz, CDCl$_3$) δ/ppm 8.43 (d, J = 1.7 Hz, 2H, H$^{\text{A3'}}$), 7.63 (dd, J = 3.7, 1.2 Hz, 2H, H$^{\text{B3'}}$), 7.41 (dd, J = 5.0, 1.2 Hz, 2H, H$^{\text{B5'}}$), 7.38 (d, J = 1.7 Hz, 2H, H$^{\text{A5'}}$), 7.15 (dd, J = 5.1, 3.6 Hz, 1H, H$^{\text{B4'}}$), 2.69 (s, 3H, H$^{\text{Me}}$). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ/ppm 158.8 (C$^{\text{A6'}}$), 156.4 (C$^{\text{A2'}}$), 142.7 (C$^{\text{B2'/A4'}}$), 142.0 (C$^{\text{B2'/A4'}}$), 128.4 (C$^{\text{B4'}}$), 127.0 (C$^{\text{B5'}}$), 125.6 (C$^{\text{B3'}}$), 119.7 (C$^{\text{A5'}}$), 115.1 (C$^{\text{A3'}}$), 24.8 (C$^{\text{Me}}$). ESI-MS *m/z* 349.1 [M+H]$^{+}$ (calc. 349.1). High resolution ESI-MS *m/z*: 349.0834 [M+H]$^{+}$ (calc. 349.0828).



□□□□□□□. 500 MHz ^{1}H NMR spectra of (a) compound **2b** (see Scheme S1), and (b) an expansion of the aromatic region; (c) 4,4'-bis(thiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine (**2c** in Scheme S1). Peaks labelled * are residual $CHCl_3$ and ^{13}C satellites. Chemical shifts in δ□□□□.

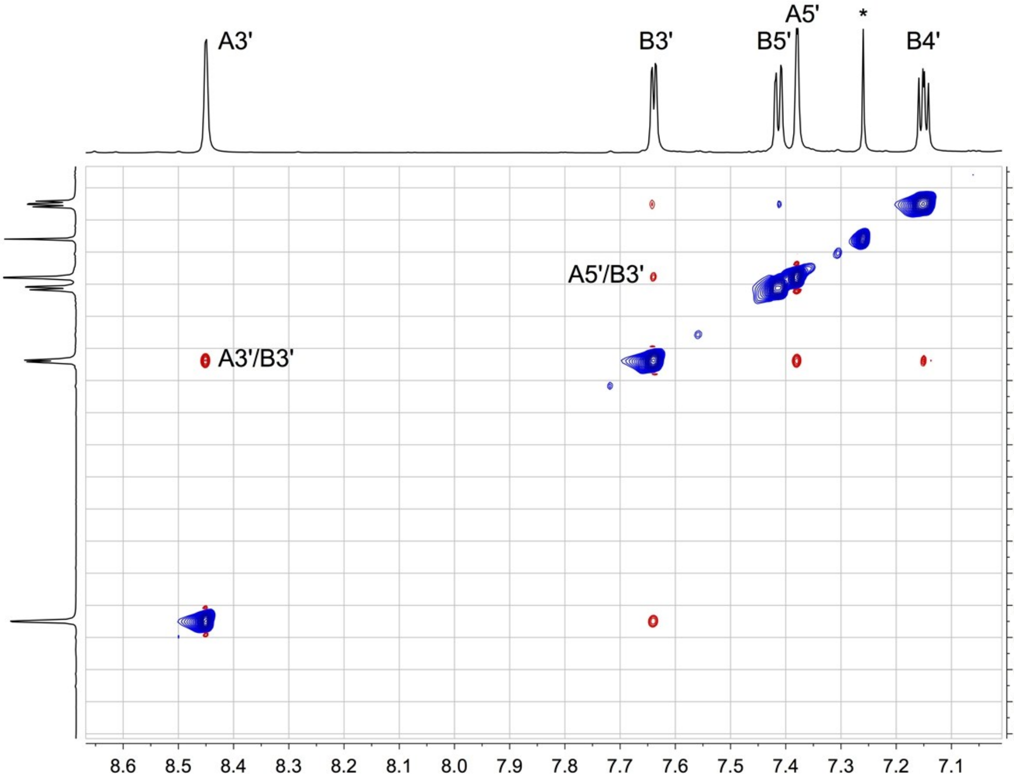
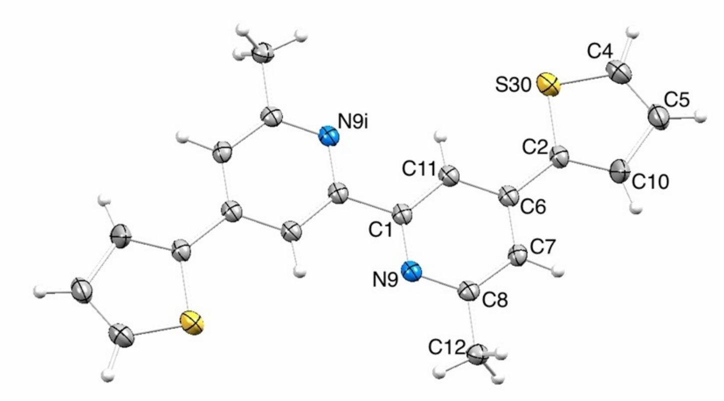


Fig. S4. 500 MHz NOESY spectrum of 4,4'-bis(thiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine (**2c** in Scheme S1) used to distinguish signals for $\mathrm{H}^{B3'}$ and $\mathrm{H}^{B5'}$. Chemical shifts in δ□□□□.



□□□□□□5□□□□□□□□□□□□□□□□ 4,4'-bis(thiophen-2-yl)-6,6'-dimethyl-2,2'-bipyridine; ellipsoids plotted at the 40% probability level. The thiophene is disordered and is modelled over two positions of 0.60 and 0.40 fractional occupancies; the major site is shown. Symmetry code i = 1–*x*, –*y*, 1–*z*. Selected bond metrics: C2–S30 = 1.673(2), C4–S30 = 1.594(3), N9–C1 = 1.348(2), C8–N9 = 1.341(2), C1–C1$^{\mathrm{i}}$ = 1.492(3), C8–C12 = 1.507(2) Å; C2–S30–C4 = 93.36(12), C8–N9–C1 = 117.59(14)$^{\circ}$.

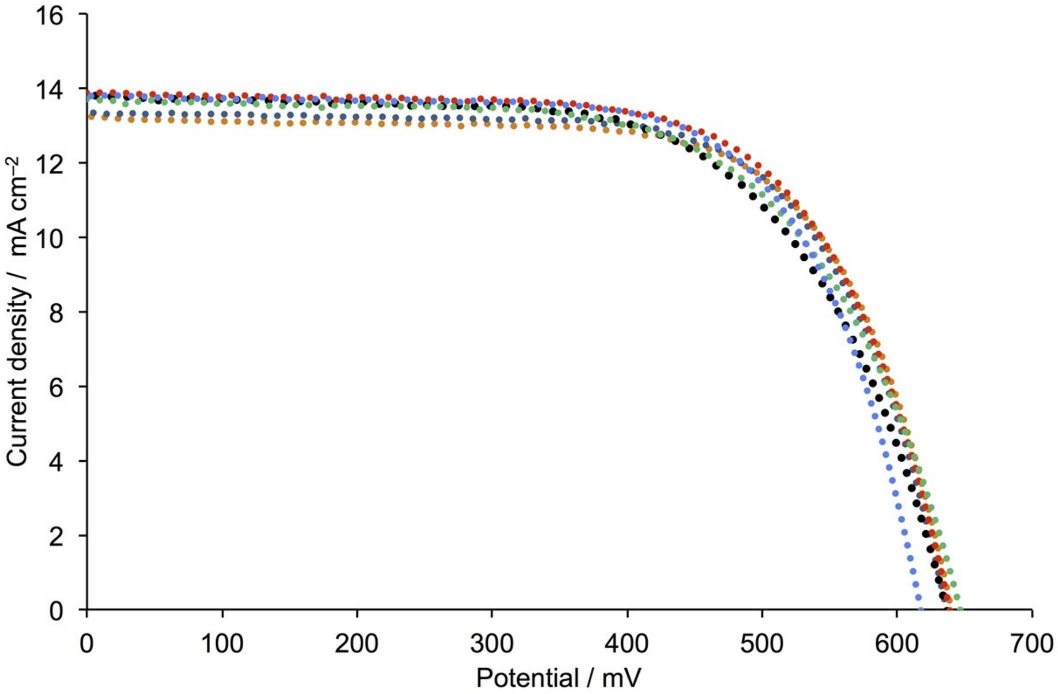


Fig. S6. *J*–*V* curves for six DSCs with N719 recorded on the day of DSC assembly to validate the reproducibility of the data.

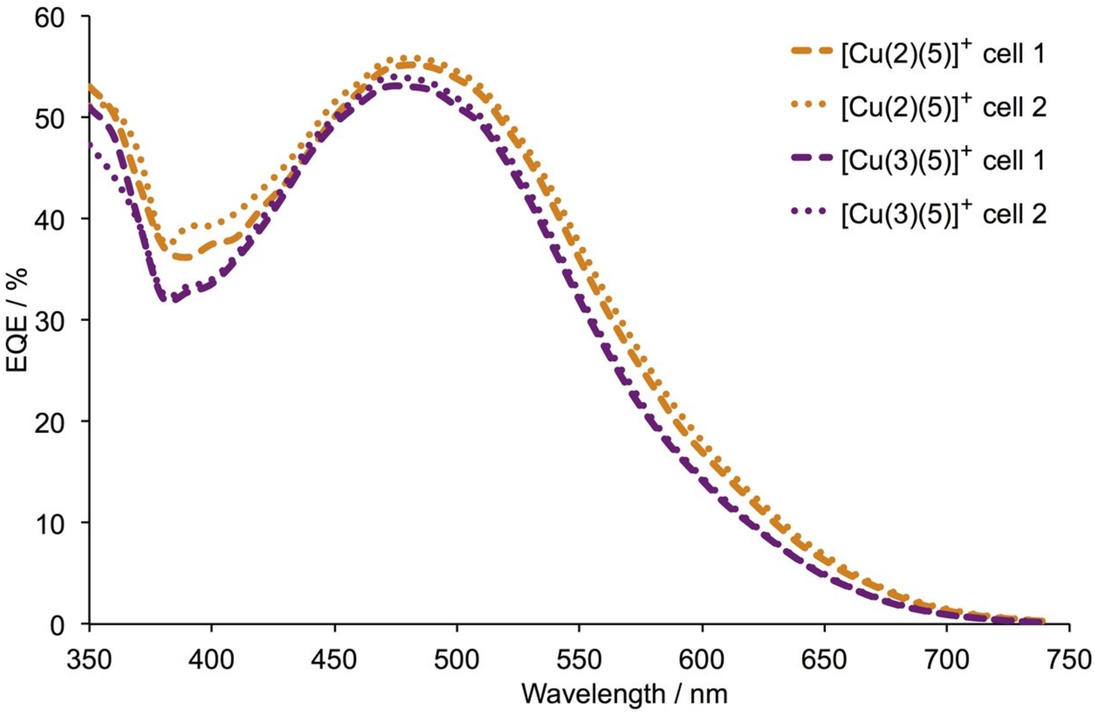


Fig. S7. EQE spectra for duplicate DSCs with [Cu(**2**)(**5**)]$^+$ and [Cu(**3**)(**5**)]$^+$ and in-house, screen-printed FTO/TiO_2 electrodes, recorded on the day of DSC assembly.

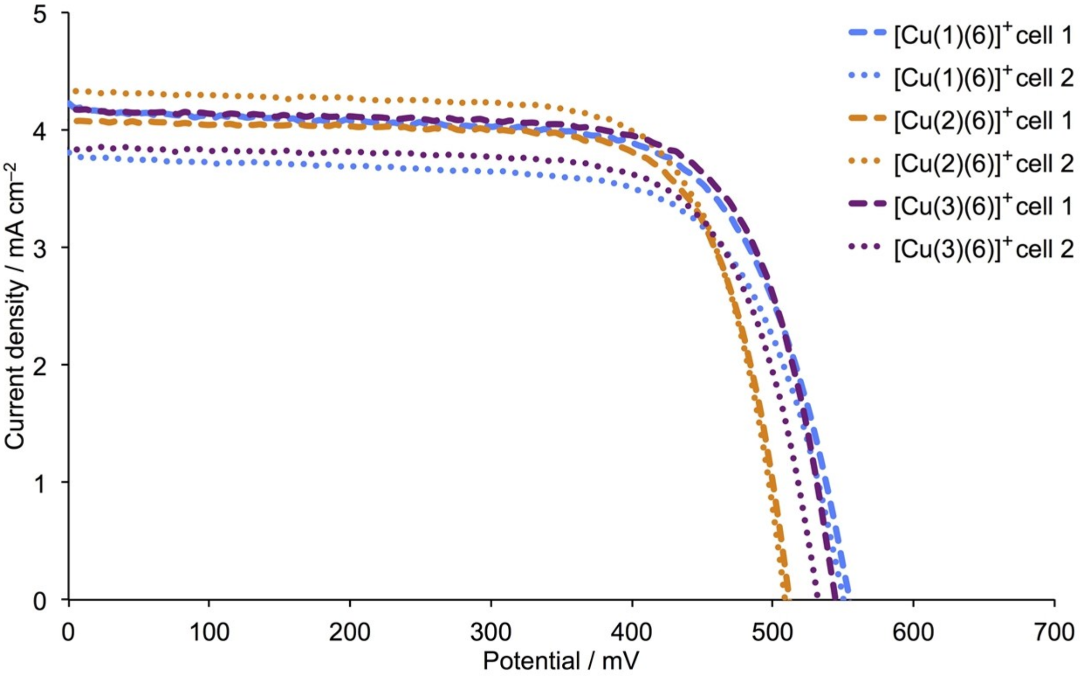


Fig. S8. *J*–*V* curves for duplicate DSCs with [Cu(**1**)(**6**)]$^{+}$, [Cu(**2**)(**6**)]$^{+}$ and [Cu(**3**)(**6**)]$^{+}$ and commercial FTO/TiO$_2$ electrodes, recorded on the day of DSC fabrication.

Table S1. Parameters for six reference DSCs with N719; commercial electrodes were used for the photoanodes and a LOT Quantum Design LS0811 was used as the light source.

Dye and cell number	J_{SC} / mA cm^{-2}	V_{OC} / mV	*ff* / %	η / %
	On the day of assembling the DSC			
N719 cell 1	13.38	636	68	5.81
N719 cell 2	13.23	640	69	5.81
N719 cell 3	13.81	636	63	5.56
N719 cell 4	13.88	639	67	5.94
N719 cell 5	13.74	646	63	5.63
N719 cell 6	13.81	617	68	5.82
Average±standard deviation[a]	13.64±0.27	636±10	66±3	5.76±0.14
	1 day after assembling the DSC			
N719 cell 1	13.30	658	67	5.90
N719 cell 2	13.49	640	65	5.65
N719 cell 3	13.65	647	64	5.64
N719 cell 4	13.24	662	64	5.61
N719 cell 5	14.00	633	67	5.98
N719 cell 6	13.60	661	67	6.00
Average±standard deviation[a]	13.55±0.27	650±12	66±2	5.80±0.18
	3 days after assembling the DSC			
N719 cell 1	12.78	688	67	5.85
N719 cell 2	12.97	680	66	5.78
N719 cell 3	13.13	684	64	5.78
N719 cell 4	13.45	687	66	6.09
N719 cell 5	12.72	700	66	5.88
N719 cell 6	13.81	668	67	6.22
Average±standard deviation[a]	13.14±0.42	684±11	66±1	5.93±0.18
	7 days after assembling the DSC			
N719 cell 1	12.61	698	66	5.80
N719 cell 2	13.13	686	65	5.82
N719 cell 3	13.30	684	63	5.72
N719 cell 4	13.29	689	65	5.93
N719 cell 5	12.43	711	68	5.99
N719 cell 6	13.55	680	67	6.14
Average±standard deviation[a]	13.05±0.44	691±11	66±2	5.90±0.15

[a] Standard deviation = $\sqrt{\frac{1}{n}\sum_{i=1}^{n}(n_i - n_{average})^2}$

Table S2. Parameters of duplicate, masked DSCs with [Cu(**2**)(**5**)]$^+$ and [Cu(**3**)(**5**)]$^+$ compared to a reference DSC with N719; in-house, screen-printed electrodes were used for the photoanodes and a LOT Quantum Design LS0811 was used as the light source.

Dye	J_{SC} / mA cm^{-2}	V_{OC} / mV	*ff* / %	η / %	Relative η / %[a]
On the day of sealing the cells					
[Cu(**2**)(**5**)]$^+$	6.18	539	69	2.31	40.1
[Cu(**2**)(**5**)]$^+$	6.53	535	69	2.41	41.8
[Cu(**3**)(**5**)]$^+$	5.91	596	67	2.37	41.1
[Cu(**3**)(**5**)]$^+$	5.75	595	69	2.38	41.3
N719	13.64	636	66	5.76	100
3 days after sealing the cells					
[Cu(**2**)(**5**)]$^+$	5.90	535	67	2.13	35.9
[Cu(**2**)(**5**)]$^+$	5.28	535	68	1.91	32.2
[Cu(**3**)(**5**)]$^+$	5.87	589	64	2.23	37.6
[Cu(**3**)(**5**)]$^+$	6.02	591	67	2.40	40.5
N719	13.14	684	66	5.93	100
7 days after sealing the cells					
[Cu(**2**)(**5**)]$^+$	5.72	548	69	2.16	36.6
[Cu(**2**)(**5**)]$^+$	5.95	541	68	2.20	37.3
[Cu(**3**)(**5**)]$^+$	5.53	626	68	2.36	40.0
[Cu(**3**)(**5**)]$^+$	5.61	603	69	2.35	39.8
N719	13.05	691	66	5.90	100

[a] Relative to N719 set at 100%. See Table S1 for N719 DSCs.

Table S3. Parameters of duplicate, masked DSCs with $[Cu(L_{anchor})(L_{ancillary})]^{+}$ (L_{anchor} = **1–3**, $L_{ancillary}$ = **6**, **7**) measured 3 and 7 days after cell fabrication compared to a reference DSC with N719; commercial FTO/TiO_2 electrodes were used. The light source was a LOT Quantum Design LS0811. See Table 6 for day 0 data.

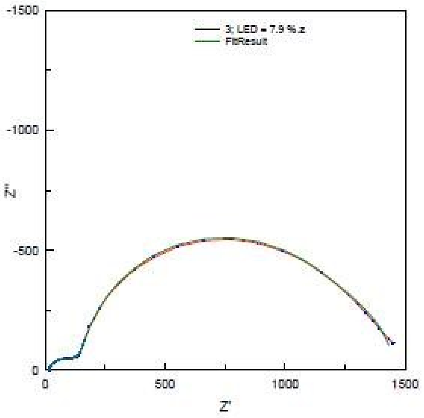
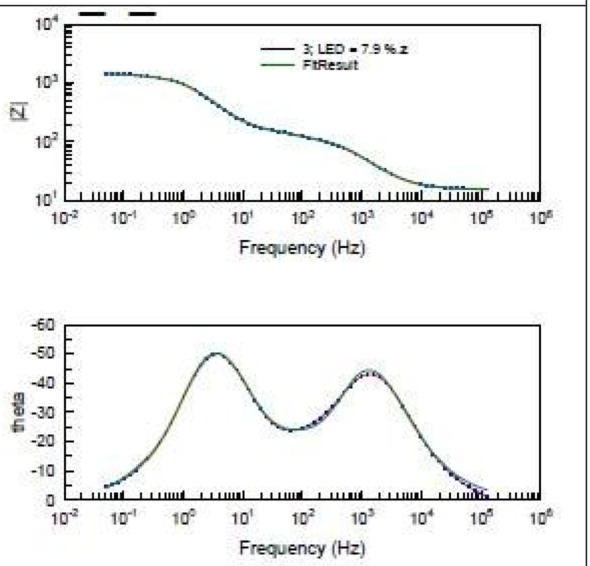
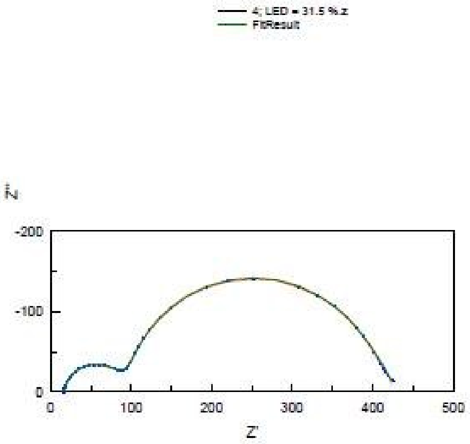
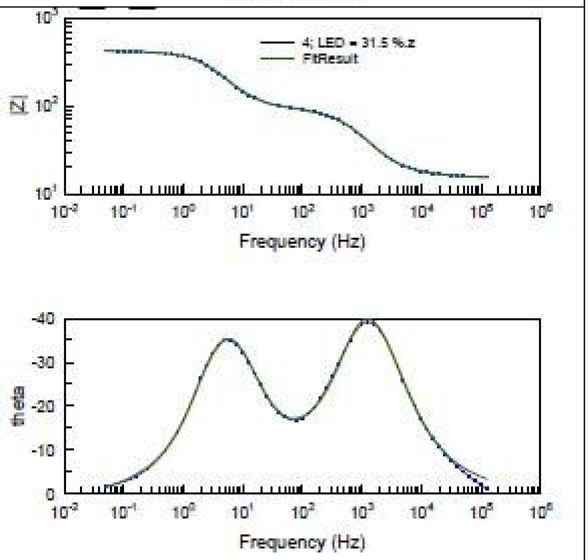
Dye	J_{SC} / mA cm^{-2}	V_{OC} / mV	*ff* / %	η / %	Relative η / %[a]
3 days after sealing the cells					
[Cu(**1**)(**6**)]$^{+}$ [b]	3.08	540	70	1.17	19.7
[Cu(**1**)(**6**)]$^{+}$ [b]	2.90	556	71	1.15	19.4
[Cu(**1**)(**7**)]$^{+}$	3.57	597	75	1.60	27.0
[Cu(**1**)(**7**)]$^{+}$	3.73	561	73	1.53	25.8
[Cu(**2**)(**6**)]$^{+}$	3.39	539	73	1.33	22.4
[Cu(**2**)(**6**)]$^{+}$	4.37	553	74	1.79	30.2
[Cu(**2**)(**7**)]$^{+}$	4.20	550	73	1.69	28.5
[Cu(**2**)(**7**)]$^{+}$	4.58	553	75	1.89	31.9
[Cu(**3**)(**6**)]$^{+}$	3.87	593	73	1.68	28.3
[Cu(**3**)(**6**)]$^{+}$	3.57	553	74	1.45	24.5
[Cu(**3**)(**7**)]$^{+}$	4.14	600	70	1.74	29.3
[Cu(**3**)(**7**)]$^{+}$	4.52	597	73	1.97	33.2
N719	13.14	684	66	5.93	100
7 days after sealing the cells					
[Cu(**1**)(**6**)]$^{+}$ [b]	3.04	537	70	1.15	19.5
[Cu(**1**)(**6**)]$^{+}$ [b]	2.82	564	70	1.12	19.0
[Cu(**1**)(**7**)]$^{+}$	3.50	590	75	1.55	26.3
[Cu(**1**)(**7**)]$^{+}$	3.79	558	73	1.55	26.3
[Cu(**2**)(**6**)]$^{+}$	3.50	551	74	1.43	24.2
[Cu(**2**)(**6**)]$^{+}$	4.31	566	75	1.82	30.8
[Cu(**2**)(**7**)]$^{+}$	4.22	563	74	1.77	30.0
[Cu(**2**)(**7**)]$^{+}$	4.59	563	75	1.94	32.9
[Cu(**3**)(**6**)]$^{+}$	3.86	594	73	1.68	28.5
[Cu(**3**)(**6**)]$^{+}$	3.54	556	74	1.46	24.7
[Cu(**3**)(**7**)]$^{+}$	4.13	604	71	1.77	30.0
[Cu(**3**)(**7**)]$^{+}$	4.44	602	73	1.96	33.2
N719	13.05	691	66	5.90	100

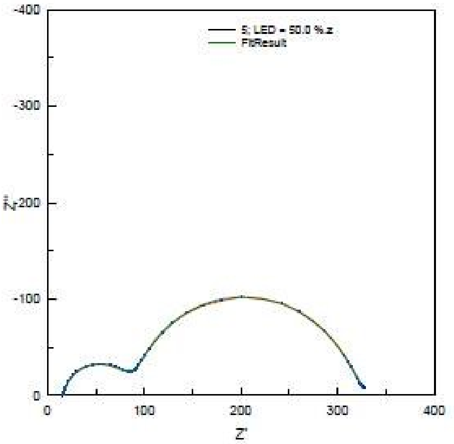
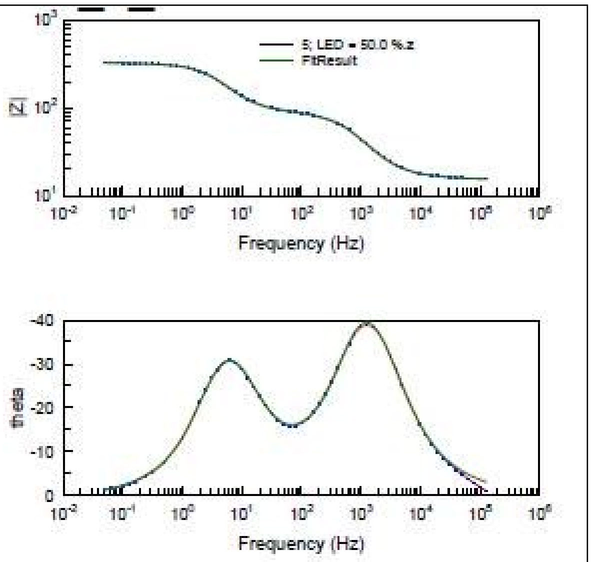
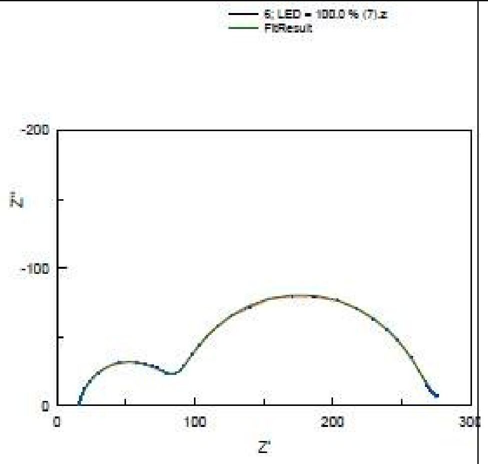
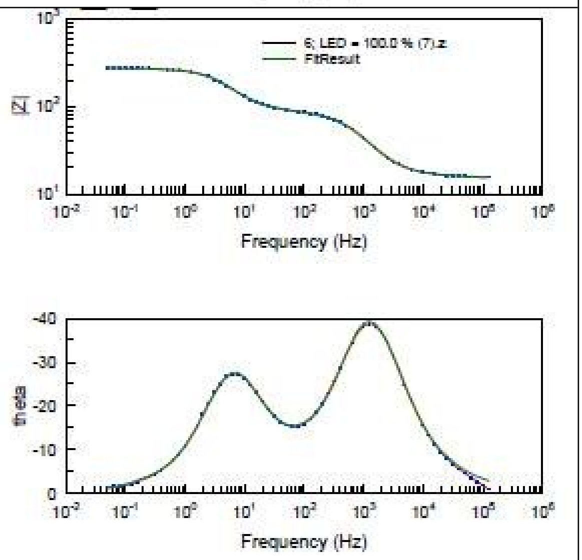
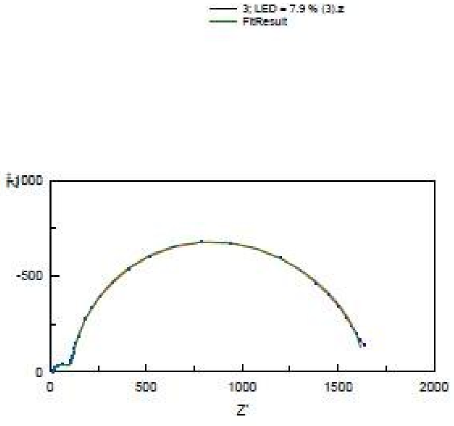
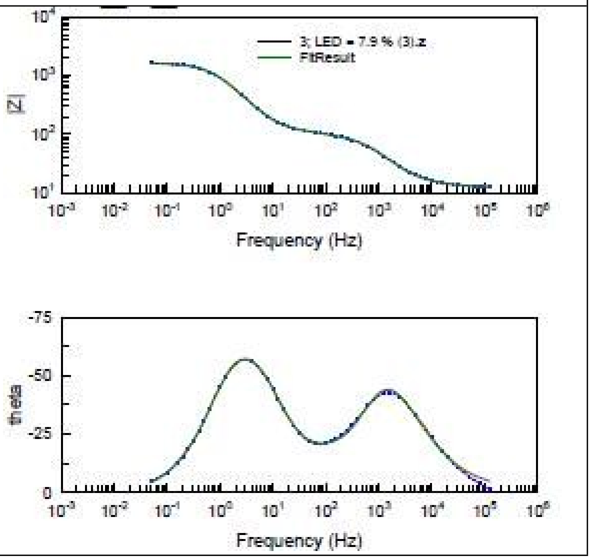
[a] Relative to N719 set at 100%. [b] Data are from Table 1.

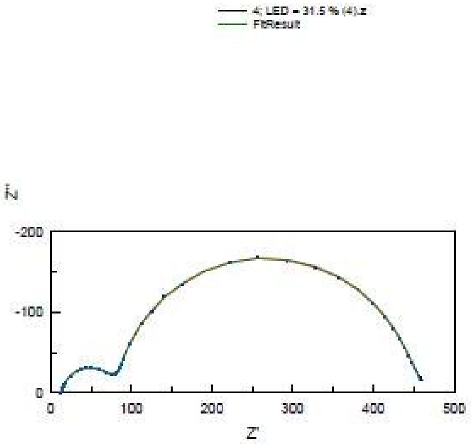
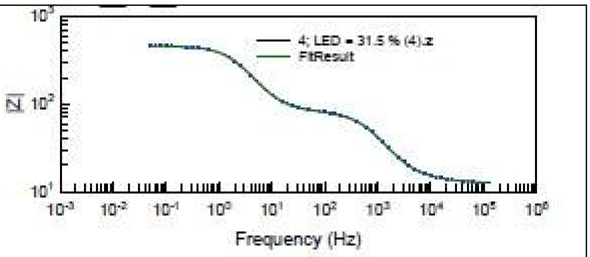
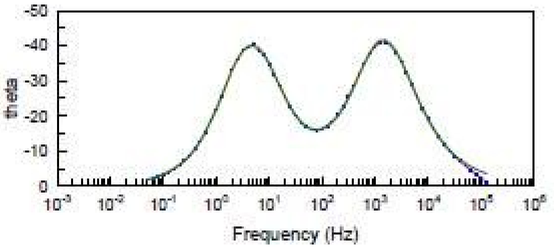
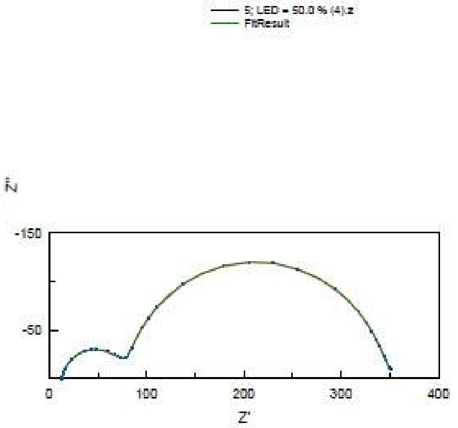
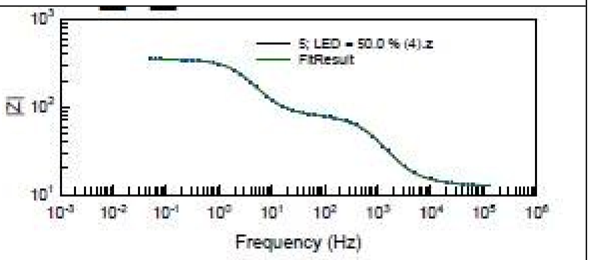
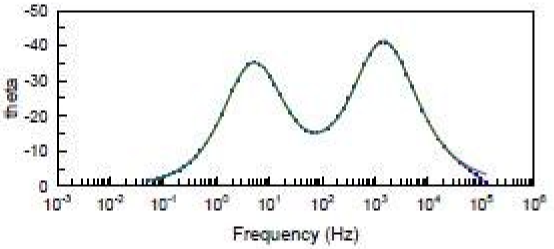
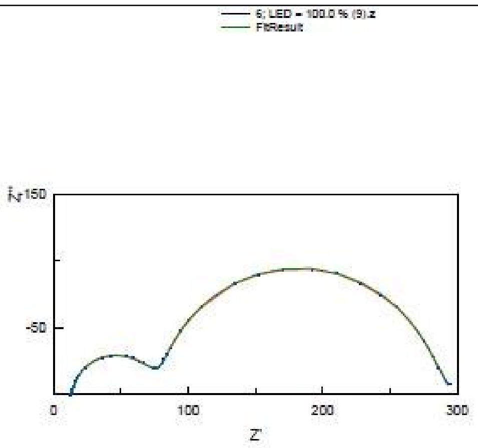
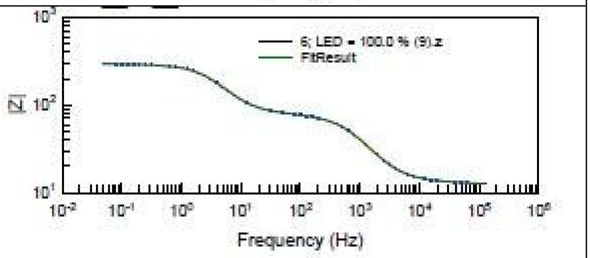
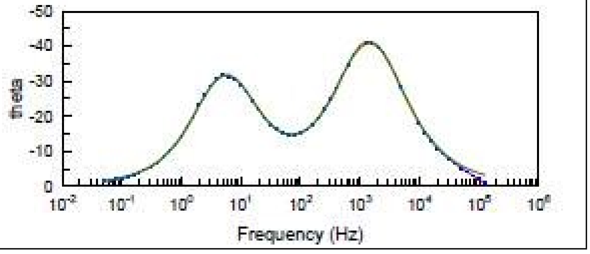
Table S4. Impedance data obtained during measurements at different light intensities (2,4, 10.0, 15.0 and 22.0 mW cm^{-2}). EIS measurements are carried out 3 days after DSC assembly.

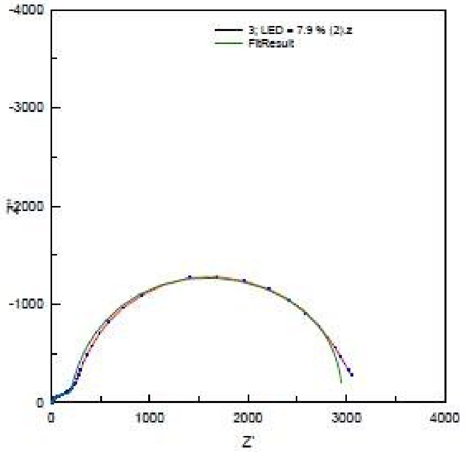
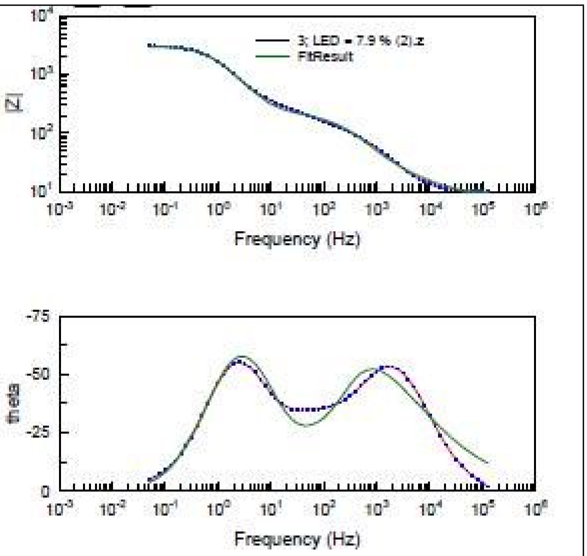
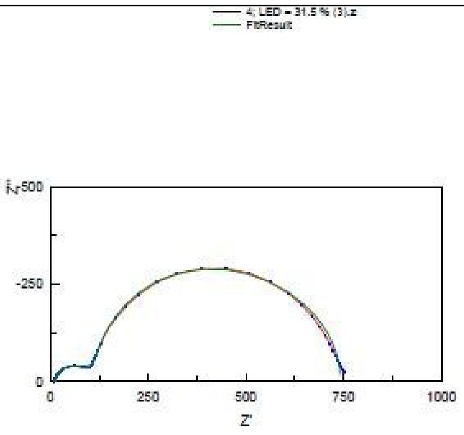
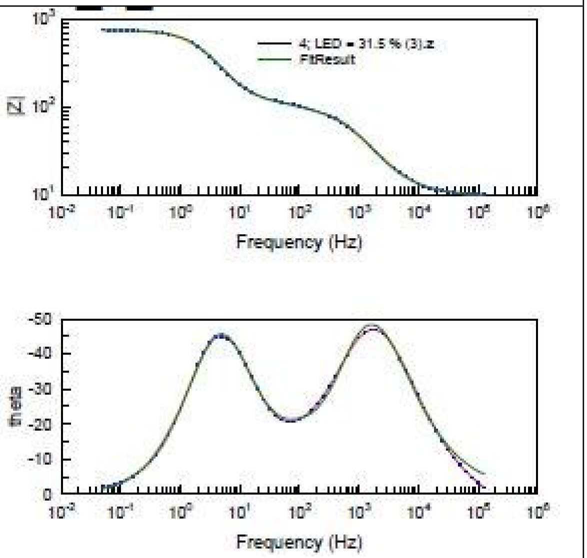
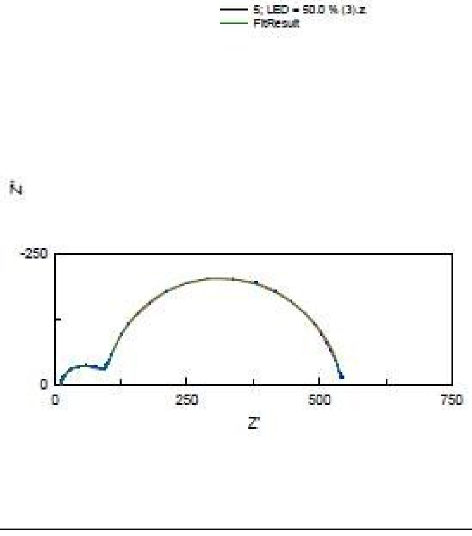
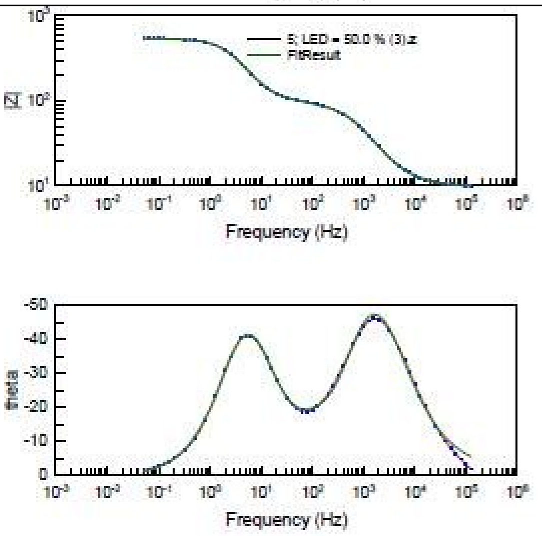
Dye	R_s / Ω	R_t / Ω	R_{rec} / Ω	C_μ / μF	R_{Pt} / Ω	C_{Pt} / μF	τ / ms	L_d/L	V_{OC} / mV	I / mW cm^{-2}
[Cu(**1**)(**4**)]$^+$	14.9	192.8	1068.0	131.0	59.0	4.8	139.9	2.4	550	2.4
[Cu(**1**)(**4**)]$^+$	14.7	87.1	303.6	206.3	50.6	5.3	62.6	1.9	600	10.0
[Cu(**1**)(**4**)]$^+$	14.8	78.9	219.3	232.1	49.8	5.4	50.9	1.7	610	15.0
[Cu(**1**)(**4**)]$^+$	14.9	74.5	172.0	251.8	49.4	5.4	43.3	1.5	630	22.0
[Cu(**1**)(**5**)]$^+$	11.7	104.3	1242.0	158.53	52.8	4.7	196.9	3.5	550	2.4
[Cu(**1**)(**5**)]$^+$	12.1	66.8	365.8	230.52	47.8	5.2	84.3	2.3	600	10.0
[Cu(**1**)(**5**)]$^+$	12.2	61.1	261.7	256.1	47.5	5.2	67.0	2.1	610	15.0
[Cu(**1**)(**5**)]$^+$	12.2	57.9	204.3	276.1	47.4	5.2	56.4	1.9	620	22.0
[Cu(**1**)(**6**)]$^+$	7.0	288.6	2420.0	88.3	91.2	6.9	213.6	2.9	440	2.4
[Cu(**1**)(**6**)]$^+$	9.2	90.5	416.0	175.6	57.4	4.5	73.0	2.1	510	10.0
[Cu(**1**)(**6**)]$^+$	9.2	90.6	361.9	178.5	54.7	4.6	64.6	2.0	520	15.0
[Cu(**1**)(**6**)]$^+$	9.3	90.3	316.0	183.3	53.3	4.7	57.9	1.9	530	22.0
[Cu(**1**)(**7**)]$^+$	13.0	228.0	1723.0	130.1	16.0	8.6	224.1	2.7	493	2.4
[Cu(**1**)(**7**)]$^+$	14.8	63.9	468.1	161.9	15.1	4.6	75.8	2.7	539	10.0
[Cu(**1**)(**7**)]$^+$	15.2	44.3	327.0	184.2	14.6	4.5	60.2	2.7	543	15.0
[Cu(**1**)(**7**)]$^+$	15.4	34.8	250.5	201.4	14.2	4.6	50.4	2.7	553	22.0
[Cu(**2**)(**5**)]$^+$	12.3	251.2	738.0	93.2	59.0	5.8	68.8	1.7	510	2.4
[Cu(**2**)(**5**)]$^+$	13.6	90.9	133.4	180.3	56.6	4.8	24.0	1.2	560	10.0
[Cu(**2**)(**5**)]$^+$	13.6	86.9	114.4	184.7	55.3	4.8	21.1	1.1	576	15.0
[Cu(**2**)(**5**)]$^+$	13.7	81.8	94.1	197.0	54.5	4.8	18.5	1.1	582	22.0
[Cu(**3**)(**5**)]$^+$	16.4	67.8	917.4	182.0	35.3	4.4	166.9	3.7	520	2.4
[Cu(**3**)(**5**)]$^+$	18.6	44.0	266.2	260.2	32.1	4.6	69.3	2.5	568	10.0
[Cu(**3**)(**5**)]$^+$	18.6	39.9	191.9	287.8	31.8	4.6	55.2	2.2	580	15.0
[Cu(**3**)(**5**)]$^+$	18.7	37.7	150.8	309.1	31.7	4.7	46.6	2.0	594	22.0
[Cu(**2**)(**7**)]$^+$	11.3	203.3	787.1	109.0	13.2	8.8	85.8	2.0	516	2.4
[Cu(**2**)(**7**)]$^+$	12.4	39.0	202.7	174.6	10.9	4.9	35.4	2.3	551	10.0
[Cu(**2**)(**7**)]$^+$	12.4	23.4	139.5	202.2	10.2	5.1	28.2	2.4	559	15.0
[Cu(**2**)(**7**)]$^+$	12.3	17.1	107.2	222.6	9.8	5.2	23.9	2.5	578	22.0
[Cu(**3**)(**7**)]$^+$	10.6	44.1	999.3	178.0	14.8	3.9	177.9	4.8	539	2.4
[Cu(**3**)(**7**)]$^+$	10.9	18.5	259.8	258.5	13.5	4.1	67.1	3.7	585	10.0
[Cu(**3**)(**7**)]$^+$	10.8	16.3	186.7	284.9	13.3	4.1	53.2	3.4	596	15.0
[Cu(**3**)(**7**)]$^+$	10.6	10.2	136.2	320.3	13.0	4.3	43.6	3.7	622	22.0

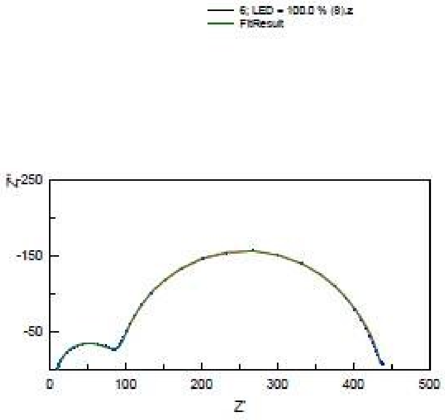
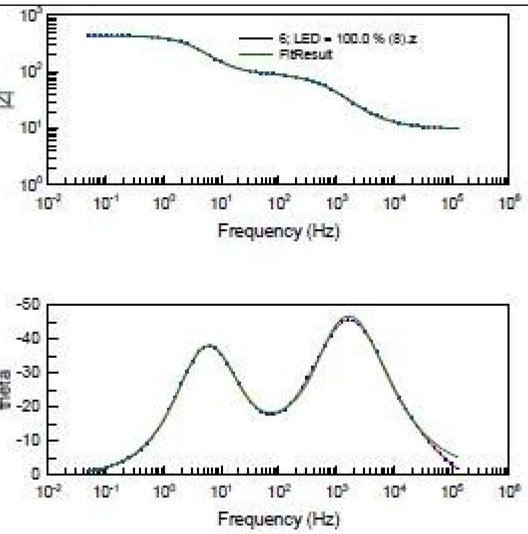
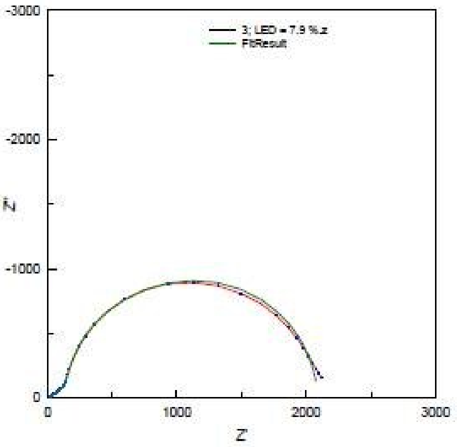
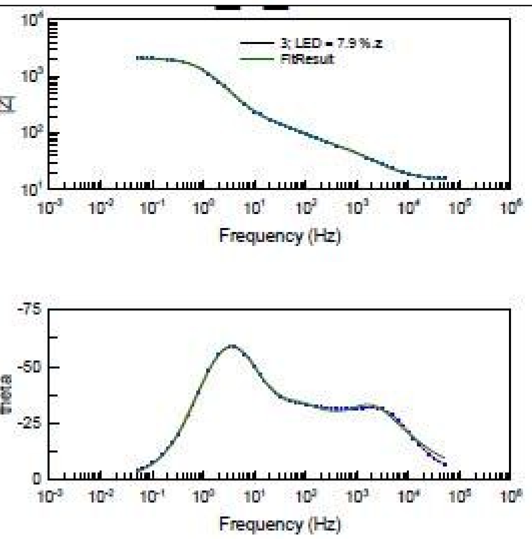
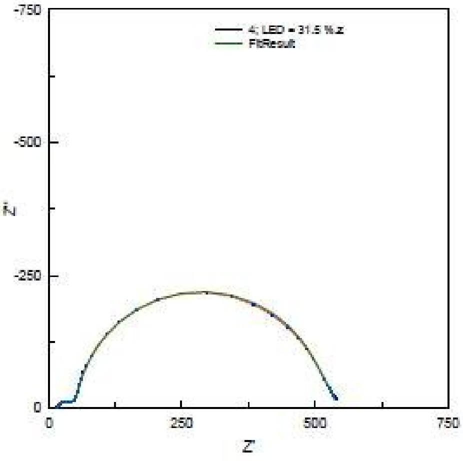
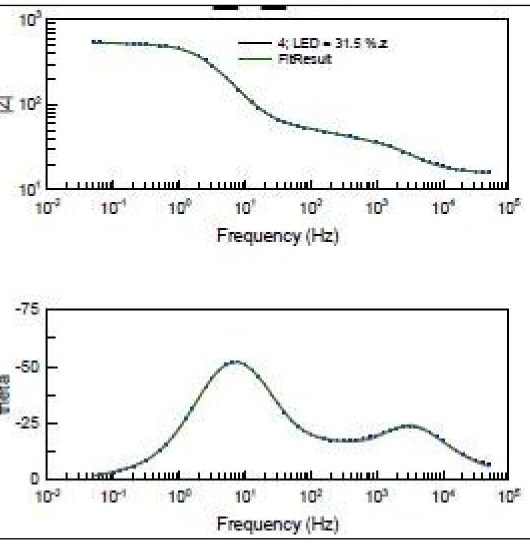
Table S5. Nyquist and Bode plots at different light intensities (2,4, 10.0, 15.0 and 22.0 mW cm^{-2}). EIS measurements are carried out 3 days after DSC assembly.

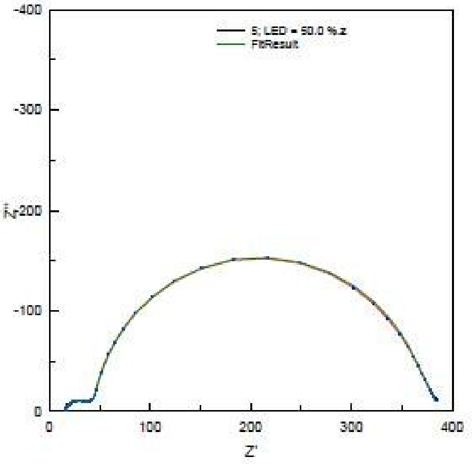
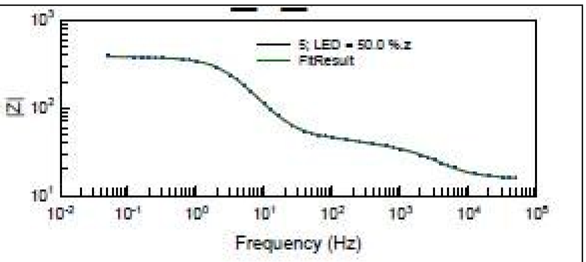
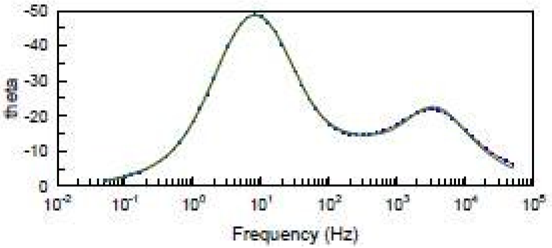
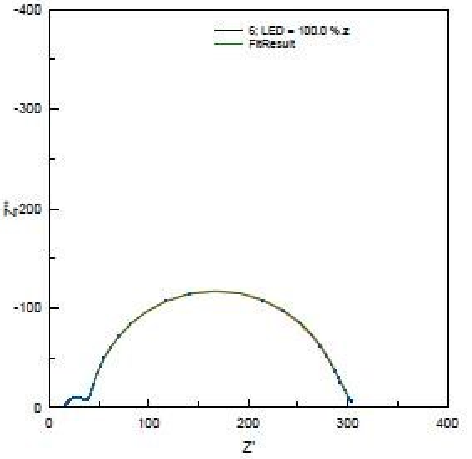
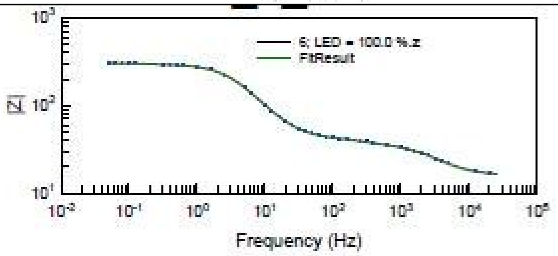
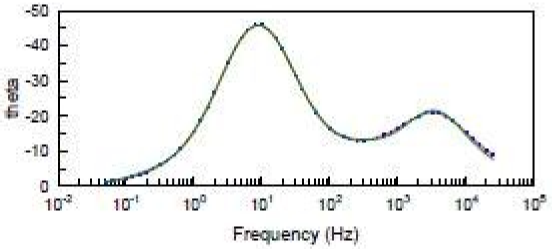
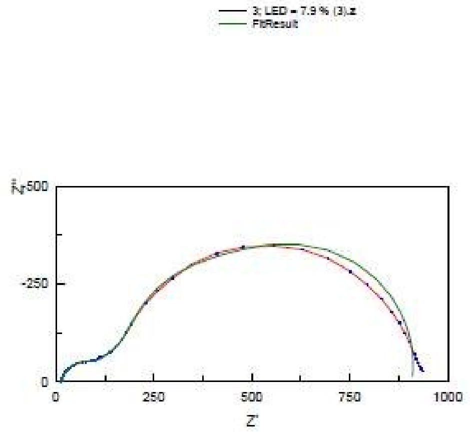
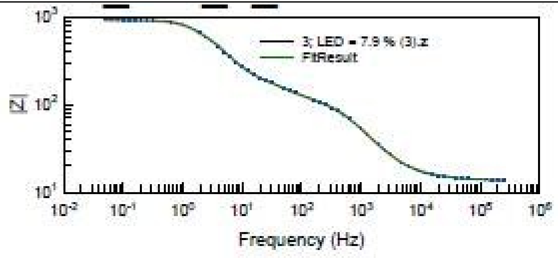
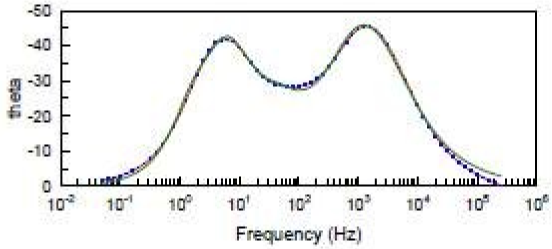
Dye/ Light intensity	Nyquist	Bode
[Cu(**1**)(**4**)]$^+$ 2.4 mW/cm^2		
[Cu(**1**)(**4**)]$^+$ 10 mW/cm^2		

[Cu(**1**)(**4**)]$^+$ 15 mW/cm^2		
[Cu(**1**)(**4**)]$^+$ 22 mW/cm^2		
[Cu(**1**)(**5**)]$^+$ 2.4 mW/cm^2		

[Cu(**1**)(**5**)]$^{+}$ 10 mW/cm^{2}		 
[Cu(**1**)(**5**)]$^{+}$ 15 mW/cm^{2}		 
[Cu(**1**)(**5**)]$^{+}$ 22 mW/cm^{2}		 

[Cu(**1**)(**6**)]$^+$ 2.4 mW/cm^2		
[Cu(**1**)(**6**)]$^+$ 10 mW/cm^2		
[Cu(**1**)(**6**)]$^+$ 15 mW/cm^2		

[Cu(**1**)(**6**)]$^+$ 22 mW/cm^2		
[Cu(**1**)(**7**)]$^+$ 2.4 mW/cm^2		
[Cu(**1**)(**7**)]$^+$ 10 mW/cm^2		

[Cu(**1**)(**7**)]$^+$ 15 mW/cm^2		 
[Cu(**1**)(**7**)]$^+$ 22 mW/cm^2		 
[Cu(**2**)(**5**)]$^+$ 2.4 mW/cm^2		 

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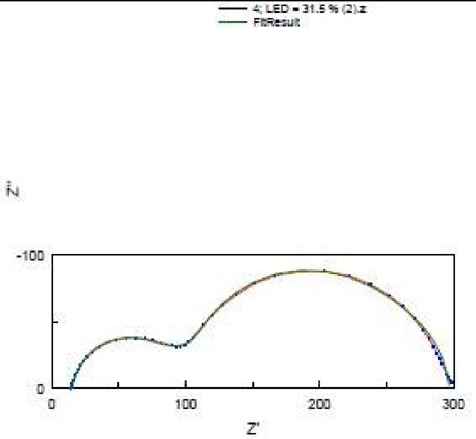
<td>
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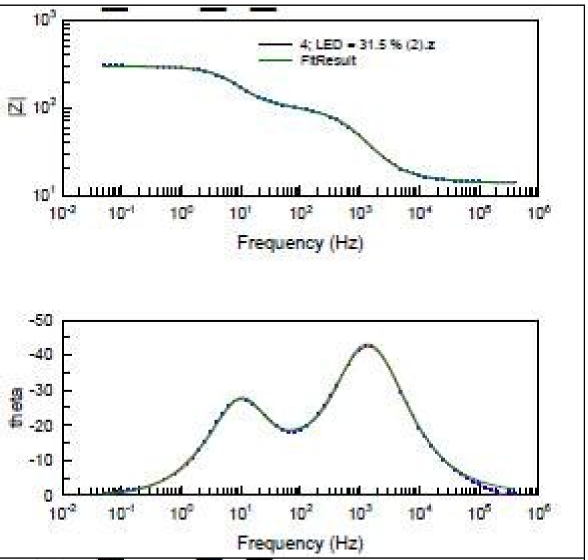
<td>
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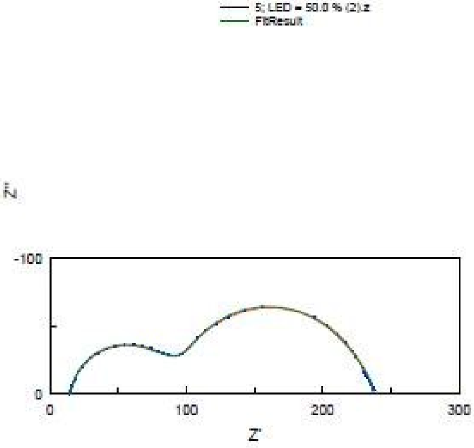
<td>
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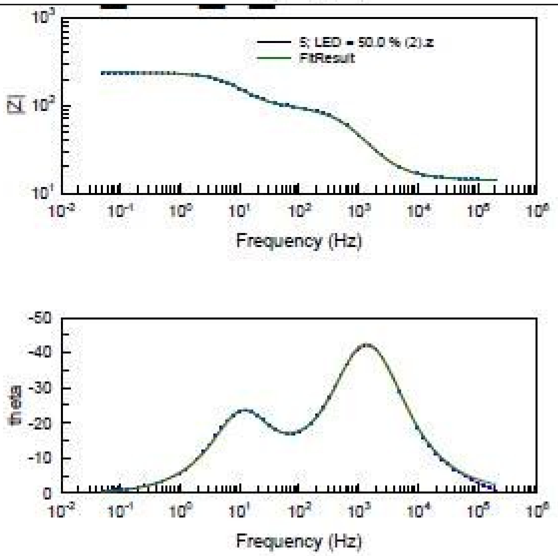
<td>
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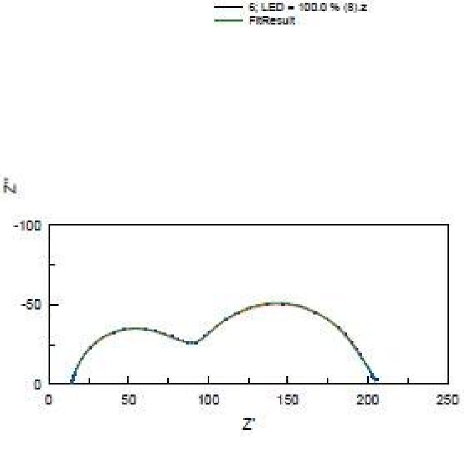
<td>
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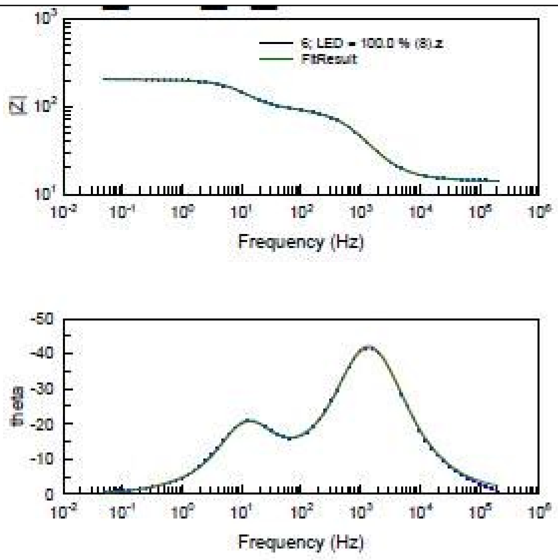
<td>
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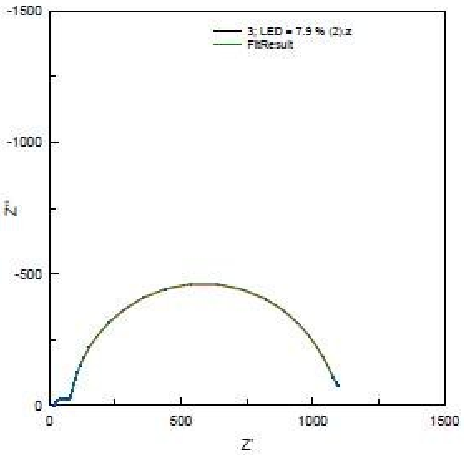
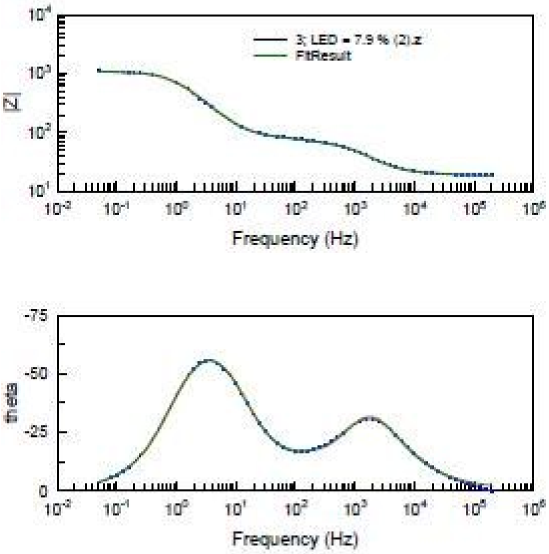
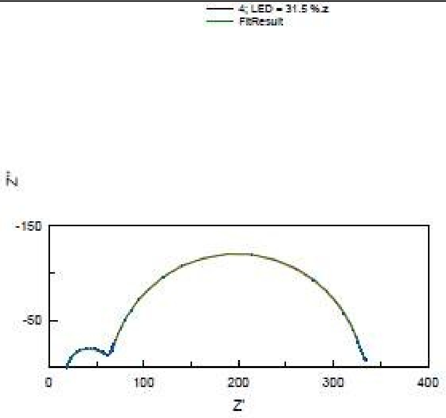
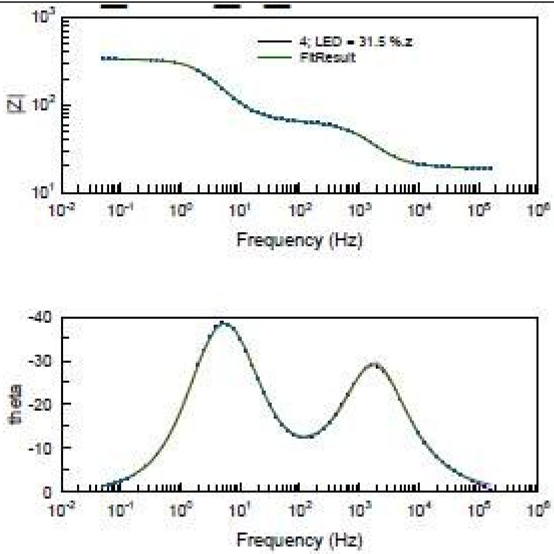
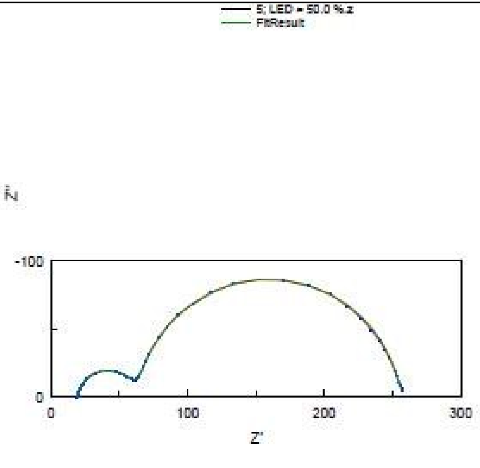
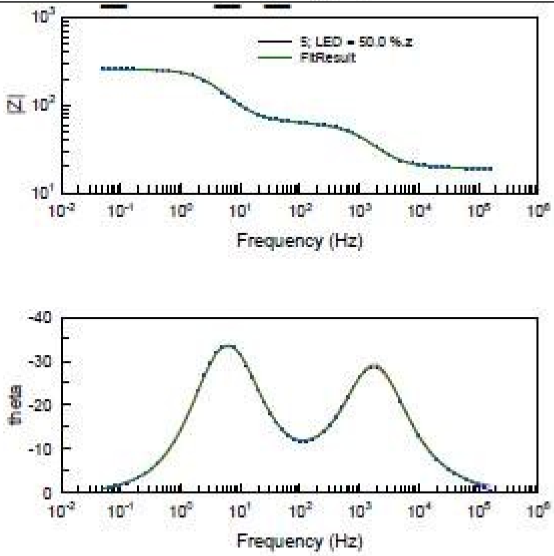
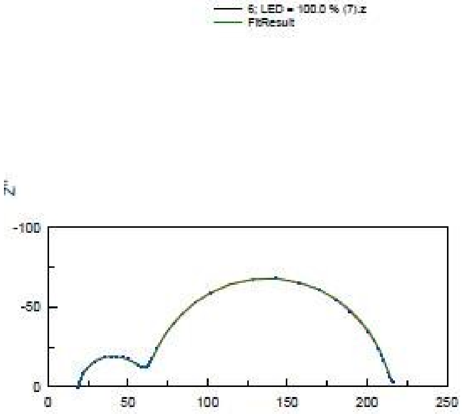
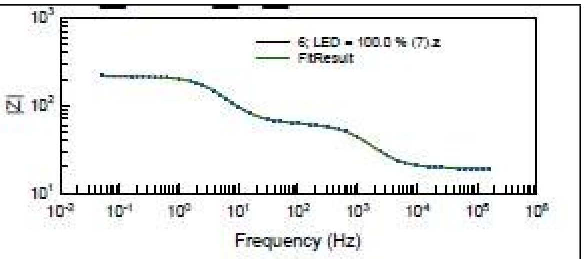
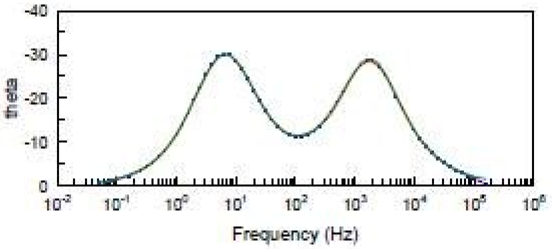
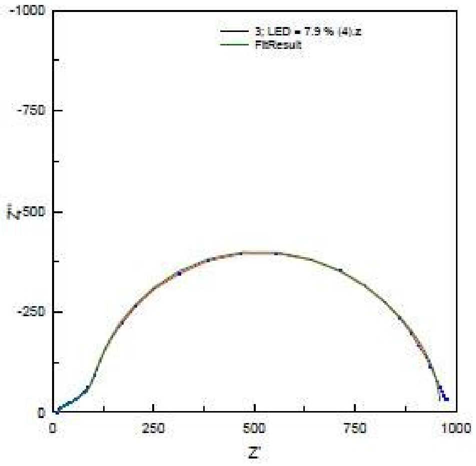
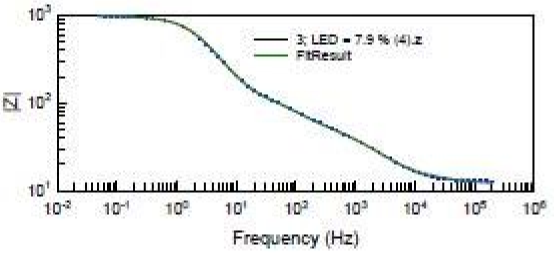
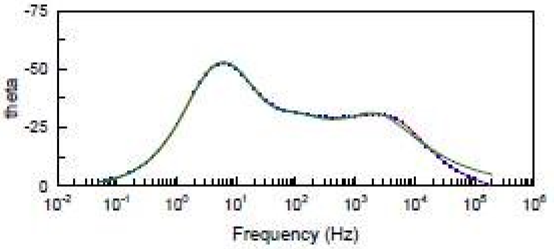
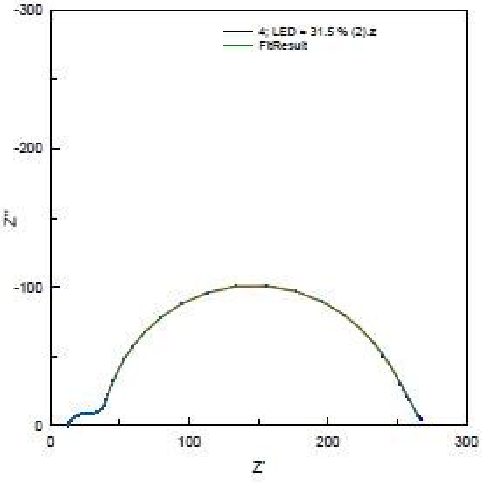
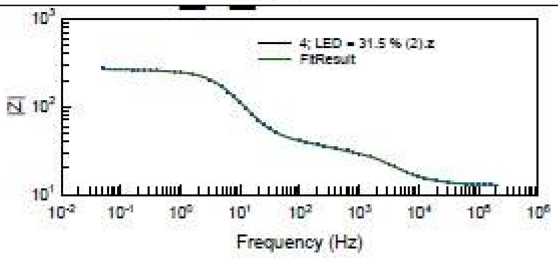
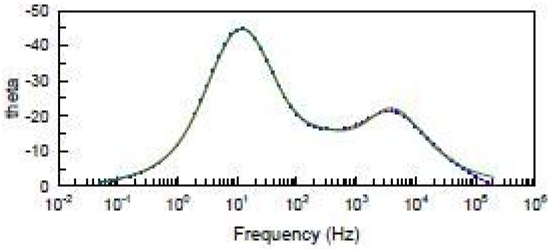
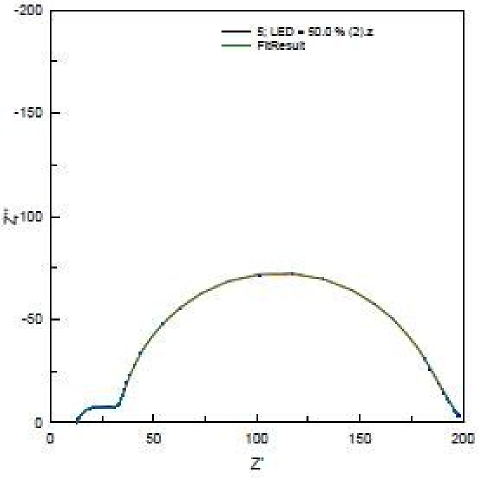
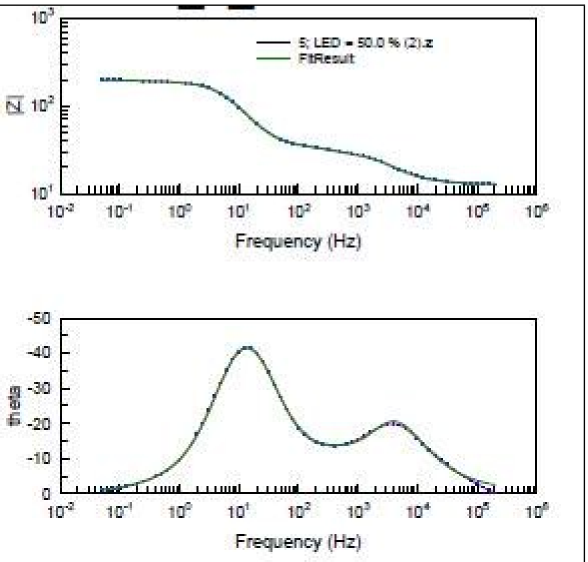
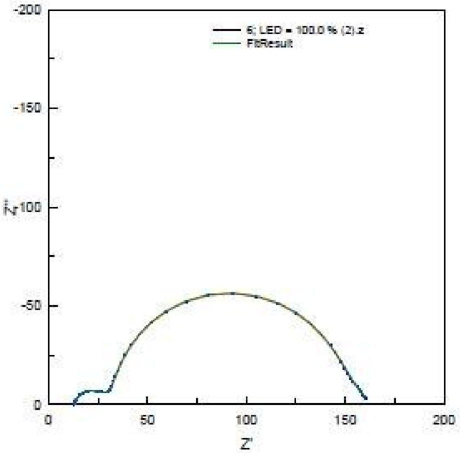
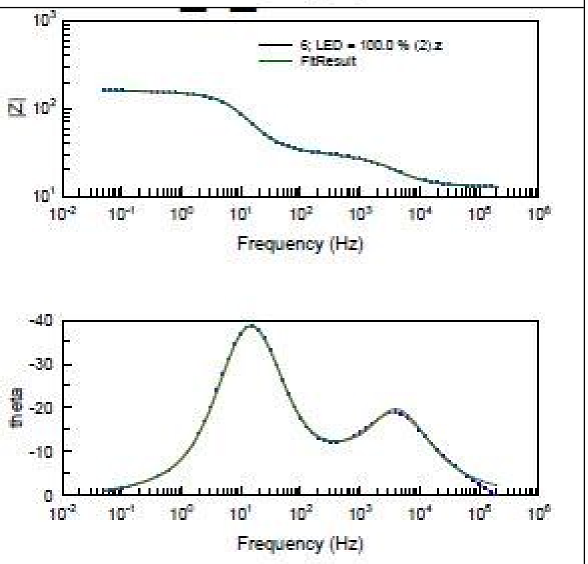
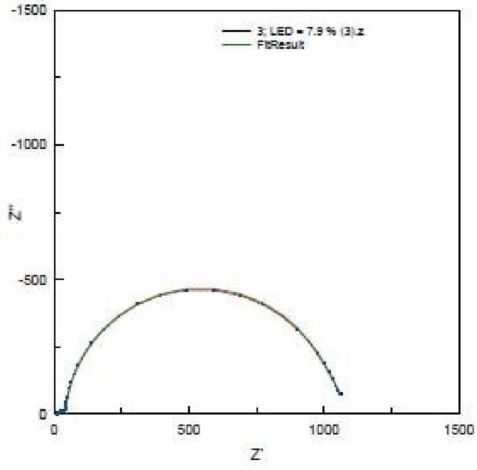
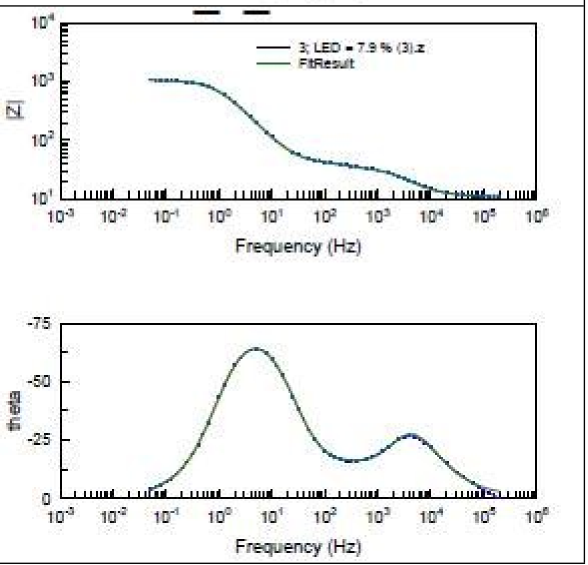
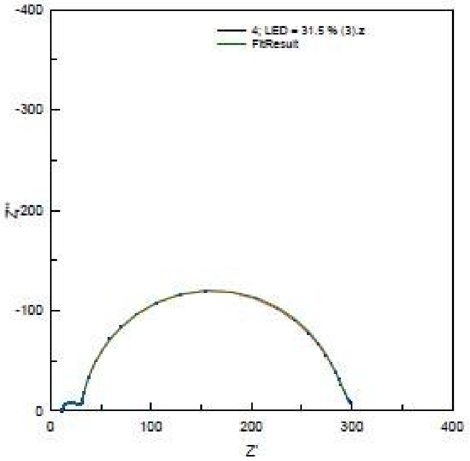
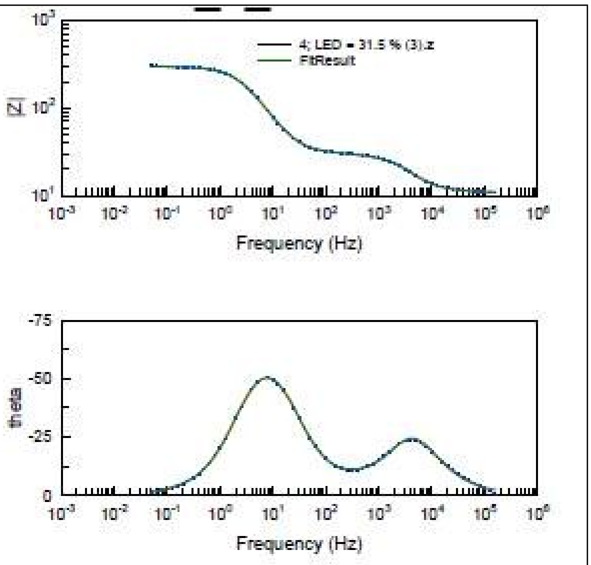
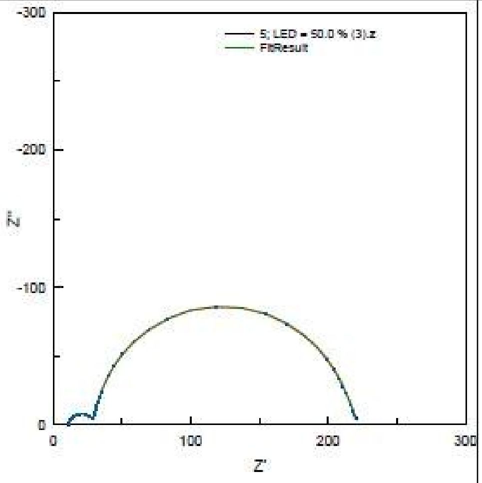
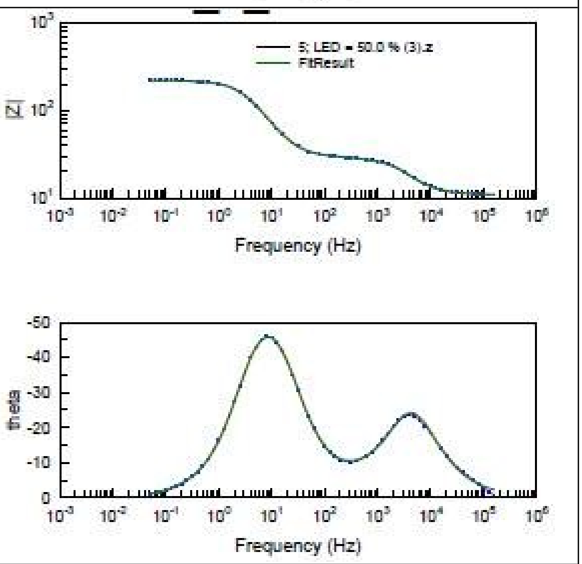
[Cu(**3**)(**5**)]$^+$ 2.4 mW/cm^2		
[Cu(**3**)(**5**)]$^+$ 10 mW/cm^2		
[Cu(**3**)(**5**)]$^+$ 15 mW/cm^2		

[Cu(**3**)(**5**)]$^+$ 22 mW/cm^2		 
[Cu(**2**)(**7**)]$^+$ 2.4 mW/cm^2		 
[Cu(**2**)(**7**)]$^+$ 10 mW/cm^2		 

[Cu(**2**)(**7**)]$^+$ 15 mW/cm^2		
[Cu(**2**)(**7**)]$^+$ 22 mW/cm^2		
[Cu(**3**)(**7**)]$^+$ 2.4 mW/cm^2		

[Cu(**3**)(**7**)]$^+$ 10 mW/cm^2		
[Cu(**3**)(**7**)]$^+$ 15 mW/cm^2		
[Cu(**3**)(**7**)]$^+$ 22 mW/cm^2