

A Simple Design for Strongly Emissive Sky-Blue Phosphorescent Neutral Rhenium Complexes: Synthesis, Photophysics and Electroluminescent Devices

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Supporting Information

Table S1. Crystal and structure determination data for **1** and **2**.

	1	2
Empirical formula	C ₃₄ H ₈ BF ₁₅ N ₃ O ₃ Re	C ₃₆ H ₁₂ BF ₁₅ N ₃ O ₃ Re
Formula weight	988.44	1016.51
Temperature / K	133(2)	133(2)
Unit cell dimensions		
<i>a</i> / Å	17.6594(4)	11.3808(6)
<i>b</i> / Å	15.9973(4)	11.7633(5)
<i>c</i> / Å	11.2462(3)	13.7533(7)
α / °	90.00	69.591(4)
β / °	90.00	78.049(4)
γ / °	90.00	87.273(4)
Volume / Å ³	3177.08(14)	1687.64(14)
Crystal system	orthorhombic	triclinic
Crystal color	colourless	yellow
Space group	P _{nma}	P $\bar{1}$
<i>Z</i>	4	2
<i>F</i> (000)	1888	976
Density (calculated) / Mgm ⁻³	2.066	2.000
Crystal size / mm	0.46 × 0.43 × 0.36	0.54 × 0.24 × 0.22
Wavelength / Å	0.7107	1.5418
Absorption coefficient / mm ⁻¹	3.96	8.22
Collection range	3.12° ≤ θ ≤ 29.03° (<i>h</i> : -21 to 10; <i>k</i> : -19 to 18; <i>l</i> : -13 to 8)	3.50° ≤ θ ≤ 71.71° (<i>h</i> : -13 to 13; <i>k</i> : -14 to 13; <i>l</i> : -16 to 12)
Completeness to theta	99.7 %	99.2 %
No. of data collected	8217	10719
No. of unique data	2893	5961
No. of data used in refinement, <i>m</i>	2637	5915
No. of parameters refined, <i>p</i>	271	534
<i>R</i> ^a	0.020	0.037
<i>wR</i> ^a	0.049	0.098
Goodness-of-fit, <i>S</i>	1.069	1.159
Maximum shift, (Δ/σ) _{max}	0.001	0.001
Residual extrema in final difference map, eÅ ⁻³	+0.591, -0.729	+1.446, -2.757

$$^a w = 1 / [\sigma^2(F_o^2) + (ap)^2 + bP], \text{ where } P = [2F_c^2 + \text{Max}(F_o^2, 0)] / 3$$

Table S2. Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for **1** and **2**

1	Re(1)–C(1)	1.943 (5)	C(1)–O(1)	1.158 (6)
	Re(1)–C(2)	1.925 (3)	C(2)–O(2)	1.149 (4)
	Re(1)–C(3)	2.099 (4)	C(3)–N(2)	1.152 (5)
	N(2)–B(1)	1.556 (5)		
	N(1)–Re(1)–N(1 ⁱ)	75.73 (12)	Re(1)–C(3)–N(2)	173.3 (3)
	C(3)–N(2)–B(1)	166.4 (4)		
2	Re(1)–C(1)	1.905 (5)	C(1)–O(1)	1.172 (7)
	Re(1)–C(2)	1.926 (4)	C(2)–O(2)	1.143 (6)
	Re(1)–C(3)	1.969 (5)	C(3)–O(3)	1.141 (6)
	Re(1)–C(4)	2.096 (4)	C(4)–N(3)	1.144 (6)
	N(3)–B(1)	1.549 (6)		
	N(1)–Re(1)–N(2)	75.46 (13)	Re(1)–C(4)–N(3)	174.8 (4)
	C(4)–N(3)–B(1)	174.0 (4)		

Table S3. HOMO, LUMO and triplet state energy of **1** and **2** estimated from electrochemical data and phosphorescence in CH₂Cl₂ solution.

	HOMO ^a	LUMO ^b	Triplet state energy ^c
1	6.55 eV	3.49 eV	2.40 eV
2	6.52 eV	3.35 eV	2.39 eV

^aEstimated from the first metal-centered oxidation potential ($E_{\text{ox}} + 4.8$).^[1] ^bEstimated from the phenanthroline-based reduction potential ($E_{\text{red}} + 4.8$).^[1] ^cBased on λ_{em} of the phosphorescence of the complexes in CH₂Cl₂ solution.

[1] Bredas, J. L.; Silbey, R.; Boudreux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555.

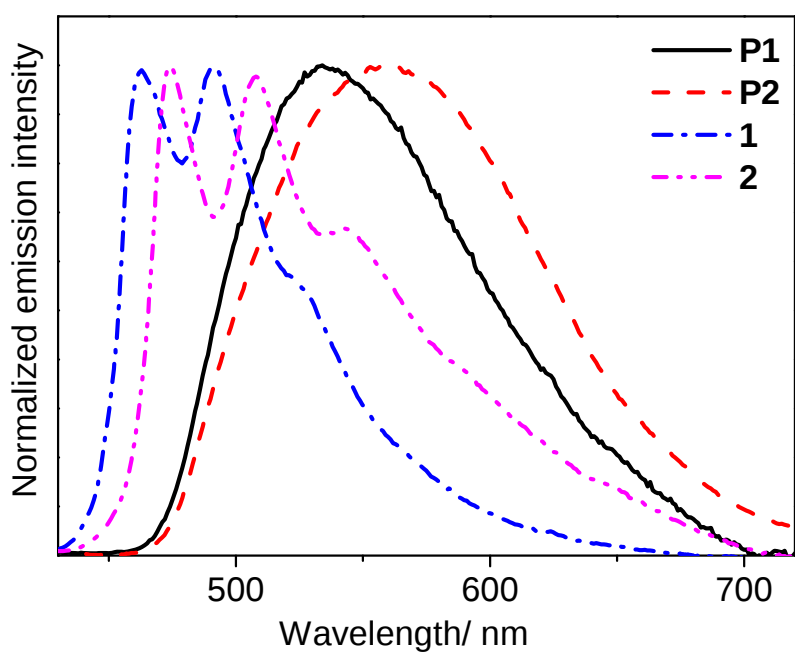


Figure S1. Overlaid corrected emission spectra of **P1**, **P2**, **1** and **2** in the solid state 298 K.

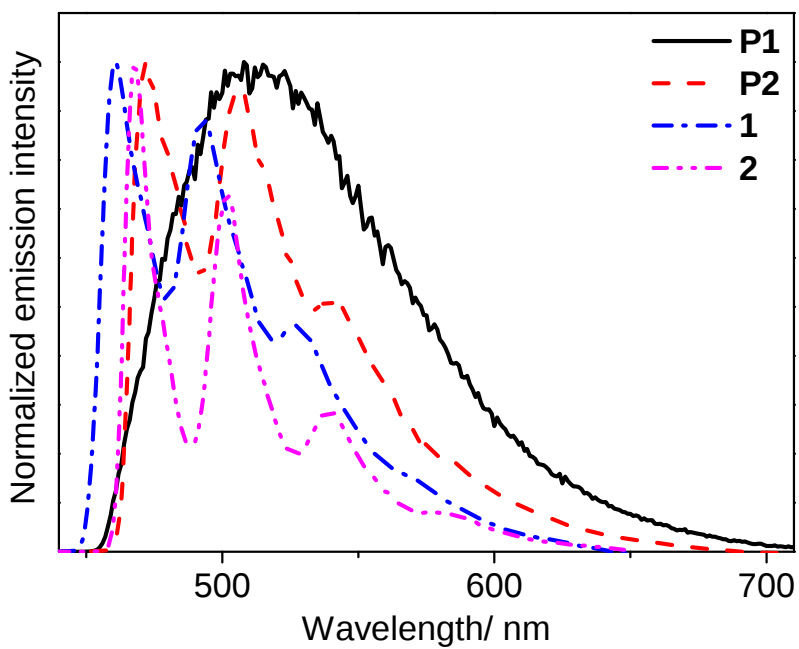


Figure S2. Overlaid corrected emission spectra of **P1**, **P2**, **1** and **2** in 4:1 (v/v) EtOH/MeOH glass at 77 K.

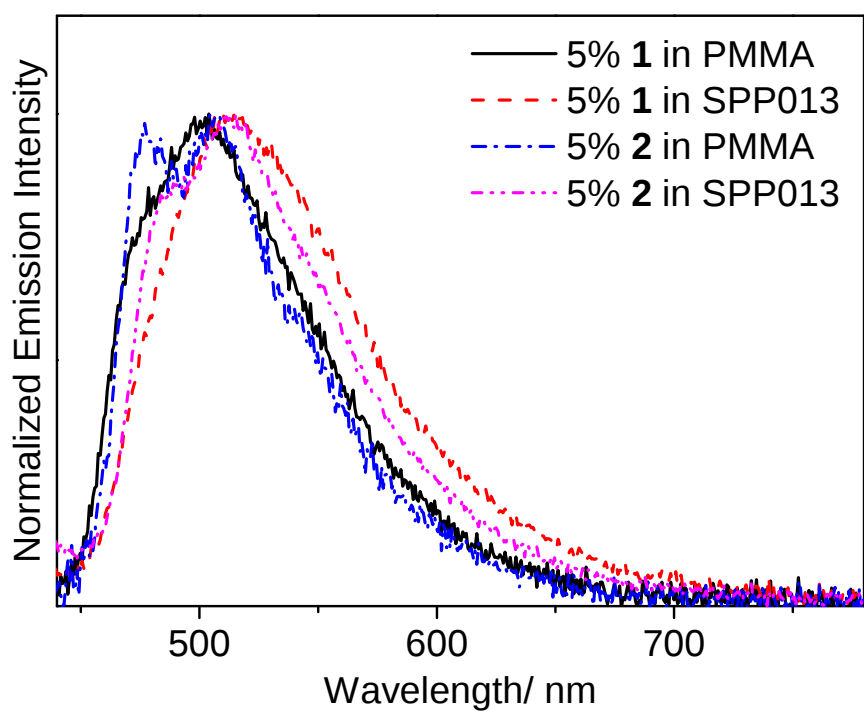


Figure S3. Overlaid emission spectra of thin films of **1** and **2** doped in PMMA and SPP013 at 5 wt % concentration at 298 K.

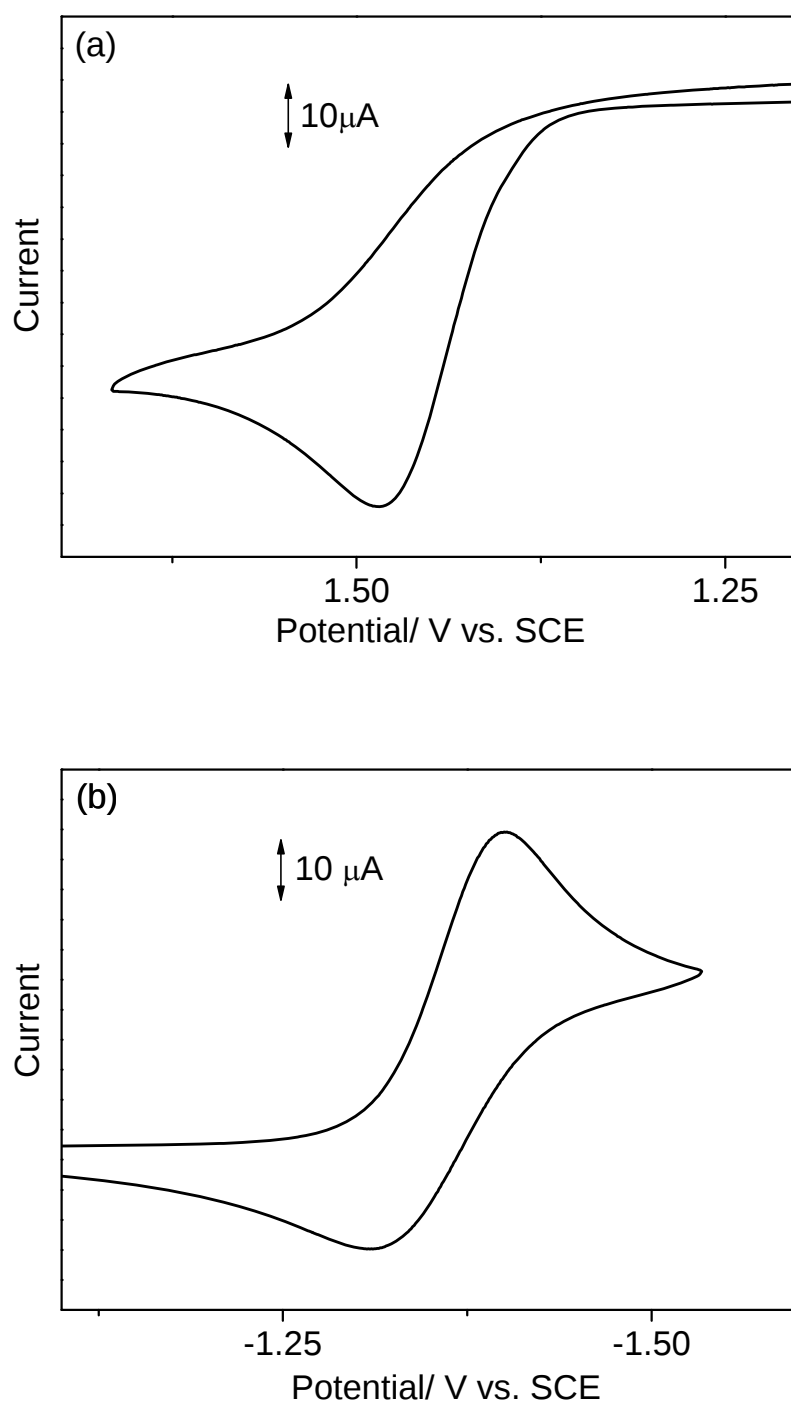


Figure S4. Cyclic voltammograms of (a) oxidative scan and (b) reductive scan of **P1** in acetonitrile solution (0.1 M $n\text{Bu}_4\text{NPF}_6$). Scan rate: 100 mVs^{-1} .

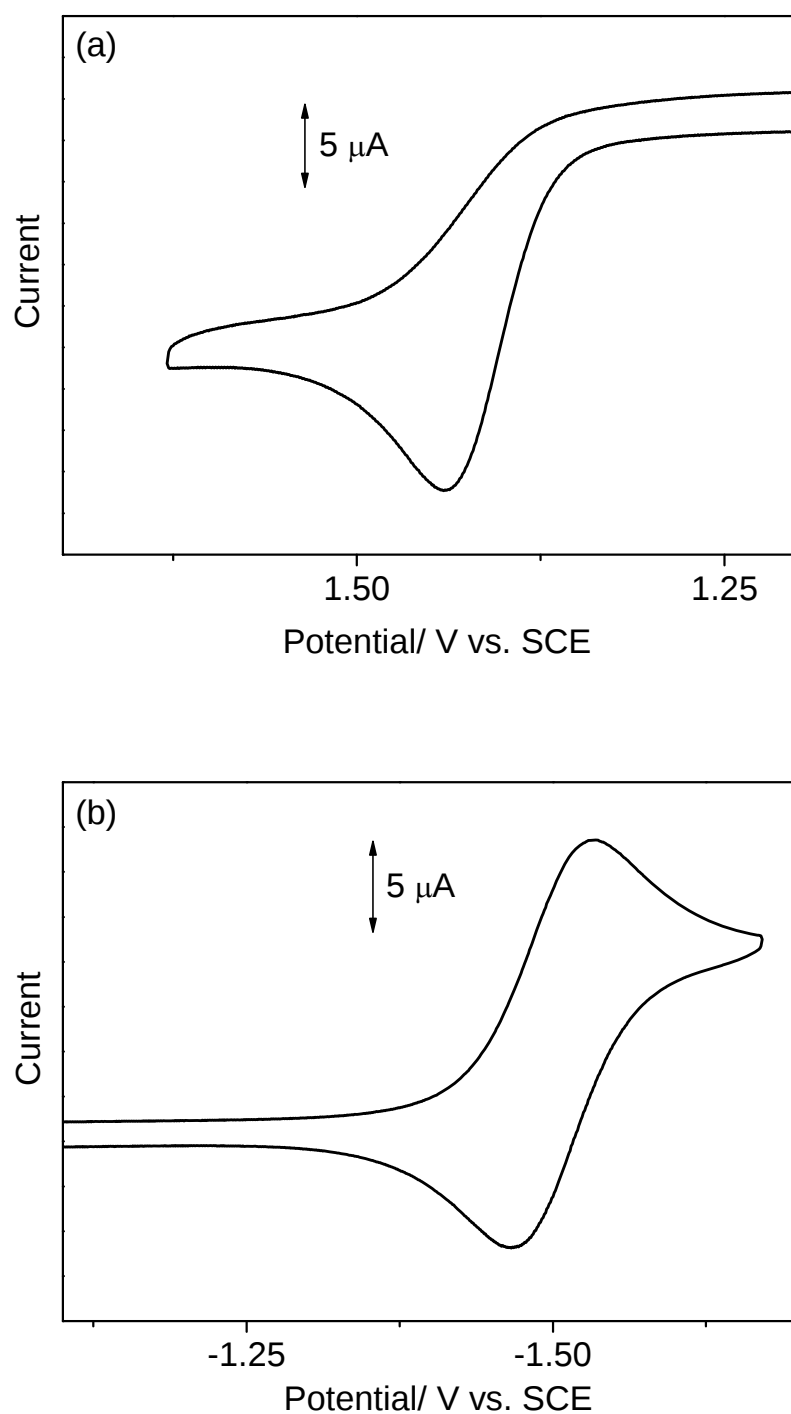


Figure S5. Cyclic voltammograms of (a) oxidative scan and (b) reductive scan of **P2** in acetonitrile solution (0.1 M $n\text{Bu}_4\text{NPF}_6$). Scan rate: 100 mVs^{-1} .

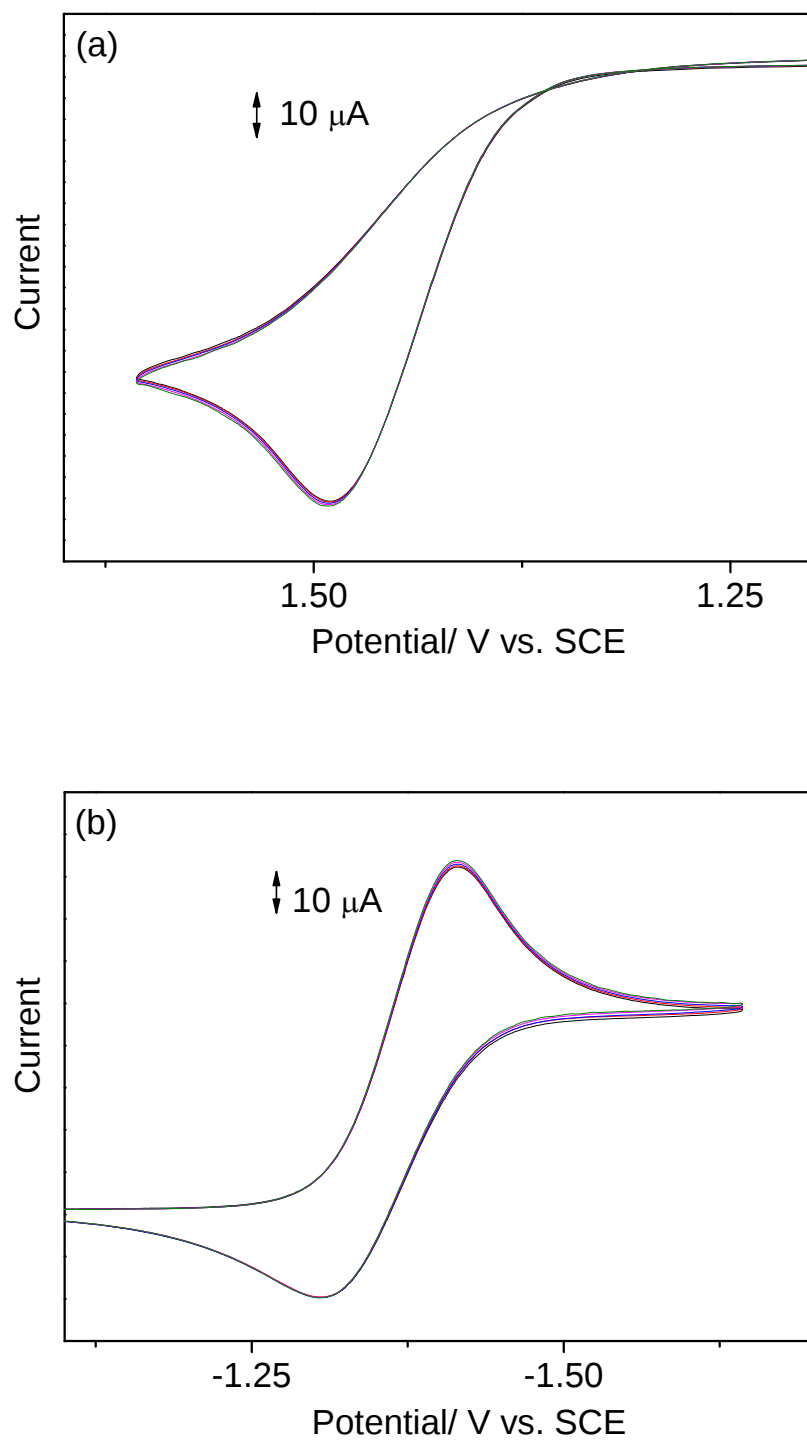


Figure S6. Cyclic voltammograms of (a) oxidative scan and (b) reductive scan of **P1** in acetonitrile solution (0.1 M $n\text{Bu}_4\text{NPF}_6$) with multiple scans. Scan rate: 100 mVs^{-1} .

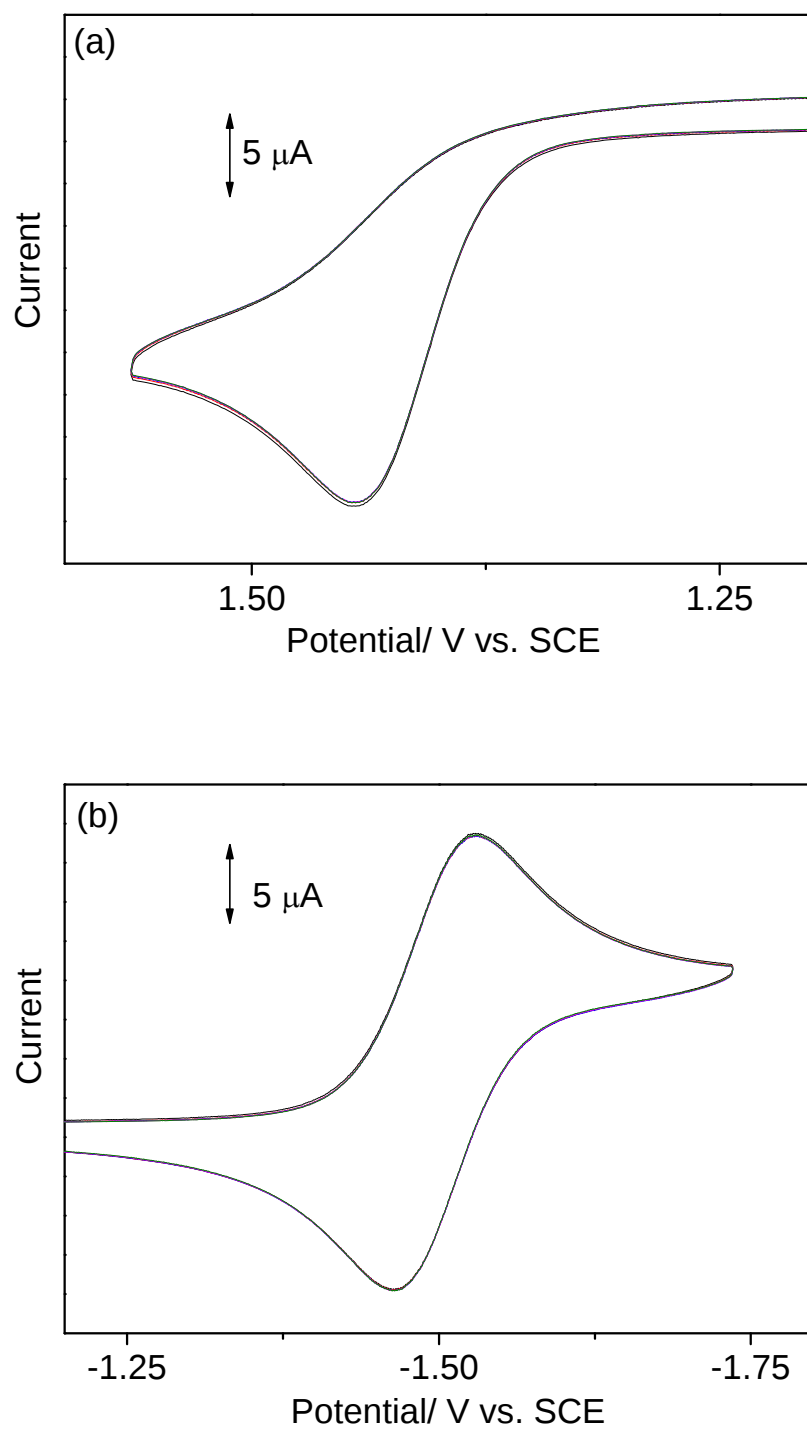


Figure S7. Cyclic voltammograms of (a) oxidative scan and (b) reductive scan of **P2** in acetonitrile solution (0.1 M $n\text{Bu}_4\text{NPF}_6$) with multiple scans. Scan rate: 100 mVs^{-1} .

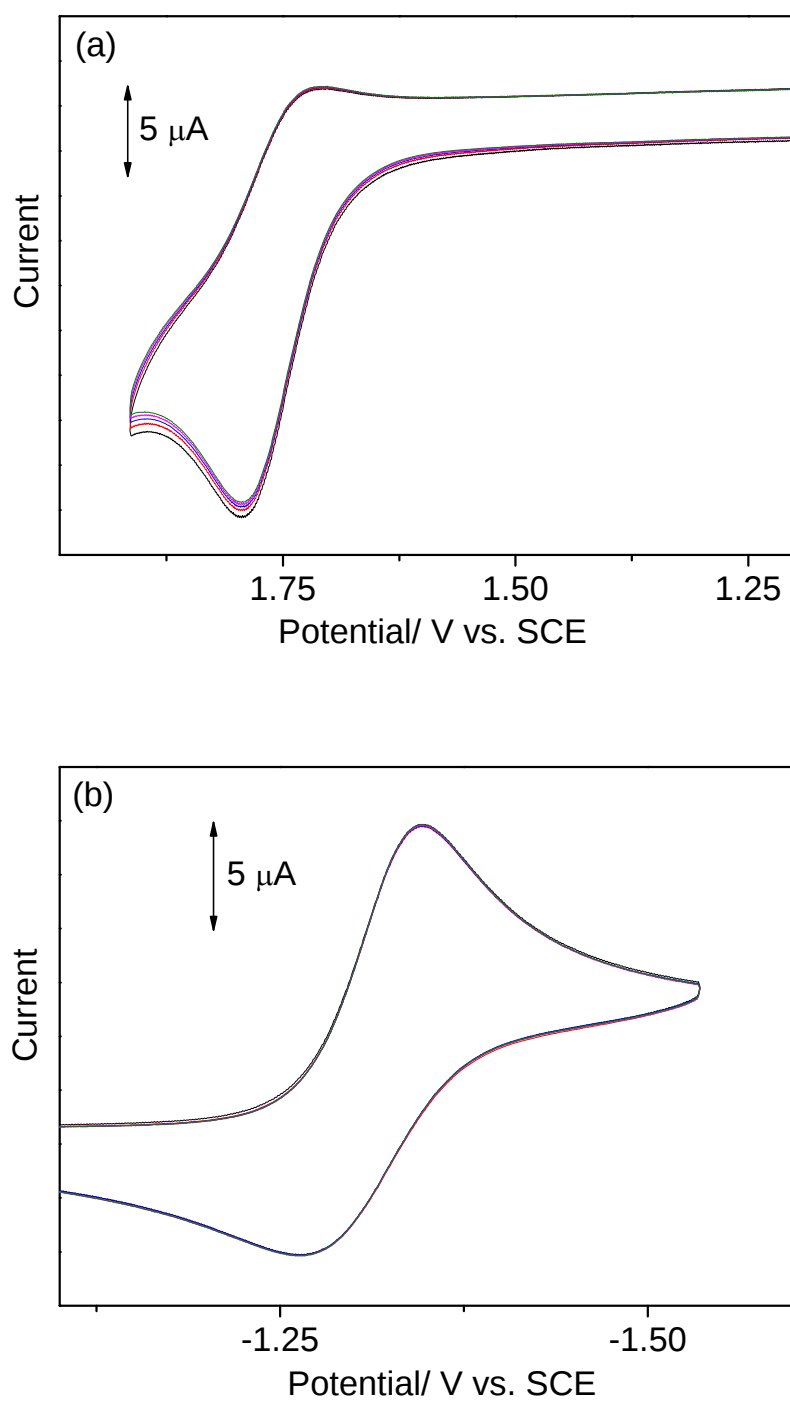


Figure S8. Cyclic voltammograms of (a) oxidative scan and (b) reductive scan of **1** in acetonitrile solution (0.1 M $n\text{Bu}_4\text{NPF}_6$) with multiple scans. Scan rate: 100 mVs^{-1} .

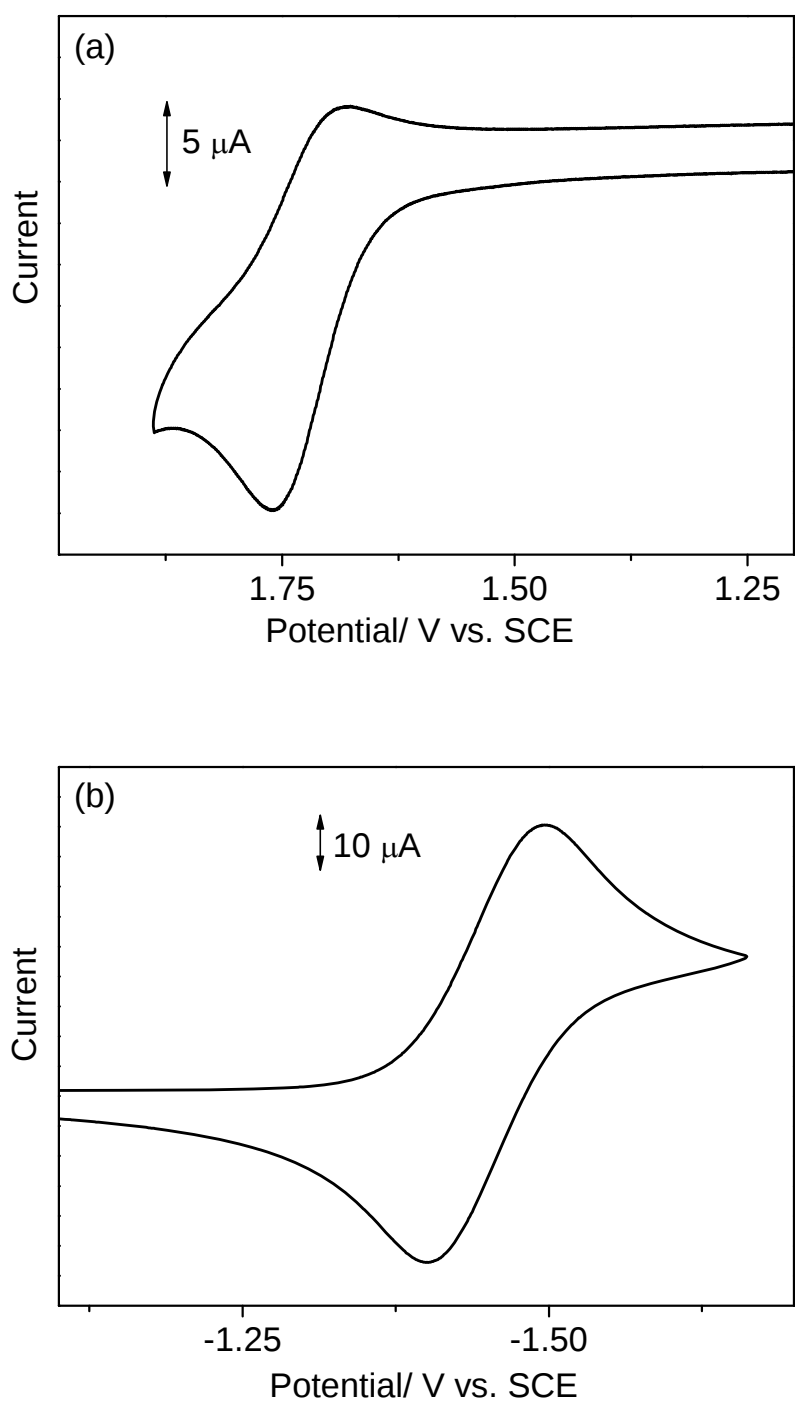


Figure S9. Cyclic voltammograms of (a) oxidative scan and (b) reductive scan of **2** in acetonitrile solution (0.1 M $n\text{Bu}_4\text{NPF}_6$). Scan rate: 100 mVs^{-1} .

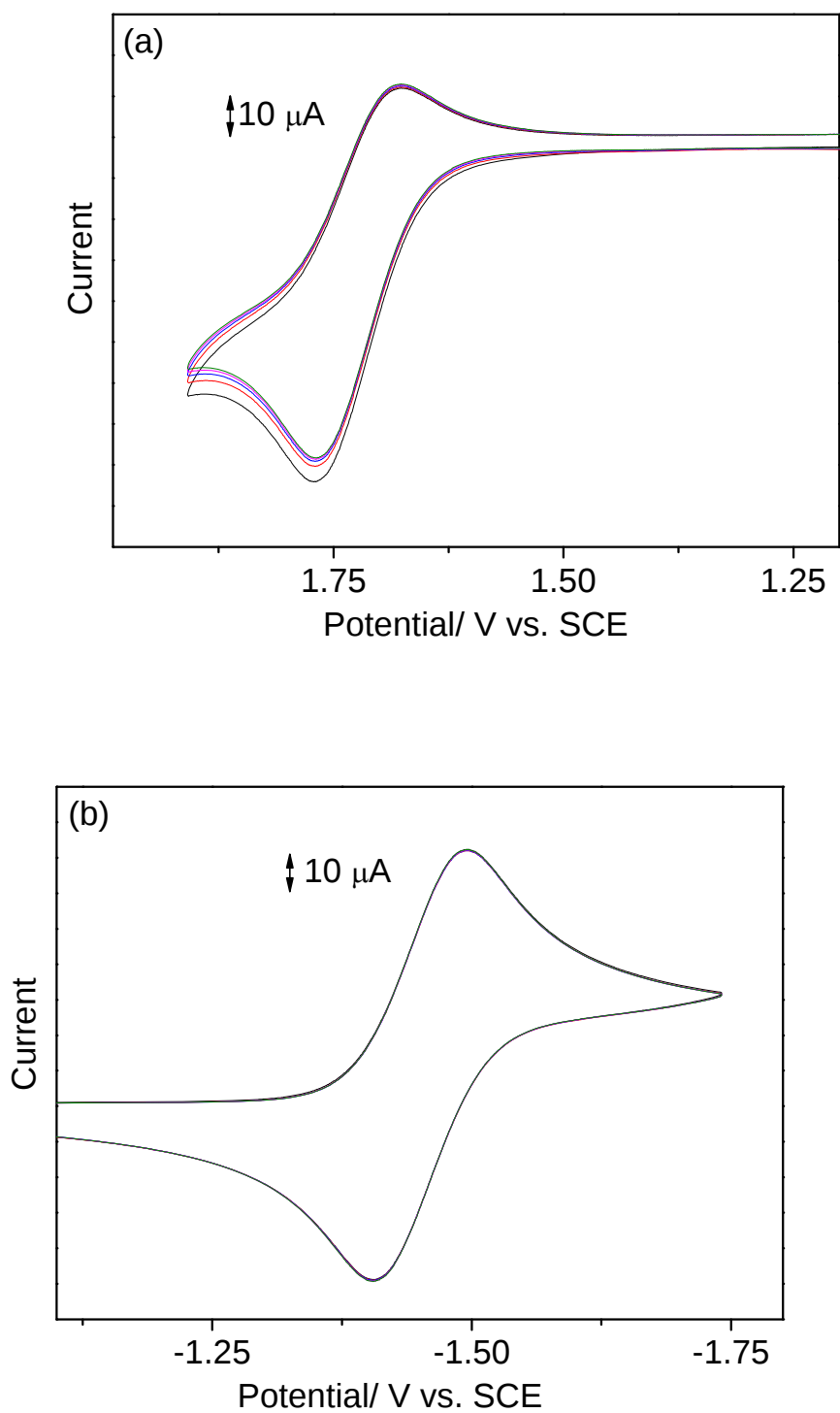


Figure S10. Cyclic voltammograms of (a) oxidative scan and (b) reductive scan of **2** in acetonitrile solution (0.1 M $n\text{Bu}_4\text{NPF}_6$) with multiple scans. Scan rate: 100 mVs^{-1} .

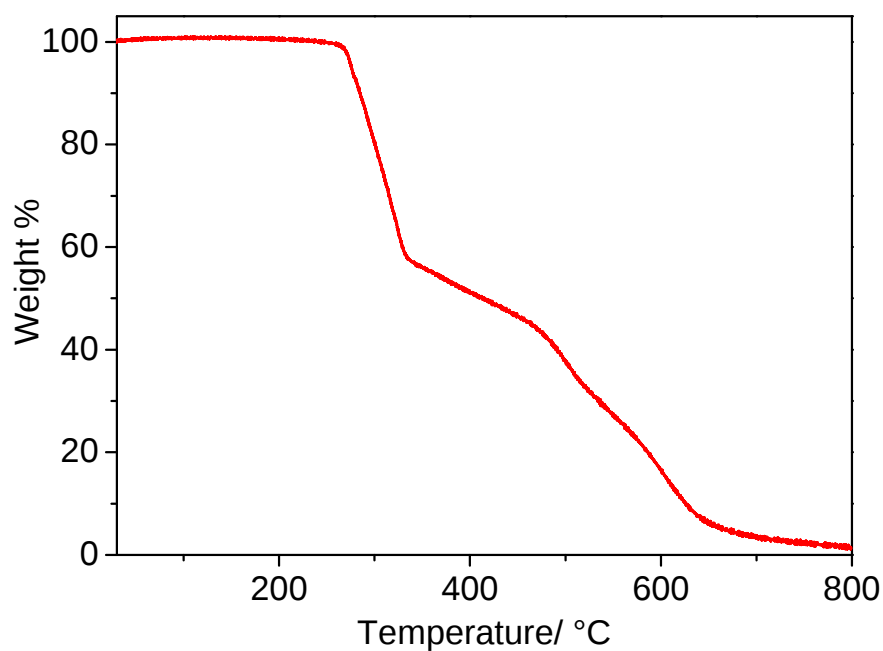


Figure S11. TGA thermogram of **1** in an atmosphere of nitrogen recorded at a heating rate of $3\text{ }^{\circ}\text{C min}^{-1}$.

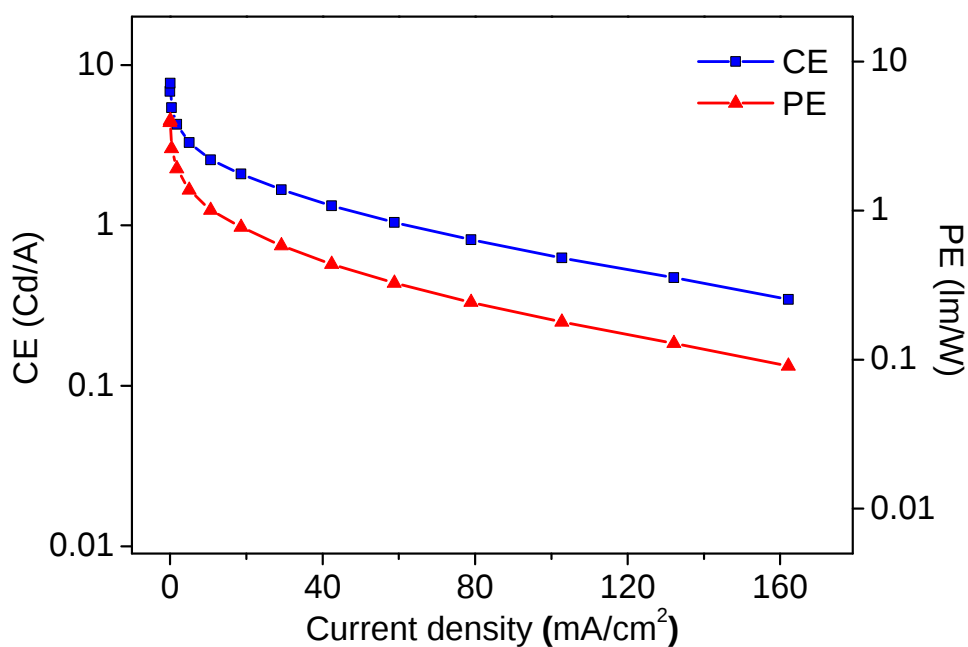


Figure S12. The current efficiency and power efficiency against current density of the doped device containing 10% of **1** as dopant.

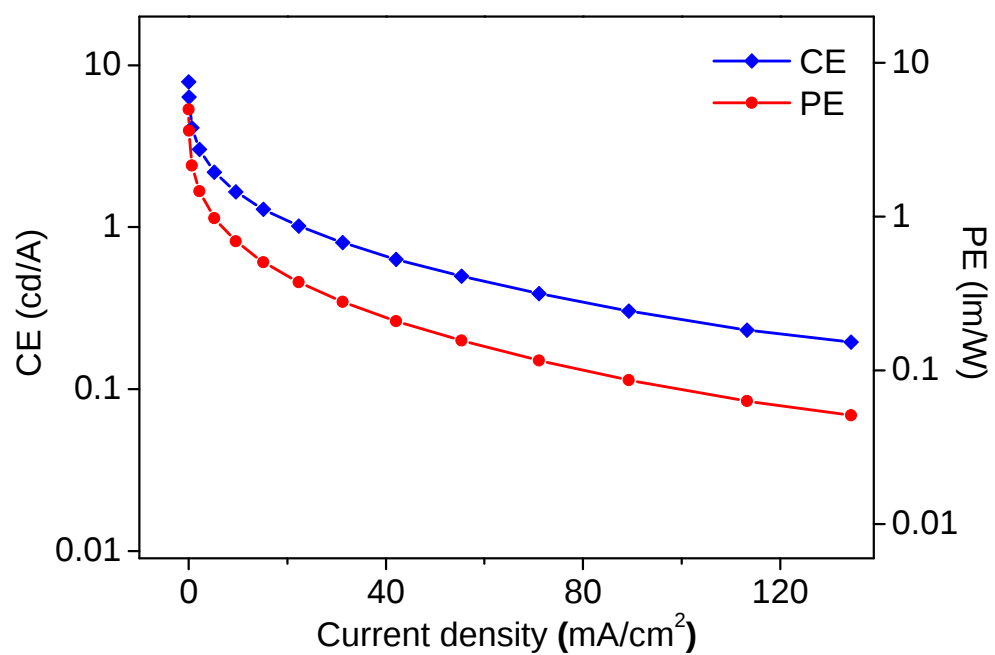


Figure S13. The current efficiency and power efficiency against current density of the doped device containing 10% of **2** as dopant.

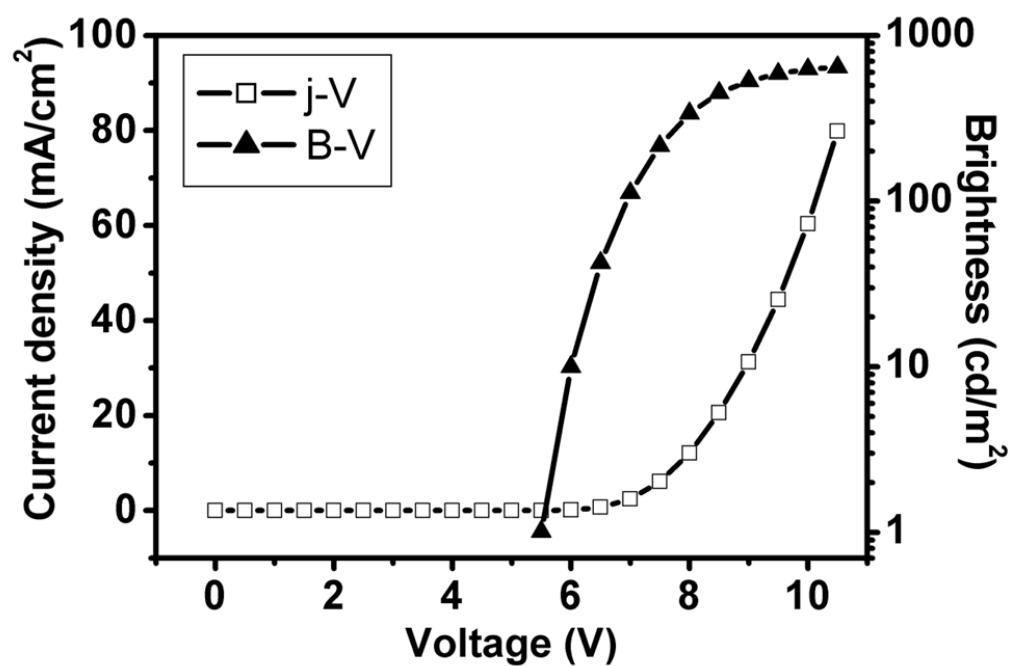


Figure S14. J-V-B characteristics of the doped device containing 10% of 1 as dopant.

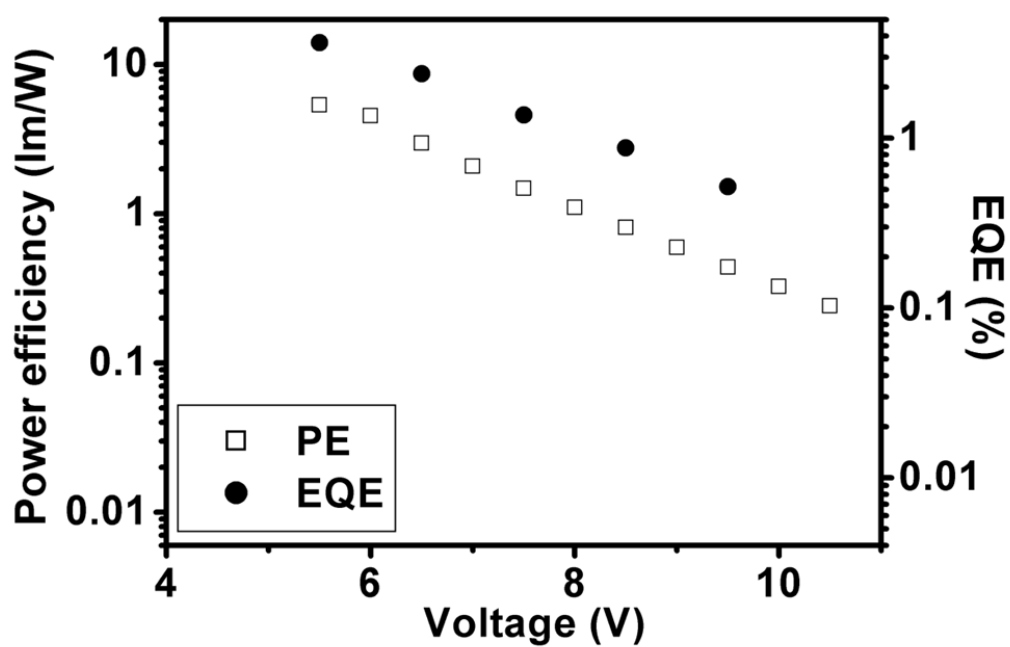


Figure S15. PE-V-EQE characteristics of the doped device containing 10% of 1 as dopant.

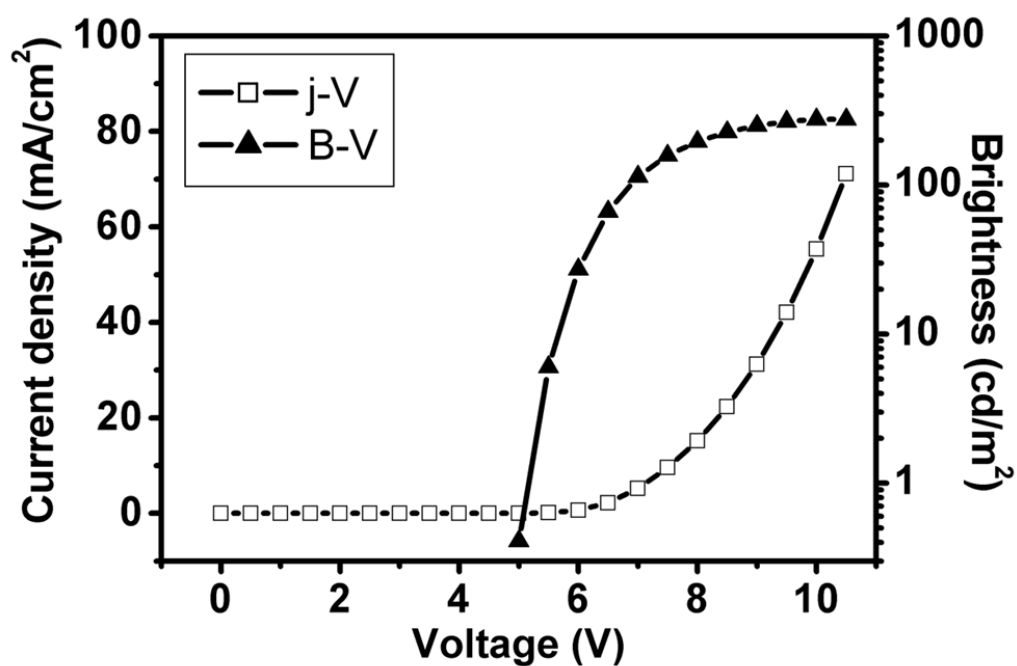


Figure S16. J-V-B characteristics of the doped device containing 10% of 2 as dopant.

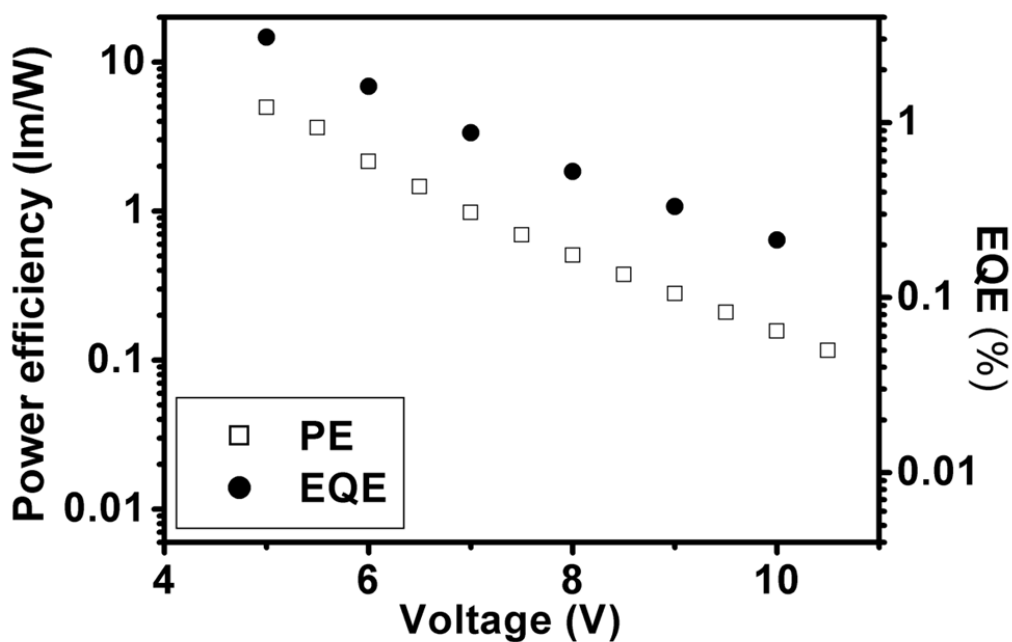


Figure S17. PE-V-EQE characteristics of the doped device containing 10% of 2 as dopant.

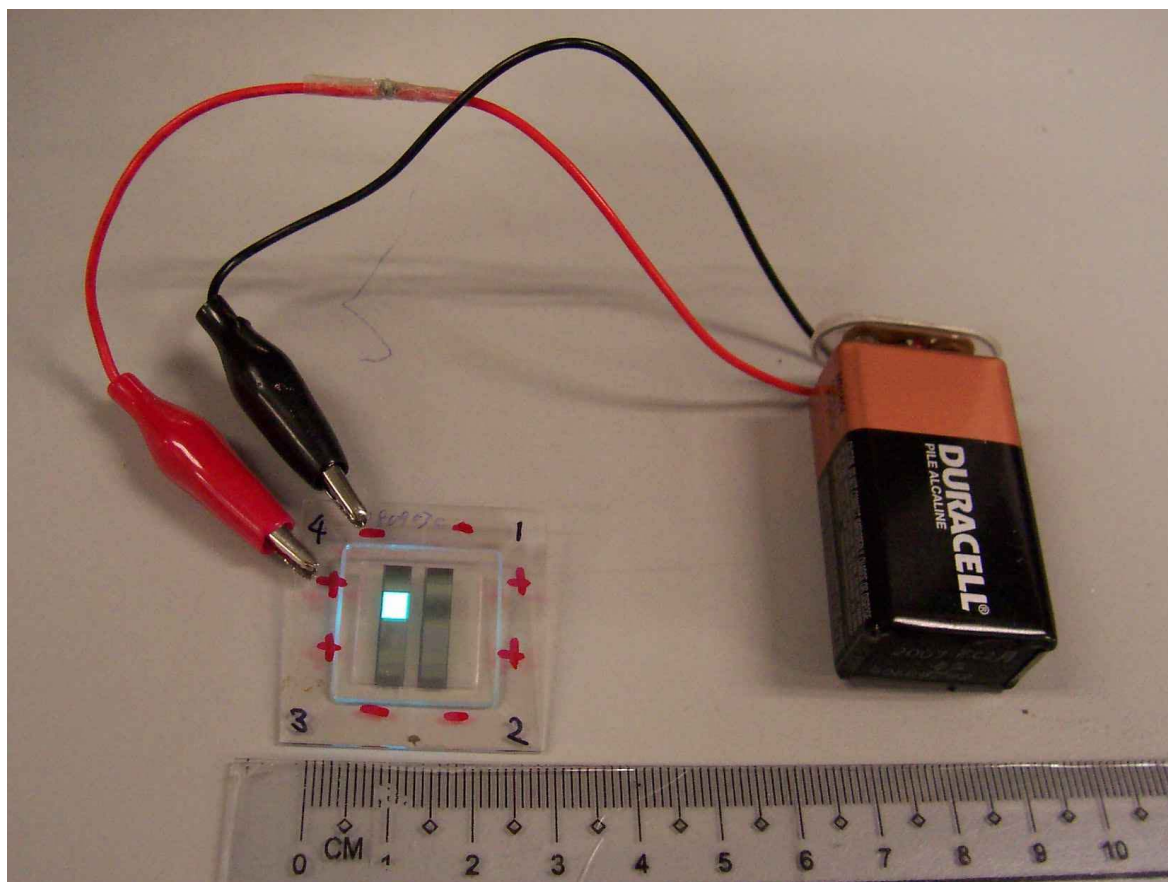


Figure S18. The OLED device with 4 light emitting pixels, each with emitting area of 0.1 cm^2 . The pixel near the left top corner was DC biased and light was emitted.