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Tuning the charge transport properties of non-planar zinc(II) complexes of azadipyrromethene using solubilizing groups

Supporting Information

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Crystal Packing and Calculated Overlap Integrals

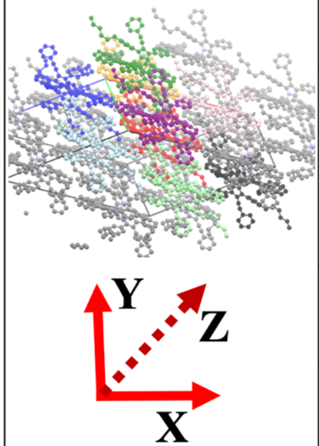
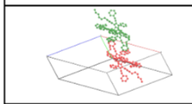
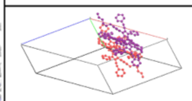
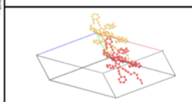
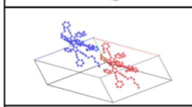
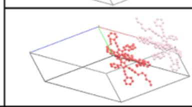
$Zn(phexWS3)_2$	Pair	Direction from red	Vh^{+} (meV)	Ve^{-} (meV)
		+Y, -Z	-1.90	0.44
		+Y	6.36	-1.64
		-Z	-2.13	-0.44
		-X	-0.05	-0.56
		+X, +Y, +Z,	0.37	-0.40

Table S1: Crystal packing, pairs, directions from red-colored compound and calculated absolute hole and electron overlap integrals for $Zn(phexWS3)_2$.

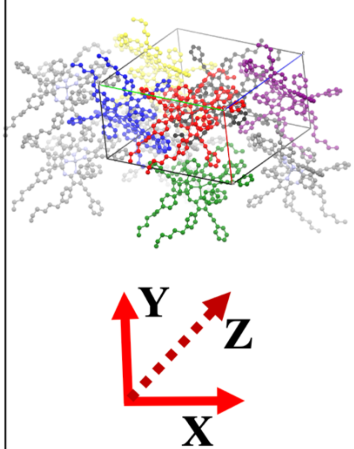
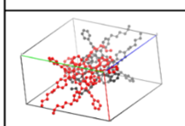
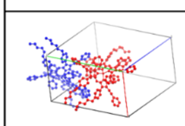
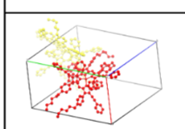
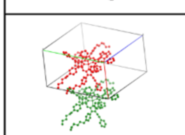
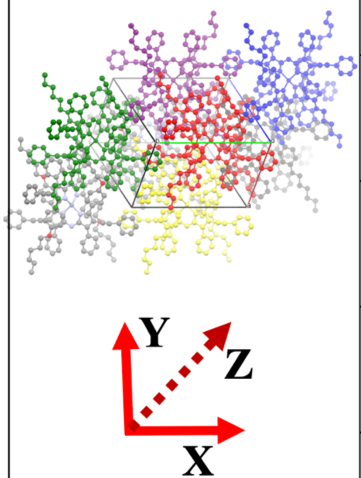
$Zn(dhexWS3)_2$	Pair	Directions from red	Vh^{+} (meV)	Ve^{-} (meV)
		-Y, -Z	-0.48	1.14
		-X	3.88	-3.18
		-X, -Z	-0.43	-0.20
		-Y	1.70	1.78

Table S2: Crystal packing, pairs, directions from red-colored compound and calculated absolute hole and electron overlap integrals for $Zn(dhexWS3)_2$.

$Zn(pOhexWS3)_2$



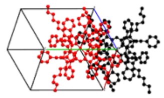
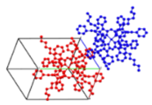
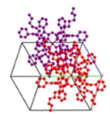
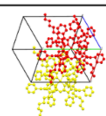
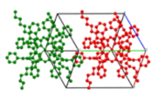
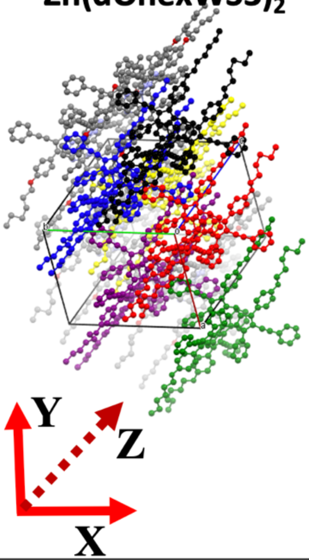
Pair	Directions from Red	Vh^+ (meV)	Ve^- (meV)
	+X, -Z	-0.42	-0.06
	+X, +Y, -Z	1.45	-0.86
	-X, -Z	3.79	-7.66
	-Y, -Z	-0.34	-1.21
	-X	-0.44	-0.47

Table S3: Crystal packing, pairs, directions from red-colored compound and calculated absolute hole and electron overlap integrals for $Zn(pOhexWS3)_2$.

$Zn(dOhexWS3)_2$



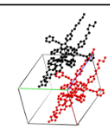
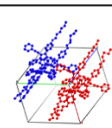
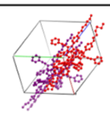
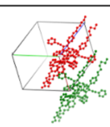
Pair	Direction from red	Vh^+ (meV)	Ve^- (meV)
	-X, +Y	-0.71	-0.16
	-X, -Y	17.94	-7.99
	-Y, +Z	-0.55	0.65
	+X, -Y	-0.71	-0.16

Table S4: Crystal packing, pairs, directions from red-colored compound and calculated absolute hole and electron overlap integrals for $Zn(dOhexWS3)_2$.

Grazing-Incident Wide-Angle X-ray Diffraction

Compound	In-plane FWHM (°, deg)	In-plane β (°, rad)	In-plane Crystallite size (nm)	Out-of-Plane FWHM (°, deg)	Out-of-Plane β (°, rad)	Out-of-Plane Crystallite Size (nm)
$Zn(phexWS3)_2^*$	----	----	----	----	----	----
$Zn(dhexWS3)_2^*$	----	----	----	----	----	---
$Zn(pOhexWS3)_2$	0.2205	0.2347	20.2	0.2407	0.2562	18.5
$Zn(dOhexWS3)_2$	0.0648	0.0690	65.7	0.2749	0.2926	16.2

Table S5: Summary of crystallite properties in annealed films. Hexyloxy substituted molecules were amorphous in film, therefore no measurements were taken.

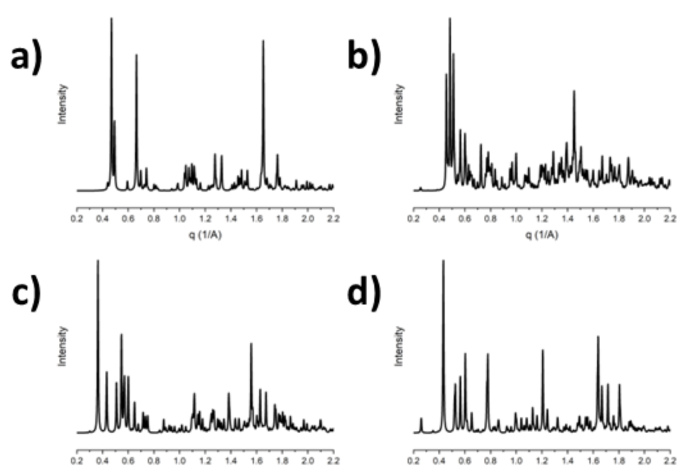


Figure S1: Powder diffraction patterns for (a) $Zn(phexWS3)_2$, (b) $Zn(dhexWS3)_2$, (c) $Zn(pOhexWS3)_2$, and (d) $Zn(dOhexWS3)_2$.

Diode Mobility

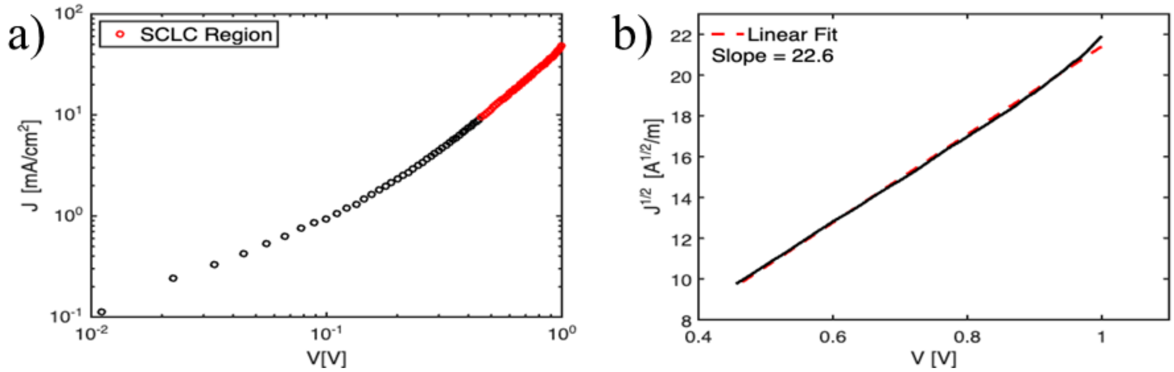


Figure S2: Electron mobility of $Zn(phexWS3)_2$ (a) plot of the double logarithm relationship between J and absolute V. The data highlighted in red shows the SCLC region which fits to the Mott-Gurney law. (b) $J^{1/2}$ characteristics shown versus V for electron mobility.

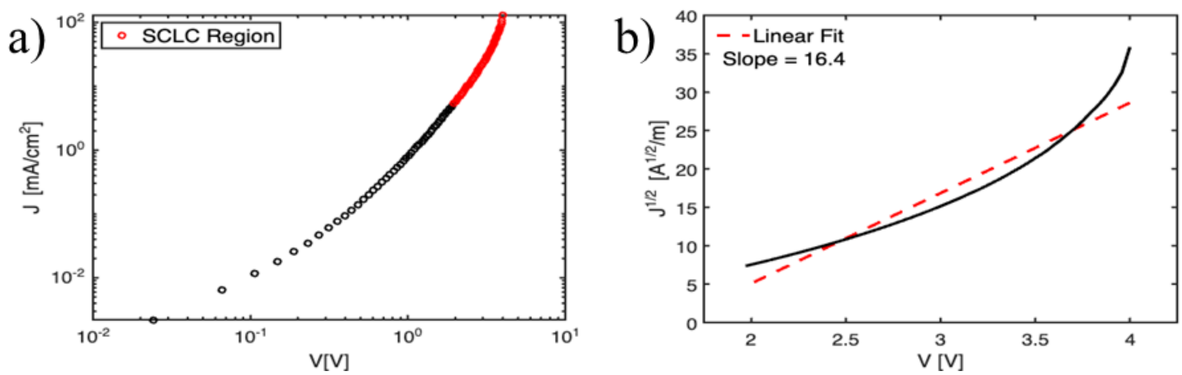


Figure S3: Electron mobility of $Zn(dhexWS3)_2$ (a) plot of the double logarithm relationship between J and absolute V. The data highlighted in red shows the SCLC region which fits to the Mott-Gurney law. (b) $J^{1/2}$ characteristics shown versus V for electron mobility.

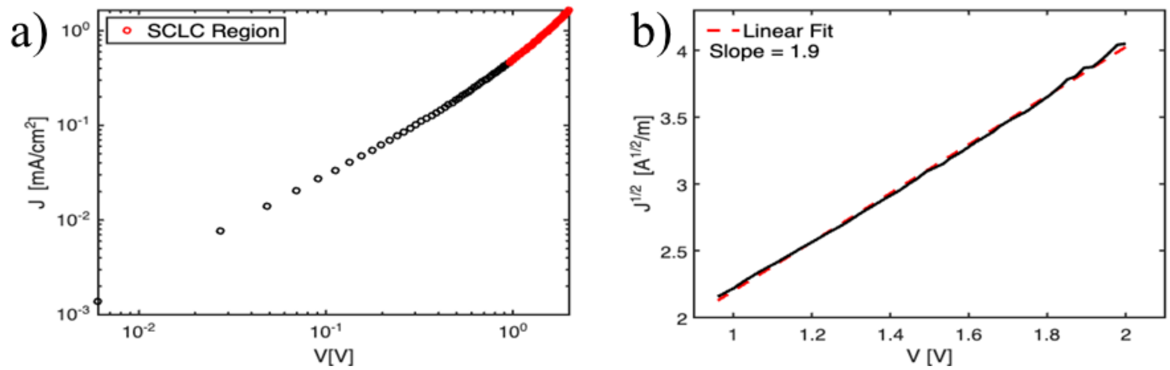


Figure S4: Electron mobility of Zn(pOhexWS3)$_2$ (a) plot of the double logarithm relationship between J and absolute V. The data highlighted in red shows the SCLC region which fits to the Mott-Gurney law. (b) $J^{1/2}$ characteristics shown versus V for electron mobility.

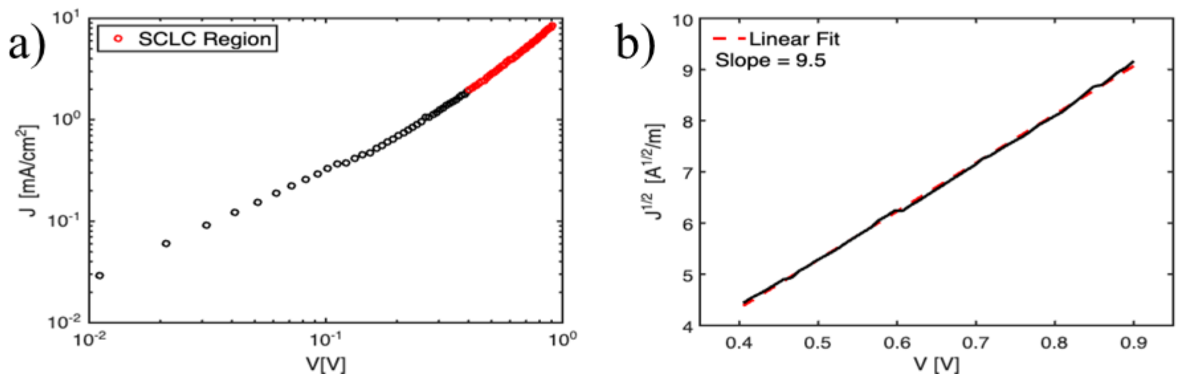


Figure S5: Electron mobility of Zn(dOhexWS3)$_2$ (a) plot of the double logarithm relationship between J and absolute V. The data highlighted in red shows the SCLC region which fits to the Mott-Gurney law. (b) $J^{1/2}$ characteristics shown versus V for electron mobility.

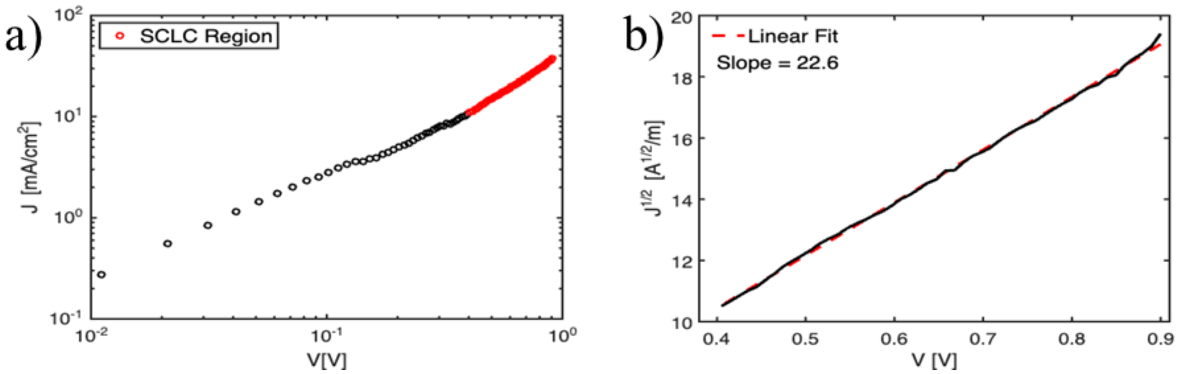


Figure S6: Electron mobility of $Zn(WS3)_2$ (a) plot of the double logarithm relationship between J and absolute V. The data highlighted in red shows the SCLC region which fits to the Mott-Gurney law. (b) $J^{1/2}$ characteristics shown versus V for electron mobility.

Organic Thin-Film Transistor Mobility

	Electron Mobility ($cm^2V^{-1}s^{-1}$)		
complex	Room Temperature	50°C	100°C
$Zn(phexWS3)_2$	$2 \pm 1 \times 10^{-4}$	$9 \pm 6 \times 10^{-5}$	$1 \pm 0.8 \times 10^{-4}$
$Zn(dhexWS3)_2$	$7 \pm 2 \times 10^{-5}$	$4 \pm 0.6 \times 10^{-5}$	$4 \pm 0.7 \times 10^{-5}$
$Zn(pOhexWS3)_2$	$3 \pm 4 \times 10^{-6}$	$1 \pm 0.1 \times 10^{-6}$	$6 \pm 3 \times 10^{-7}$
$Zn(dOhexWS3)_2$	$1 \pm 2 \times 10^{-5}$	$2 \pm 0.2 \times 10^{-4}$	$4 \pm 4 \times 10^{-5}$
$Zn(WS3)_2$	–	–	–

Table S6: Summary of average electron mobility in OTFTs at varying annealing temperatures

	Hole Mobility ($cm^2V^{-1}s^{-1}$)		
complex	Room Temperature	50°C	100°C
$Zn(phexWS3)_2$	$5 \pm 3 \times 10^{-5}$	$3 \pm 3 \times 10^{-5}$	$2 \pm 2 \times 10^{-5}$

Zn(dhexWS3)₂	$2 \pm 0.6 \times 10^{-5}$	$1 \pm 0.3 \times 10^{-5}$	$2 \pm 0.2 \times 10^{-5}$
Zn(pOhexWS3)₂	$1 \pm 0.5 \times 10^{-5}$	$9 \pm 2 \times 10^{-6}$	$8 \pm 3 \times 10^{-5}$
Zn(dOhexWS3)₂	$1 \pm 1 \times 10^{-5}$	$4 \pm 2 \times 10^{-6}$	$5 \pm 5 \times 10^{-6}$
Zn(WS3)₂	–	–	–

Table S7: Summary of average hole mobility in OTFTs at varying annealing temperatures

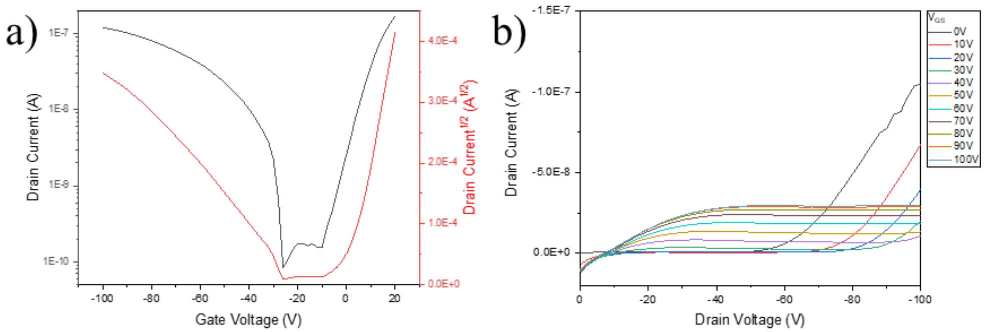


Figure S7: The (a) power transfer drain voltage (V_{DS} = -100 V) and (b) power output characteristics of prepared OTFT devices of p-type Zn(phexWS3)₂.

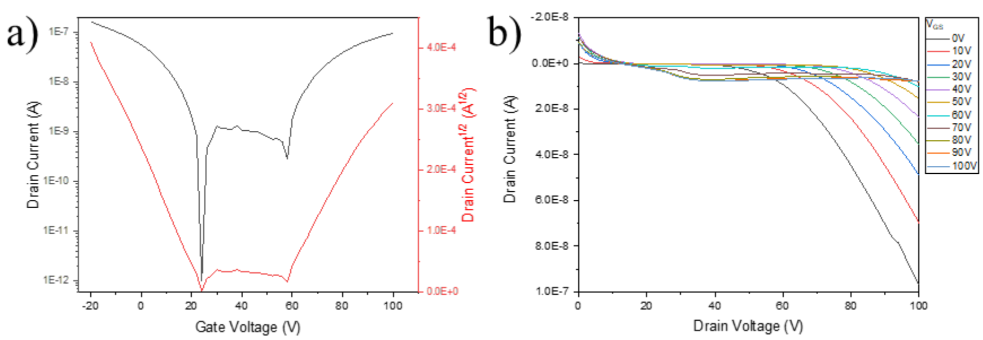


Figure S8: The (a) power transfer drain voltage (V_{DS} = 100 V) and (b) power output characteristics of prepared OTFT devices of n-type Zn(phexWS3)₂.

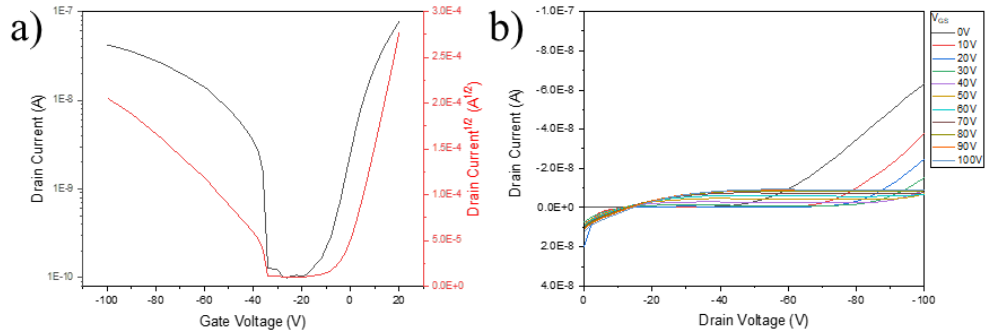


Figure S9: The (a) power transfer drain voltage (V_{DS} = -100 V) and (b) power output characteristics of prepared OTFT devices of p-type Zn(dhexWS3)$_2$.

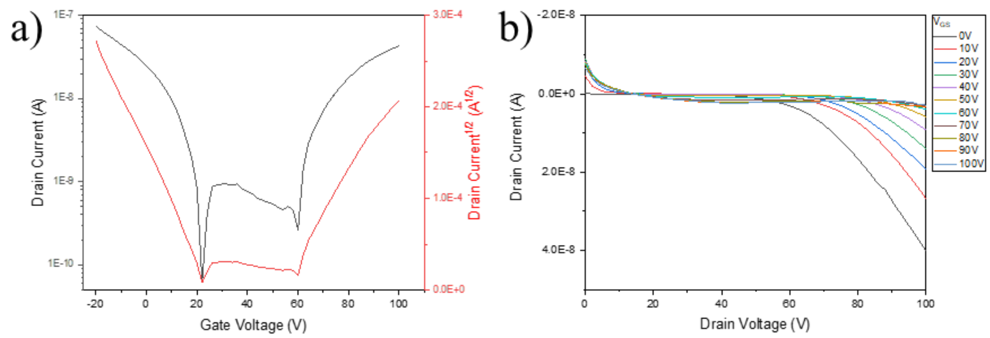


Figure S10: The (a) power transfer drain voltage (V_{DS} = 100 V) and (b) power output characteristics of prepared OTFT devices of n-type Zn(dhexWS3)$_2$.

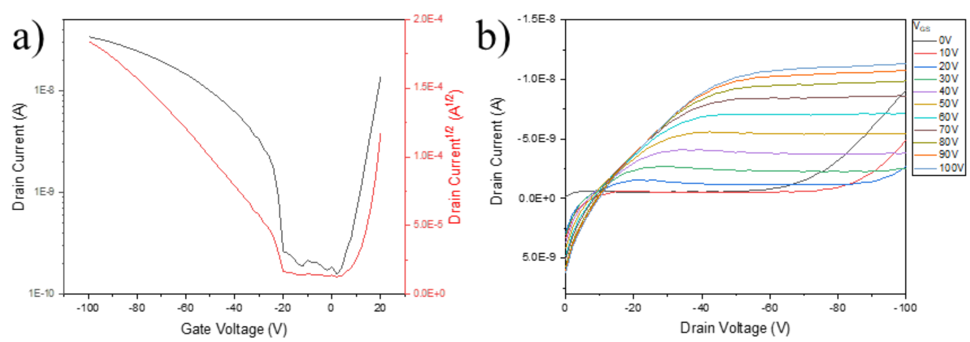


Figure S11: The (a) power transfer drain voltage (V_{DS} = -100 V) and (b) power output characteristics of prepared OTFT devices of p-type Zn(pOhexWS3)$_2$.

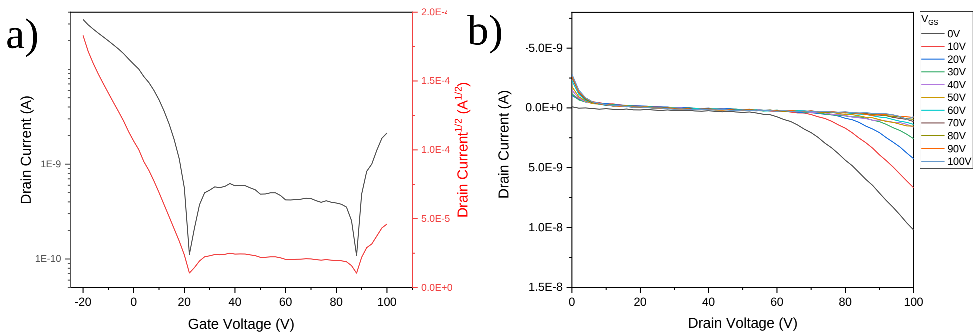


Figure S12: The (a) power transfer drain voltage (V_{DS} = 100 V) and (b) power output characteristics of prepared OTFT devices of n-type Zn(pOhexWS3)$_2$.

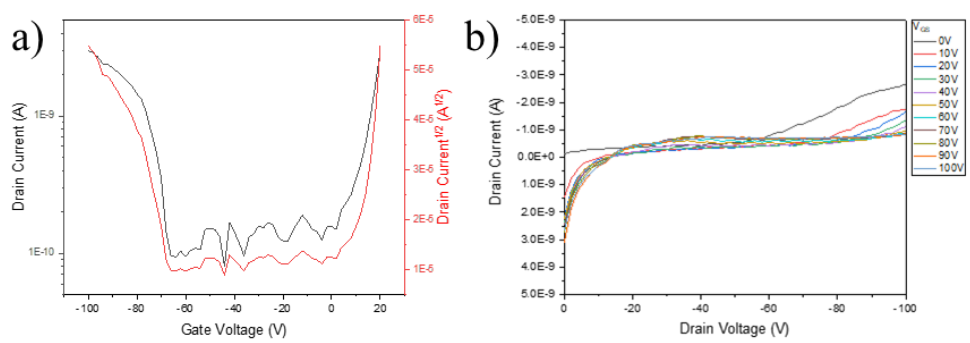


Figure S13: The (a) power transfer drain voltage (V_{DS} = -100 V) and (b) power output characteristics of prepared OTFT devices of p-type Zn(dOhexWS3)$_2$.

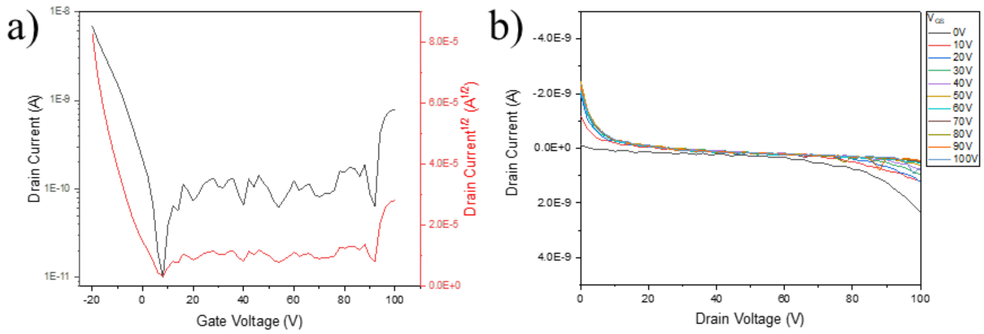


Figure S14: The (a) power transfer drain voltage (V_{DS} = 100 V) and (b) power output characteristics of prepared OTFT devices of n-type Zn(dOhexWS3)$_2$.