

Electronic Supplementary Information (ESI)

Band gap engineering in pyridyl-functionalized two-dimensional (2D) CuSCN coordination polymers

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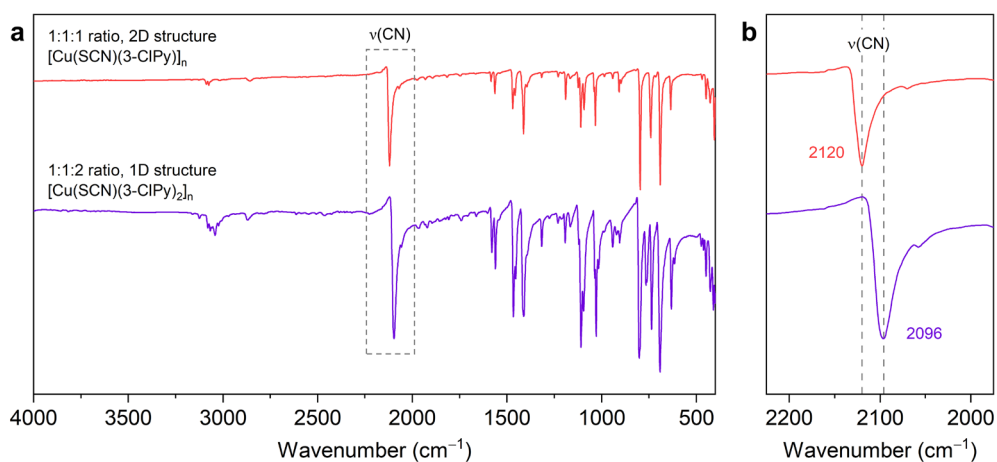


Figure S1. (a) Attenuated total reflectance-infrared spectroscopy (ATR-IR) spectra of $[\text{Cu}(\text{SCN})(3\text{-CIPy})]_n$ (1:1:1 ratio) and $[\text{Cu}(\text{SCN})(3\text{-CIPy})_2]_n$ (1:1:2 ratio). (b) Close-up of the $\nu(\text{CN})$ region. The structures of the two samples used for this measurement were confirmed by single-crystal X-ray diffraction.

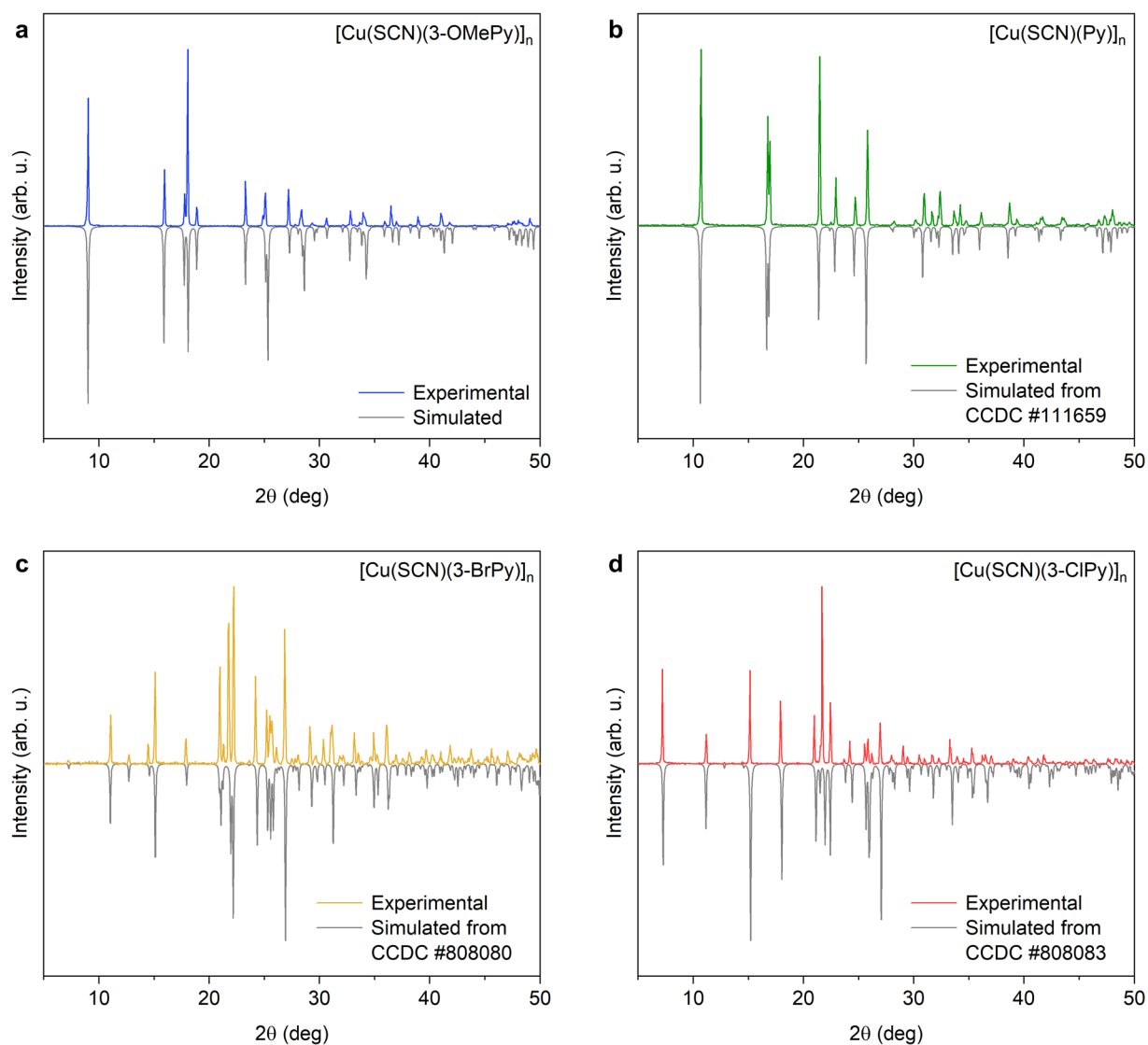


Figure S2. Powder X-ray diffraction (PXRD) patterns of $[\text{Cu}(\text{SCN})(3\text{-XPy})]_n$ complexes where X = (a) OMe, (b) H, (c) Br, and (d) Cl. The experimental data are shown against reference data simulated from single-crystal structures (CCDC numbers given in the plot legends). For $[\text{Cu}(\text{SCN})(3\text{-OMe})]_n$, the single-crystal data was collected in this work.

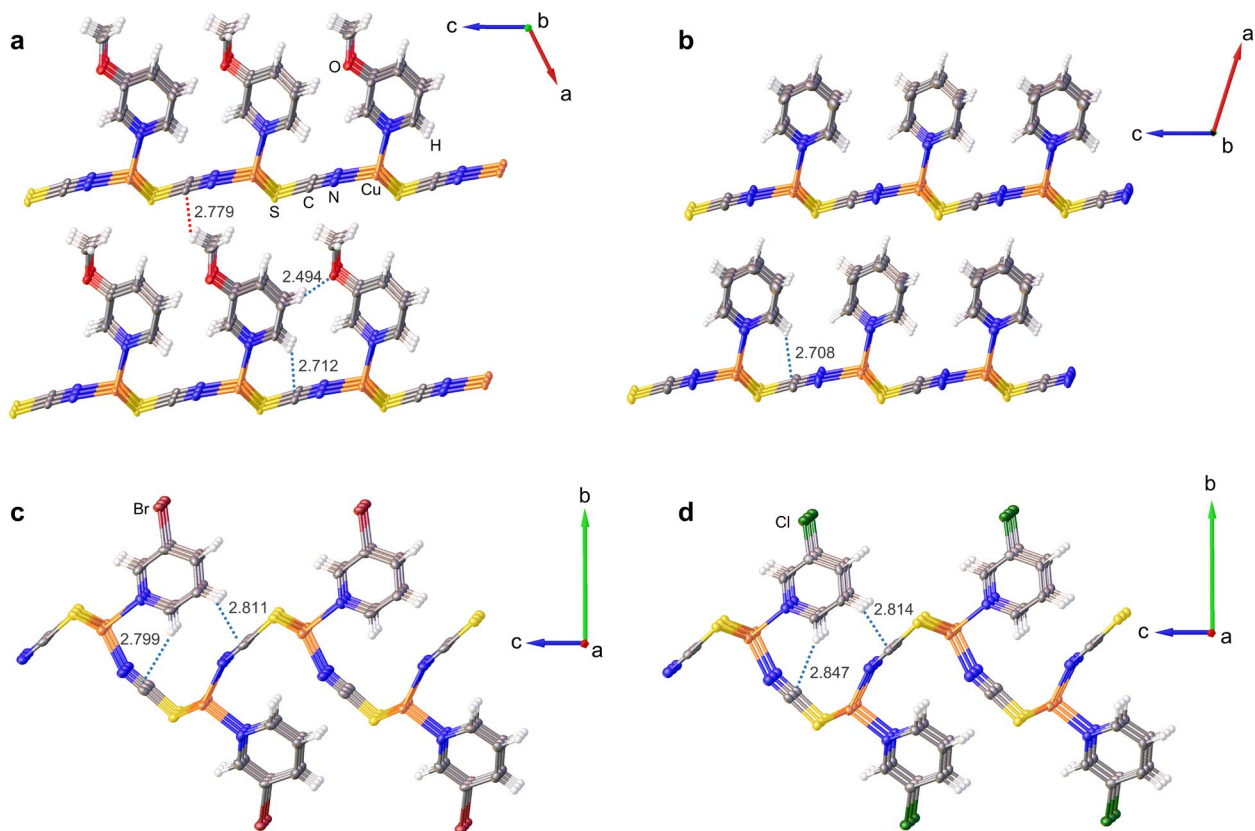


Figure S3. (a) and (b) 2D buckled sheet structures of $[\text{Cu}(\text{SCN})(3\text{-OMePy})]_n$ and $[\text{Cu}(\text{SCN})(\text{Py})]_n$, respectively. (c) and (d) 2D puckered/rippled sheet structures of $[\text{Cu}(\text{SCN})(3\text{-BrPy})]_n$ and $[\text{Cu}(\text{SCN})(3\text{-ClPy})]_n$, respectively. Short contacts are shown as dashed lines with units in Å.

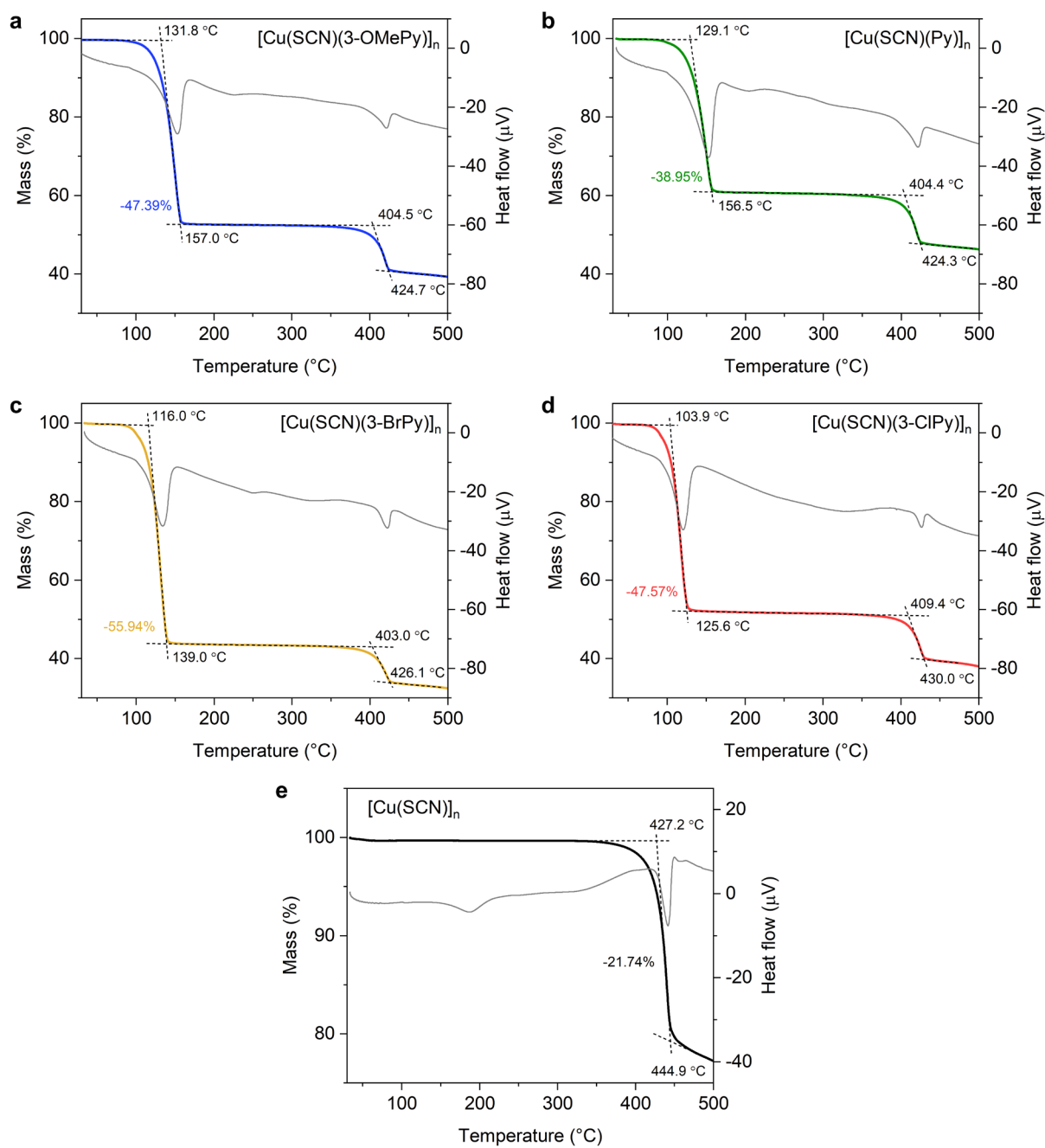


Figure S4. Thermogravimetric analysis (TGA) data of $[\text{Cu}(\text{SCN})(3\text{-XPy})]_n$ complexes with X = (a) OMe, (b) H, (c) Br, and (d) Cl, respectively. The data for $[\text{Cu}(\text{SCN})]_n$ (CuSCN treated with acetonitrile but without additional ligands) is shown as reference in (e).

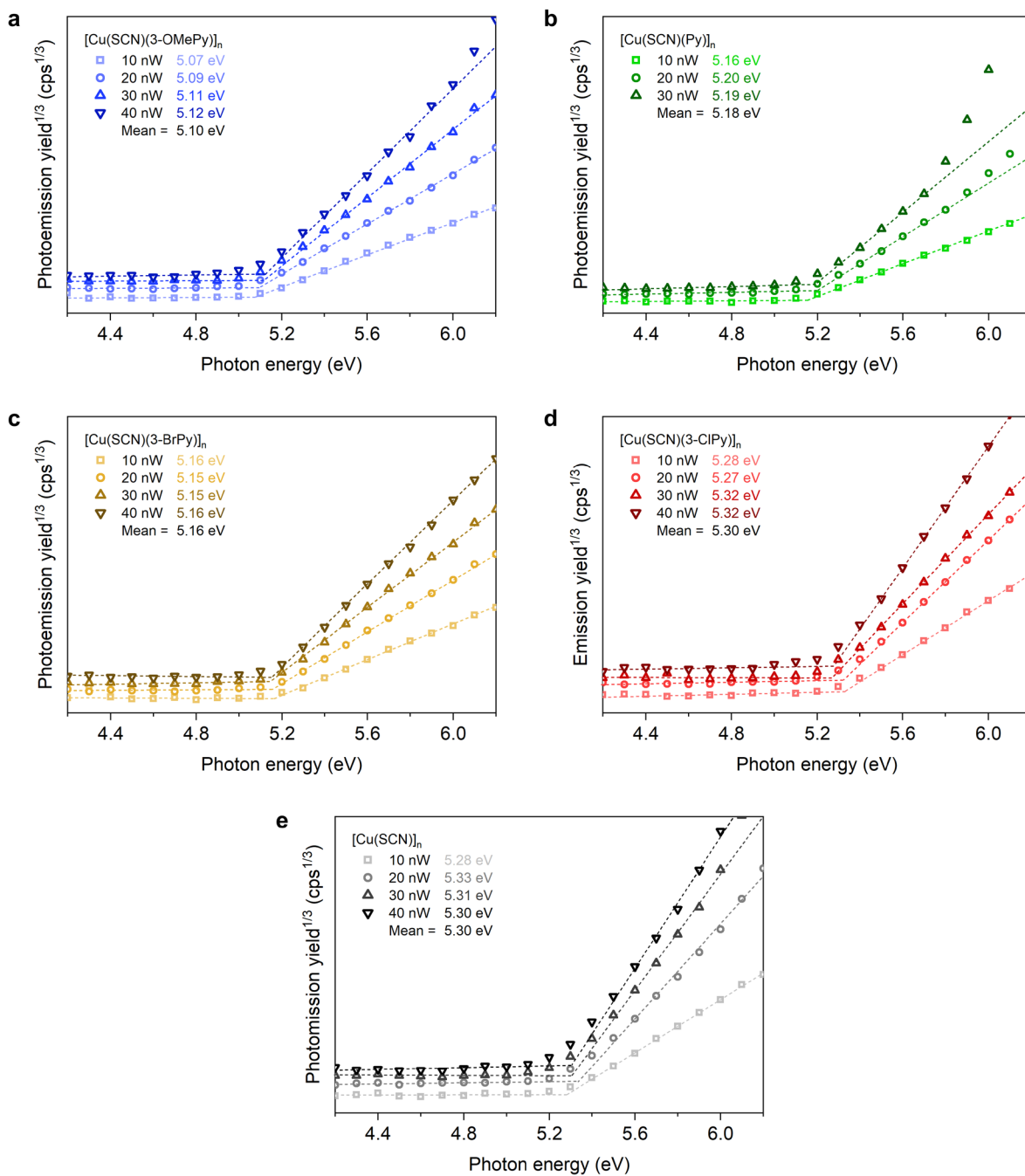


Figure S5. Photoelectron yield spectroscopy (PYS) results of $[\text{Cu}(\text{SCN})(3\text{-XPy})]_n$ complexes with $X =$ (a) OMe, (b) H, (c) Br, and (d) Cl, respectively. The data for $[\text{Cu}(\text{SCN})]_n$ is shown as reference in (e).

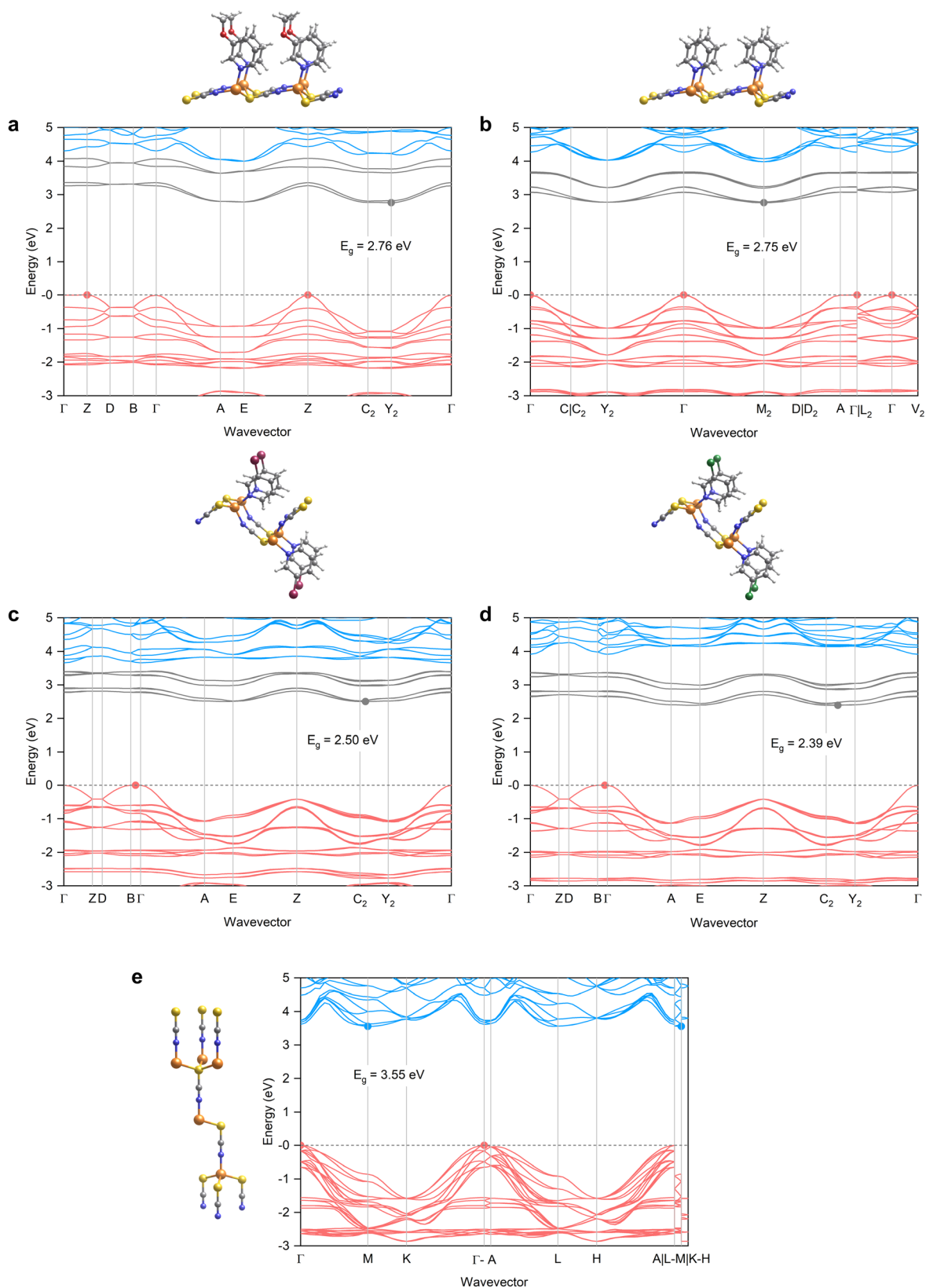


Figure S6. (a)-(e) Computed electronic band structures of $[\text{Cu}(\text{SCN})(3\text{-OMePy})]_n$, $[\text{Cu}(\text{SCN})(\text{Py})]_n$, $[\text{Cu}(\text{SCN})(3\text{-BrPy})]_n$, $[\text{Cu}(\text{SCN})(3\text{-ClPy})]_n$, and reference $3\text{R-}\beta\text{-CuSCN}$, respectively. Valence bands (VBs) are plotted as light red lines, conduction bands (CBs) from ligands as gray, and CBs from SCN states as light blue. Solid circles mark the valence band maximum and conduction band minimum.

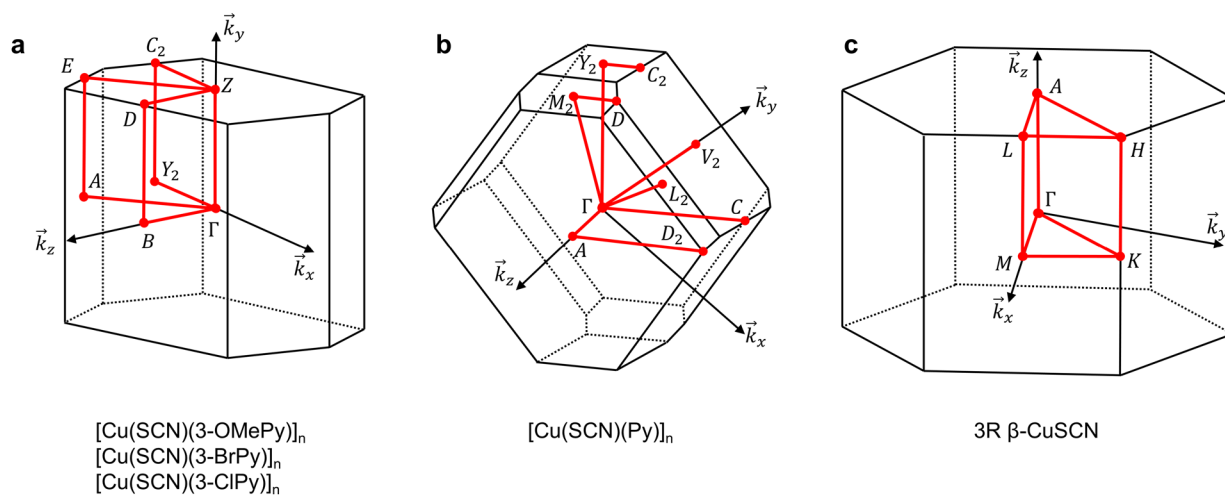


Figure S7. Brillouin zones of (a) $[\text{Cu}(\text{SCN})(3\text{-OMePy})]_n$, $[\text{Cu}(\text{SCN})(3\text{-BrPy})]_n$, and $[\text{Cu}(\text{SCN})(3\text{-ClPy})]_n$; (b) $[\text{Cu}(\text{SCN})(\text{Py})]_n$; and (c) $3\text{R-}\beta\text{-CuSCN}$.

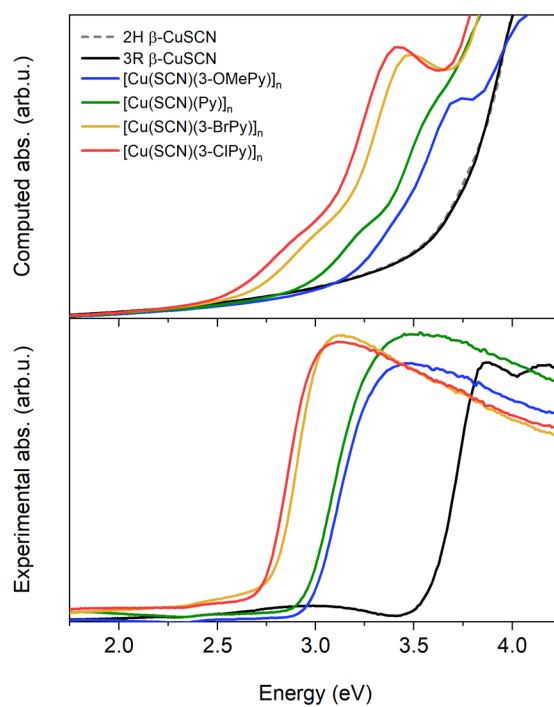


Figure S8. Comparison of the computed (top panel) and experimental (bottom panel) absorption spectra.

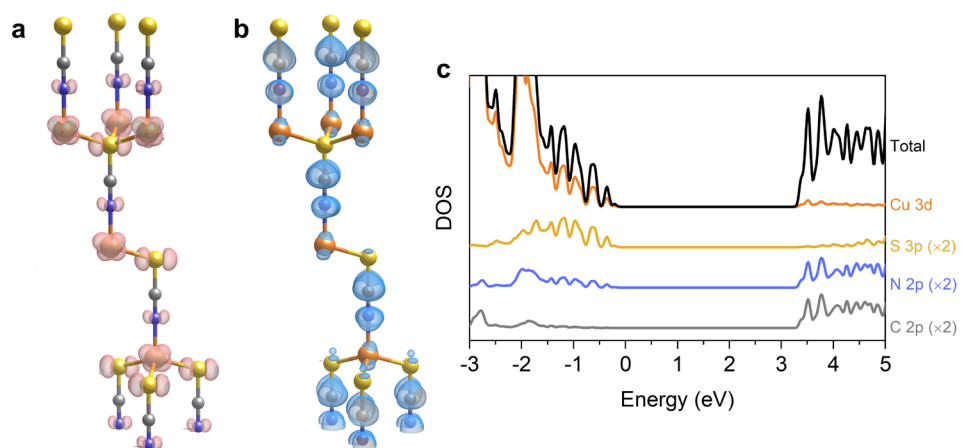


Figure S9. Isosurfaces of (a) valence band maximum (VBM) and (b) conduction band minimum (CBM) states of 3R- β -CuSCN. (c) Total and partial density of states (DOS).

Table S1. Crystal data and structural refinement parameters of [Cu(SCN)(3-OMePy)]_n.

Compound	[Cu(SCN)(3-OMePy)]_n
CCDC no.	2329055
Empirical formula	C ₇ H ₇ CuN ₂ OS
Formula weight	230.75
Temperature (K)	150(2)
Crystal system	monoclinic
Space group	Pc
<i>a</i> (Å)	10.9519(9)
<i>b</i> (Å)	3.7899(3)
<i>c</i> (Å)	11.1736(8)
<i>α</i> (deg)	90
<i>β</i> (deg)	116.487(2)
<i>γ</i> (deg)	90
Volume (Å ³)	415.10(6)
<i>Z</i>	2
ρ_{calc} (g/cm ³)	1.846
μ (mm ⁻¹)	2.828
<i>F</i> (000)	232.0
Crystal size (mm ³)	0.15 × 0.12 × 0.06
Radiation	Mo K α (λ = 0.71073 Å)
2 θ range for data collection (deg)	4.156 to 60.31
Index ranges	-15 ≤ <i>h</i> ≤ 15, -5 ≤ <i>k</i> ≤ 5, -15 ≤ <i>l</i> ≤ 15
Reflections collected	19382
Independent reflections	2447 [<i>R</i> _{int} = 0.0330, <i>R</i> _{sigma} = 0.0256]
Data/restraints/parameters	2447/2/110
Goodness-of-fit on <i>F</i> ²	1.174
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0279, <i>wR</i> ₂ = 0.0635
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0314, <i>wR</i> ₂ = 0.0671
Largest diff. peak/hole (e Å ⁻³)	0.81/-0.94
Flack parameter	0.056(5)

Table S2. Comparison of lattice parameters and band gaps between experimental values and computed values.

Compound	Method	a (Å)	b (Å)	c (Å)	V (Å ³)	α (deg)	β (deg)	γ (deg)	E _g (eV)
3R- β -CuSCN	Experimental	3.856	3.856	32.905	423.708	90.00	90.00	120.00	3.65
	HSE06-D3	3.831	3.831	32.821	417.105	90.00	90.00	120.00	3.55
	PBE-D3	3.783	3.783	32.917	407.972	90.00	90.00	120.00	2.18
[Cu(SCN)(3-OMePy)] _n	Experimental	3.790	10.952	11.174	415.098	116.49	90.00	90.00	3.05
	HSE06-D3	3.797	10.926	11.149	413.531	116.60	90.00	90.00	2.76
	PBE-D3	3.762	10.915	11.168	409.468	116.77	90.00	90.00	1.45
[Cu(SCN)(Py)] _n	Experimental	3.855	11.159	17.435	715.108	107.55	90.00	90.00	3.03
	HSE06-D3	3.806	11.112	17.313	697.386	107.72	90.00	90.00	2.75
	PBE-D3	3.760	11.124	17.230	686.279	107.75	90.00	90.00	1.41
[Cu(SCN)(3-BrPy)] _n	Experimental	3.817	8.492	24.288	786.876	90.00	90.00	91.71	2.84
	HSE06-D3	3.847	8.535	24.334	798.454	90.00	90.00	91.93	2.50
	PBE-D3	3.798	8.532	24.149	782.077	90.00	90.00	91.86	1.22
[Cu(SCN)(3-ClPy)] _n	Experimental	3.781	8.386	24.283	769.866	90.00	90.00	91.01	2.79
	HSE06-D3	3.812	8.385	24.329	777.414	90.00	90.00	91.29	2.39
	PBE-D3	3.765	8.383	24.179	762.907	90.00	90.00	91.19	1.10

Table S3. Hole and electron effective masses (m_h^* and m_e^* expressed in multiples of an electron rest mass m_0) calculated along Brillouin zone paths near the valence band maximum (VBM), conduction band minimum (CBM), or points near VBM and CBM with high band dispersions. For simple k -paths, the approximate direction in the real lattice space is also denoted.

Compound	Direction	m_h^*	Direction	m_e^*
3R- β -CuSCN	$\Gamma \rightarrow K$ (Cu-S plane)	0.39 ^a , 1.20 ^b	$M \rightarrow \Gamma$ (Cu-S plane)	1.22
	$\Gamma \rightarrow M$ (Cu-S plane)	0.39 ^a , 1.20 ^b	$M \rightarrow K$ (Cu-S plane)	3.96
	$\Gamma \rightarrow A$ (c-axis, along SCN)	0.70	$M \rightarrow L$ (c-axis, along SCN)	3.24
			$\Gamma \rightarrow M$ (Cu-S plane)	0.38
			$\Gamma \rightarrow K$ (Cu-S plane)	0.38
[Cu(SCN)(3-OMePy)] _n	$Z \rightarrow \Gamma$ (Interlayer)	> 4 ^c	$Y_2 \rightarrow C_2$ (Interlayer)	> 4 ^c
	$Z \rightarrow C_2$ (Along Cu-S chain)	0.50	$Y_2 \rightarrow \Gamma$ (Along π - π stacking)	2.24
	$Z \rightarrow E$ (Within 2D layer)	0.53	$E \rightarrow Z$ (Within 2D layer)	2.67
	$Z \rightarrow D$ (Along SCN)	0.79		
	$\Gamma \rightarrow B$ (Along SCN)	0.80		
	$\Gamma \rightarrow A$ (Within 2D layer)	0.52		
	$\Gamma \rightarrow Y_2$ (Along Cu-S chain)	0.50		
[Cu(SCN)(Py)] _n	$\Gamma \rightarrow C$ (Within 2D layer)	0.49	$M_2 \rightarrow \Gamma$ (Within 2D layer)	> 4 ^c
	$\Gamma \rightarrow Y_2$ (Within 2D layer)	0.49	$M_2 \rightarrow D$	> 4 ^c
	$\Gamma \rightarrow M_2$ (Within 2D layer)	0.53	$Y_2 \rightarrow C_2$ (Within 2D layer)	> 4 ^c
	$\Gamma \rightarrow A$ (Interlayer)	> 4 ^c	$Y_2 \rightarrow \Gamma$ (Within 2D layer)	> 4 ^c
	$\Gamma \rightarrow L_2$	1.13		
	$\Gamma \rightarrow V_2$ (Along SCN)	0.67		
[Cu(SCN)(3-BrPy)] _n	VBM $\rightarrow \Gamma$ (Interlayer)	> 4 ^c	CBM $\rightarrow C_2$ (Along undulating dir.)	> 4 ^c
	VBM $\rightarrow B$ (Interlayer)	> 4 ^c	CBM $\rightarrow Y_2$ (Along undulating dir.)	> 4 ^c
	$\Gamma \rightarrow A$ (Within 2D layer)	0.50	$E \rightarrow Z$	> 4 ^c
	$\Gamma \rightarrow Y_2$ (Along Cu-S chain)	0.49		
[Cu(SCN)(3-ClPy)] _n	VBM $\rightarrow \Gamma$ (Interlayer)	> 4 ^c	CBM $\rightarrow C_2$ (Along undulating dir.)	> 4 ^c
	VBM $\rightarrow B$ (Interlayer)	> 4 ^c	CBM $\rightarrow Y_2$ (Along undulating dir.)	> 4 ^c
	$\Gamma \rightarrow A$ (Within 2D layer)	0.50	$E \rightarrow Z$	3.53
	$\Gamma \rightarrow Y_2$ (Along Cu-S chain)	0.49		

Note: ^a Light hole; ^b Heavy hole ^c Large effective masses (> 4 m_0 in this case) due to very low band curvatures such that the parabola fitting contained uncertainty too large for exact value determination.