

# Enhanced plant growth and harvestable yield through fluorescent copper-based composites

## Supporting Information

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**Crystallographic dataset**

New Tetragonal Polymorph of  $C_{56}H_{60}I_4P_4Cu_4$ .

<b>Table 1 Crystal data and structure refinement for tetragonal <math>C_{56}H_{60}I_4P_4Cu_4</math>.</b>	
Empirical formula	$C_{56}H_{60}I_4P_4Cu_4$
Formula weight	1618.68
Temperature/K	140
Crystal system	Tetragonal
Space group	I-4
a/Å	16.6953(2)
b/Å	16.6953(2)
c/Å	10.2819(2)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å <sup>3</sup>	2865.91(9)
Z	2
$\rho_{calc}/cm^3$	1.876
$\mu/mm^{-1}$	3.766
F(000)	1568
Crystal size/mm <sup>3</sup>	0.44 × 0.24 × 0.16
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection/ $^\circ$	4.652 to 61.12
Index ranges	-20 ≤ h ≤ 20, -16 ≤ k ≤ 21, -13 ≤ l ≤ 12
Reflections collected	10170
Independent reflections	3466 [ $R_{int} = 0.0493$ , $R_{sigma} = 0.0438$ ]
Data/restraints/parameters	3466/0/155
Goodness-of-fit on F <sup>2</sup>	1.123
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0375$ , $wR_2 = 0.0904$
Final R indexes [all data]	$R_1 = 0.0385$ , $wR_2 = 0.0908$
Largest diff. peak/hole / e Å <sup>-3</sup>	1.36/-1.23
Flack parameter	0.02(2)
CCDC deposition number	2501638

<b>Table 2 Fractional Atomic Coordinates (<math>\times 10^4</math>) and Equivalent Isotropic Displacement Parameters (<math>\text{Å}^2 \times 10^3</math>) for tetragonal <math>C_{56}H_{60}I_4P_4Cu_4</math>. <math>U_{eq}</math> is defined as 1/3 of the trace of the orthogonalised <math>U_{ij}</math> tensor.</b>				
Atom	X	Y	Z	U(eq)
I1	5858.7(3)	9122.6(3)	972.8(4)	19.16(13)
Cu1	5694.0(6)	9237.1(7)	3558.3(10)	27.3(2)
P1	6496.0(13)	8401.8(12)	4668.6(19)	21.6(4)
C1	6396(5)	7332(5)	4365(8)	21.5(15)
C2	6401(6)	6733(7)	5350(10)	37(2)
C3	6431(7)	5926(6)	5011(11)	43(2)
C4	6414(6)	5700(6)	3738(10)	37(2)
C5	6401(6)	6282(6)	2767(9)	35(2)
C6	6379(6)	7065(6)	3082(9)	32.2(19)

C7	7565(4)	8532(5)	4323(7)	20.9(15)
C8	7816(5)	9248(5)	3784(9)	28.4(18)
C9	8627(6)	9373(6)	3582(10)	34(2)
C10	9184(5)	8776(6)	3878(9)	32.2(19)
C11	8925(6)	8063(6)	4366(9)	34(2)
C12	8115(5)	7929(6)	4596(8)	28.7(18)
C13	6444(6)	8494(6)	6451(9)	34.5(19)
C14	6486(10)	9307(9)	6963(13)	64(4)

**Table 3 Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for tetragonal  $\text{C}_{56}\text{H}_{60}\text{I}_4\text{P}_4\text{Cu}_4$ . The Anisotropic displacement factor exponent takes the form: -  $2\pi^2[h^2a^*U_{11}+2hka^*b^*U_{12}+\dots]$ .**

Atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
I1	19.5(3)	15.2(2)	22.8(2)	-1.23(18)	1.91(18)	1.24(16)
Cu1	21.5(5)	30.3(6)	29.9(5)	-0.5(4)	-1.2(4)	8.9(3)
P1	20.4(10)	25.7(11)	18.7(9)	-3.0(7)	-0.3(7)	6.4(7)
C1	19(4)	27(4)	19(4)	-3(3)	2(3)	4(3)
C2	45(6)	44(6)	24(5)	3(4)	5(4)	5(4)
C3	65(7)	30(5)	34(5)	14(4)	-6(5)	-6(4)
C4	50(6)	25(4)	35(6)	4(4)	-4(4)	-5(4)
C5	42(5)	39(5)	24(4)	-6(4)	-5(4)	-2(4)
C6	38(5)	38(5)	21(4)	3(4)	-4(4)	0(4)
C7	18(4)	26(4)	19(4)	-3(3)	0(3)	1(3)
C8	32(4)	24(4)	28(5)	1(3)	3(3)	-4(3)
C9	33(5)	36(5)	33(5)	-2(4)	3(4)	-10(4)
C10	21(4)	48(5)	28(5)	-6(4)	4(3)	-8(3)
C11	33(5)	41(5)	26(4)	-5(4)	-2(3)	9(4)
C12	28(5)	35(5)	23(4)	3(3)	0(3)	7(3)
C13	32(5)	47(6)	24(4)	-4(4)	3(4)	10(4)
C14	85(11)	74(9)	34(6)	-10(6)	3(6)	-6(7)

**Table 4 Bond Lengths for tetragonal  $\text{C}_{56}\text{H}_{60}\text{I}_4\text{P}_4\text{Cu}_4$**

Atom	Atom	Length/ $\text{\AA}$	Atom	Atom	Length/ $\text{\AA}$
I1	Cu1 <sup>1</sup>	2.6722(11)	C3	C4	1.362(15)
I1	Cu1	2.6794(11)	C4	C5	1.393(14)
I1	Cu1 <sup>2</sup>	2.7669(12)	C5	C6	1.349(14)
Cu1	P1	2.245(2)	C7	C8	1.382(11)
P1	C1	1.820(8)	C7	C12	1.392(11)
P1	C7	1.832(8)	C8	C9	1.387(13)
P1	C13	1.841(9)	C9	C10	1.396(14)
C1	C2	1.424(13)	C10	C11	1.362(14)
C1	C6	1.393(12)	C11	C12	1.391(13)
C2	C3	1.392(15)	C13	C14	1.458(16)

<sup>1</sup>3/2-Y, 1/2+X, 1/2-Z; <sup>2</sup>-1/2+Y, 3/2-X, 1/2-Z

**Table 5 Bond Angles for tetragonal  $\text{C}_{56}\text{H}_{60}\text{I}_4\text{P}_4\text{Cu}_4$**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cu1 <sup>1</sup>	I1	Cu1	75.22(4)		C6	C1	P1	118.6(7)
Cu1 <sup>1</sup>	I1	Cu1 <sup>2</sup>	78.55(3)		C6	C1	C2	116.7(8)
Cu1	I1	Cu1 <sup>2</sup>	73.67(3)		C3	C2	C1	120.2(9)
I1 <sup>2</sup>	Cu1	I1 <sup>1</sup>	97.80(3)		C4	C3	C2	120.5(9)
I1	Cu1	I1 <sup>1</sup>	103.37(4)		C3	C4	C5	119.8(9)
I1 <sup>2</sup>	Cu1	I1	105.99(4)		C6	C5	C4	120.2(9)
P1	Cu1	I1 <sup>1</sup>	116.95(7)		C5	C6	C1	122.5(9)
P1	Cu1	I1	113.51(6)		C8	C7	P1	118.4(6)
P1	Cu1	I1 <sup>2</sup>	117.17(7)		C8	C7	C12	120.4(8)
C1	P1	Cu1	117.9(3)		C12	C7	P1	121.2(6)
C1	P1	C7	99.9(3)		C7	C8	C9	119.1(8)
C1	P1	C13	104.4(4)		C8	C9	C10	120.7(8)
C7	P1	Cu1	114.1(3)		C11	C10	C9	119.5(8)
C7	P1	C13	103.2(4)		C10	C11	C12	120.8(9)
C13	P1	Cu1	115.2(3)		C11	C12	C7	119.4(8)
C2	C1	P1	124.6(7)		C14	C13	P1	115.8(8)

<sup>1</sup>3/2-Y, 1/2+X, 1/2-Z; <sup>2</sup>-1/2+Y, 3/2-X, 1/2-Z

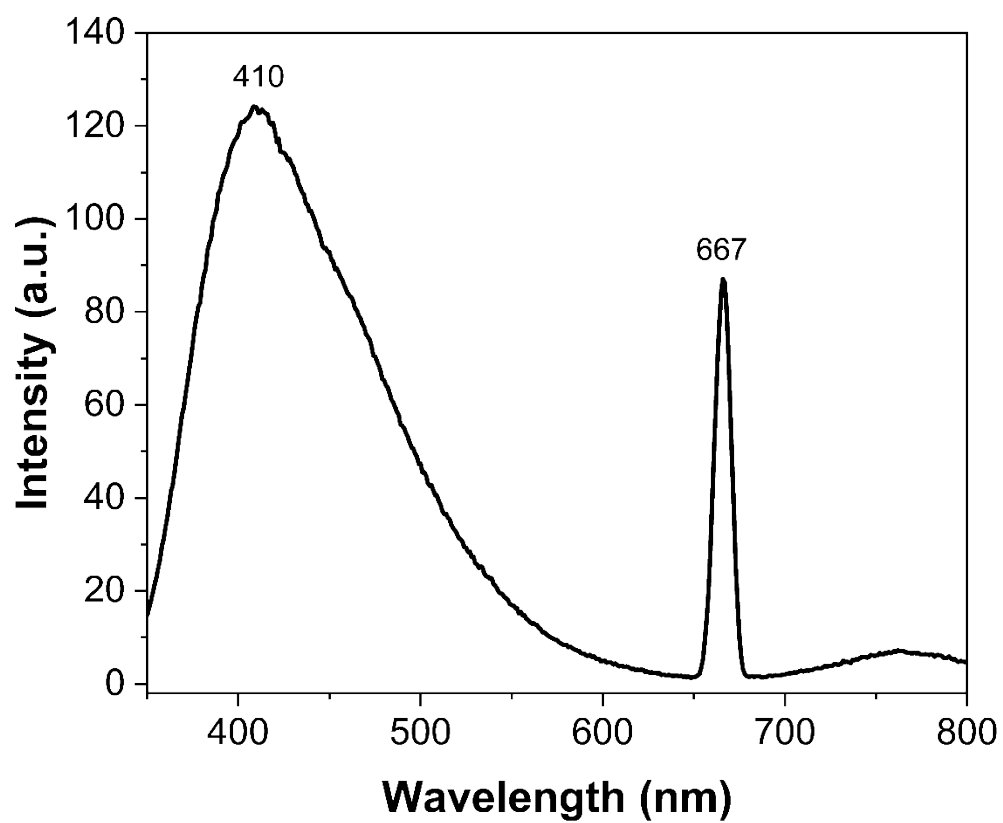
Table 6 Torsion Angles for tetragonal C <sub>56</sub> H <sub>60</sub> I <sub>4</sub> P <sub>4</sub> Cu <sub>4</sub>										
A	B	C	D	Angle/°		A	B	C	D	Angle/°
Cu1	P1	C1	C2	-137.4(7)		C4	C5	C6	C1	2.2(15)
Cu1	P1	C1	C6	48.1(8)		C6	C1	C2	C3	3.4(14)
Cu1	P1	C7	C8	20.0(7)		C7	P1	C1	C2	98.4(8)
Cu1	P1	C7	C12	-160.1(6)		C7	P1	C1	C6	-76.1(7)
Cu1	P1	C13	C14	-47.4(10)		C7	P1	C13	C14	0)
P1	C1	C2	C3	-171.2(8)		C7	C8	C9	C10	2.1(14)
P1	C1	C6	C5	172.1(8)		C8	C7	C12	C11	2.3(12)
P1	C7	C8	C9	176.5(7)		C8	C9	C10	C11	0.2(14)
P1	C7	C12	C11	-177.5(7)		C9	C10	C11	C12	-1.3(14)
C1	P1	C7	C8	146.8(7)		C10	C11	C12	C7	0.0(13)
C1	P1	C7	C12	-33.3(7)		C12	C7	C8	C9	-3.3(13)
C1	P1	C13	C14	-178.2(9)		C13	P1	C1	C2	-8.1(8)
C1	C2	C3	C4	-3.5(17)		C13	P1	C1	C6	177.4(7)
C2	C1	C6	C5	-2.8(14)		C13	P1	C7	C8	-105.7(7)
C2	C3	C4	C5	2.8(17)		C13	P1	C7	C12	74.1(8)
C3	C4	C5	C6	-2.1(16)						

Table 7 Hydrogen Atom Coordinates (Å×10 <sup>4</sup> ) and Isotropic Displacement Parameters (Å <sup>2</sup> ×10 <sup>3</sup> ) for tetragonal C <sub>56</sub> H <sub>60</sub> I <sub>4</sub> P <sub>4</sub> Cu <sub>4</sub>				
Atom	X	Y	Z	U(eq)
H2	6382.81	6883.57	6240.71	45
H3	6464.38	5530.08	5672.75	52
H4	6411.62	5148.26	3514.25	44
H5	6407.13	6125.34	1878.2	42
H6	6351.27	7450.23	2403.29	39

<b>H8</b>	7437.02	9648.66	3555.05	34
<b>H9</b>	8806.36	9869.92	3238.2	41
<b>H10</b>	9739.15	8866.57	3739.41	39
<b>H11</b>	9302	7652.8	4551.09	40
<b>H12</b>	7939.3	7430.49	4936.09	34
<b>H13A</b>	5936.57	8248.46	6749.26	41
<b>H13B</b>	6888.65	8179.82	6831.86	41
<b>H14A</b>	7007.74	9541.65	6750.52	97
<b>H14B</b>	6417.88	9294.63	7909.97	97
<b>H14C</b>	6059.67	9632.42	6574.53	97

The tetragonal polymorph crystallised from chloroform/ether as large colourless blocks, in contrast to the known orthorhombic polymorph<sup>1</sup> which produced much smaller crystals from the same solvent system. The space group is I-4, and only one quarter of the molecular structure of the functionalised Cu<sub>4</sub>I<sub>4</sub> cube is crystallographically unique, since it lies on a four-fold rotoinversion axis. The Cu-I bond lengths (2.6722(11), 2.6794(11) and 2.7669(12) Å) and I-Cu-I angles (97.80(3), 103.37(4) and 105.99(4)°) are very similar to those observed in the orthorhombic polymorph where half the molecule is crystallographically unique (2.678-2.721 Å, 98.03 & 98.62, 103.88, 106.51, 107.20 & 107.31°). The Cu-I-Cu angles (73.67(3), 75.22(4) & 78.55(3)°) are also similar to those in the orthorhombic polymorph (71.91-77.34°).

For the triphenyl phosphine complex, the data recorded corresponds to the monoclinic polymorph of this substance which has been reported in the Cambridge Structural Database a number of times as refcodes: DEWJUK, DEWJUK8-DEWJUK17 and DEWJUK20. There is also a cubic polymorph which has been reported (DEWJUK1-DEWJUK7, DEWJUK18-DEWJUK19, DEWJUK21-DEWJUK28).



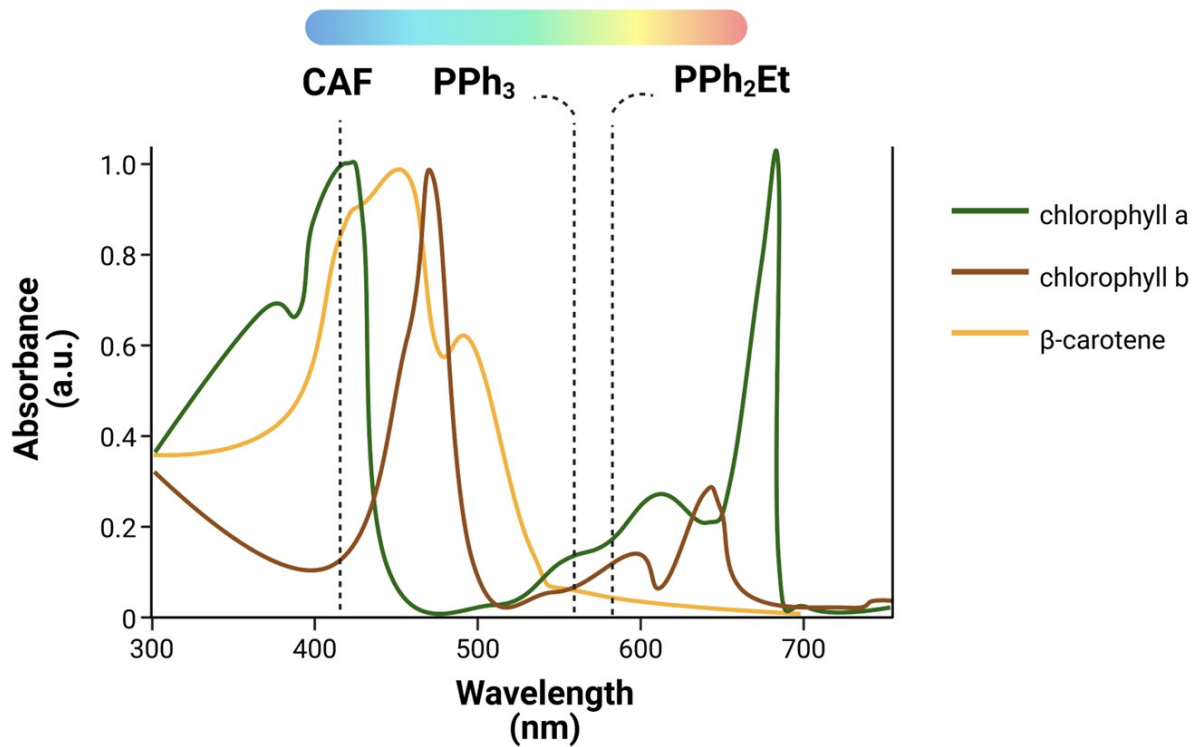
**Supplementary Figure 1.** Fluorescence emission spectrum of Cu-CNAS in solution at 333nm excitation.



**Supplementary Figure 2.** Photographs of solid samples of [Cu<sub>4</sub>I<sub>4</sub>(PPh<sub>2</sub>Et)<sub>4</sub>] (left) and their emission under 365 nm UV excitation (right).



**Supplementary Figure 3.** Indirect trial setup at AutoPotUK. Back left is the modified chamber using CA/Cu-CNA, back right is the control using the original Autopot polypropylene chamber, front left is the  $[\text{Cu}_4\text{I}_4(\text{PPh}_2\text{Et})_4]$  coating and front right is the  $[\text{Cu}_4\text{I}_4(\text{PPh}_3)_4]$  coating.



**Supplementary Figure 4.** Spectral overlap between copper-based composite emission maxima and photosynthetic pigment absorption profiles. Vertical dashed lines indicate the peak emission wavelengths for the developed spectral-converting materials: CAF (410 nm), PPh<sub>3</sub> (570 nm), and PPh<sub>2</sub>Et (585 nm).

Chlorophyll and Carotenoid quantification, adapted from Patricio et al.<sup>1</sup>

$$\text{Eq.1} \quad \text{Chlorophyll A} \left( \frac{\text{mg}}{\text{L}} \right) = 12.7 \times OD_{663} - 2.69 \times OD_{645}$$

$$\text{Eq.2} \quad \text{Chlorophyll B} \left( \frac{\text{mg}}{\text{L}} \right) = 22.9 \times OD_{645} - 4.86 \times OD_{663}$$

$$\text{Eq.3} \quad \text{Total Chlorophyll} \left( \frac{\text{mg}}{\text{L}} \right) = 8.02 \times OD_{663} + 20.20 \times OD_{645}$$

$$\text{Eq.4} \quad \text{Carotenoids} \left( \frac{\text{mg}}{\text{L}} \right) = 4.7 \times OD_{440} - 0.27 \times (\text{Total Chlorophyll})$$

## References

1. M. Pérez-Patricio, J. Camas-Anzueto, A. Sanchez-Alegría, A. Aguilar-González, F. Gutiérrez-Miceli, E. Escobar-Gómez, Y. Voisin, C. Rios-Rojas and R. Grajales-Coutiño, *Sensors*, 2018, **18**, 650.DOI:10.3390/s18020650.