A rare structural motif for a luminescent Cu(I) coordination polymer with 3-(pyridin-2-yl)triimidazotriazine

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SUPPORTING INFORMATION

Table S1 Crystal data, data collection and refinement details for **1**.

	1
Crystal data	
Chemical formula	$C_{14}H_9Cu_2I_2N_7$
M_r [g mol^{-1}]	656.16
Crystal system	monoclinic
Space group	*P21/n* (No. 14)
Temperature [K]	293(2)
a [Å]	4.2715(4)
b [Å]	18.1144(19)
c [Å]	21.199(2)
β [°]	94.098(2)
V [Å^3]	1636.1(3)
Z	4
μ(Mo *K*α) [mm^{-1}]	6.387
Crystal size [mm]	0.200 × 0.040 × 0.020
Data collection	
T_{min}, T_{max}	0.743, 0.880
No. of measured reflections	20443
No. of independent reflections	3303
No. of observed reflections [$I > 2\sigma(I)$]	2422
R_{int}	0.0720
R_σ	0.0550
$(\sin\theta/\lambda)_{max}$ [Å^{-1}]	0.600
Refinement	
$R[F^2 > 2\sigma(F^2)]$	0.0431
$wR(F^2)$	0.0704
S	1.081
No. of reflections	3303
No. of parameters	226
No. of restraints	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (*e* Å^{-3})	0.126, –0.869

Table S2 Selected bond distances [Å] and angles [°] for coordination network **1**.

1			
Cu1–N1	2.028(5)	Cu2–N3	2.075(5)
Cu1–I1	2.7555(9)	Cu2–N7	2.059(5)
Cu1–I1#1	2.6185(10)	Cu2–I2	2.6400(9)
Cu1–I1#2	2.6501(10)	Cu2–I2#4	2.5439(9)
N1–Cu1–I1	102.45(14)	N7–Cu2–N3	95.8(2)
N1–Cu1–I1#1	112.64(14)	N7–Cu2–I2#4	119.34(15)
N1–Cu1–I1#2	115.58(14)	N3–Cu2–I2#4	114.19(14)
I1#1–Cu1–I1#2	116.76(3)	N7–Cu2–I2	114.03(14)
I1#1–Cu1–I1	105.25(3)	N7–Cu2–I2	114.03(14)
I1#2–Cu1–I1	101.71(3)	I2#4–Cu2–I2	110.96(3)

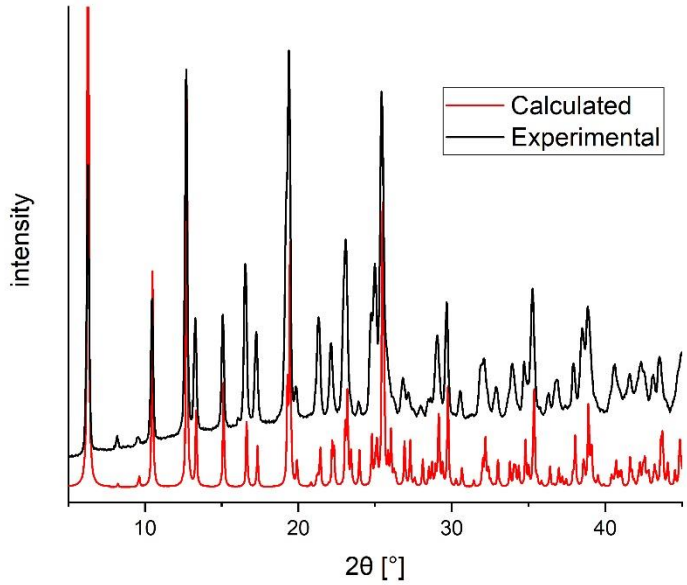


Figure S1. Simulated and experimental XRPD patterns of **1**.

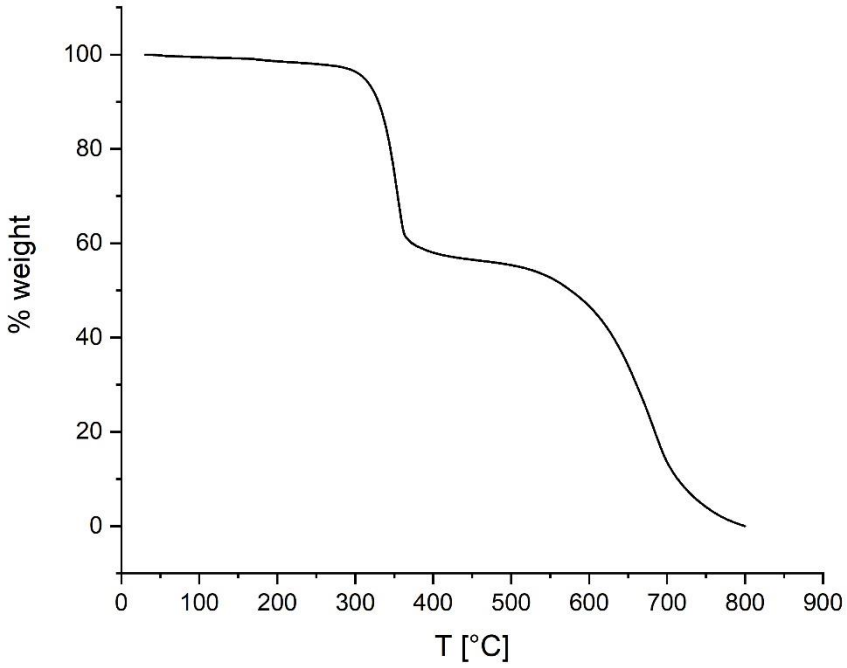


Figure S2. TGA analysis of **1**.

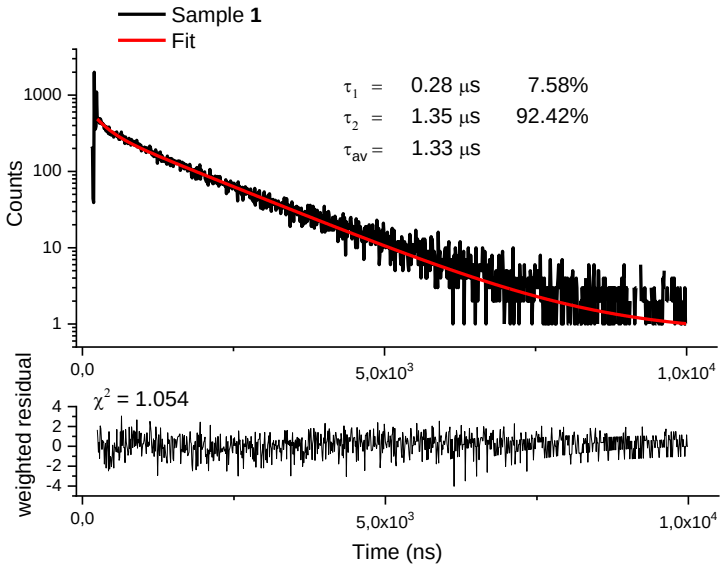


Figure S3. Lifetime measurement (λ_{exc} = 374 nm, λ_{em} = 588 nm) of **1** microcrystalline powders at 298 K.

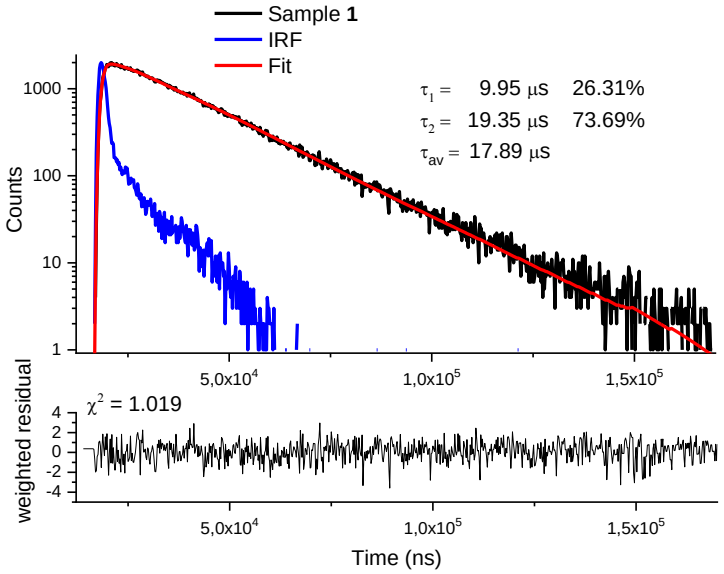


Figure S4. Lifetime measurement (λ_{exc} = 374 nm, λ_{em} = 580 nm) of **1** microcrystalline powders at 77 K.

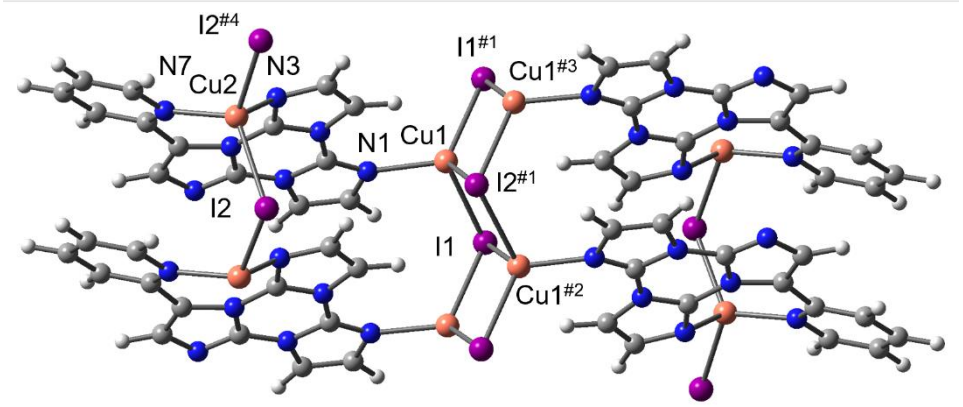
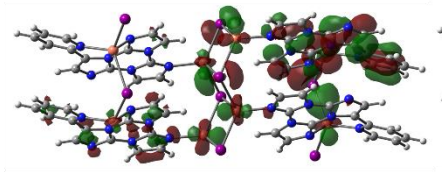


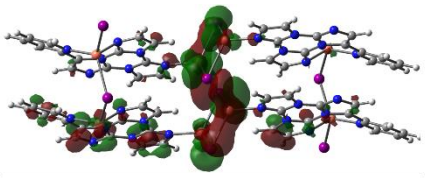
Figure S5. Model compound of **[Cu_2I_2(TT-Py)]$_n$** with labelling scheme.

Table S3 Selected optimized bond distances [Å] for the model compound of **[Cu_2I_2(TT-Py)]$_n$** (in parentheses the corresponding X-ray values).

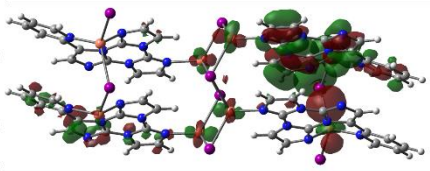
Cu1–Cu1$^{\#3}$	2.783 [2.762(1)]	Cu2–N3	2.100 [2.075(5)]
Cu1–Cu1$^{\#2}$	3.529 [3.413(1)]	Cu2–N7	2.094 [2.059(5)]
Cu1–N1	2.121 [2.028(5)]	Cu2–I2	2.830 [2.640(1)]
Cu1–I1	2.784 [2.755(1)]	Cu2–I2#4	2.594 [2.544(1)]
Cu1–I1$^{\#1}$	2.610 [2.618(1)]		
Cu1–I1$^{\#2}$	2.661 [2.650(1)]		



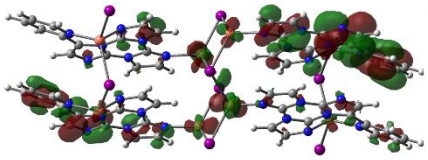
HOMO – 41 (MO 571)



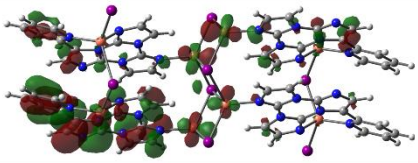
HOMO – 40 (MO 572)



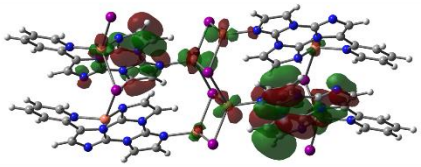
HOMO – 39 (MO 573)



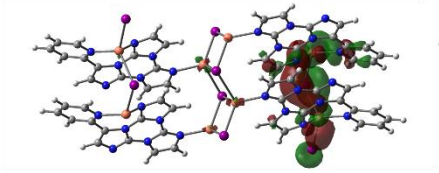
HOMO – 38 (MO 574)



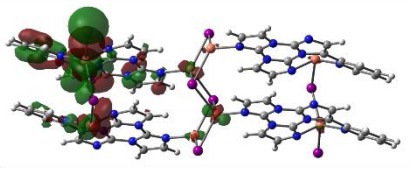
HOMO – 37 (MO 575)



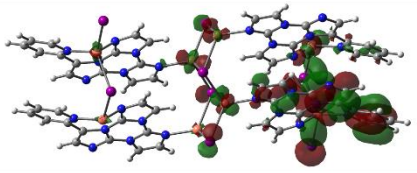
HOMO – 33 (MO 579)



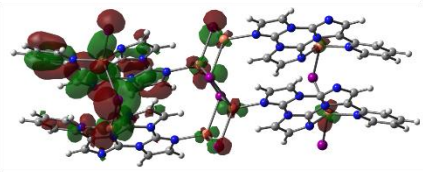
HOMO – 32 (MO 580)



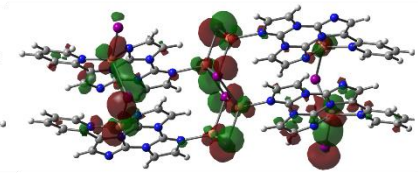
HOMO – 31 (MO 581)



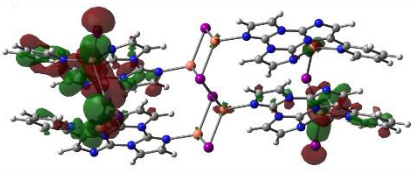
HOMO – 30 (MO 582)



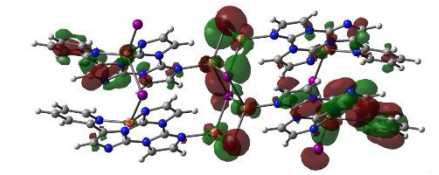
HOMO – 29 (MO 583)



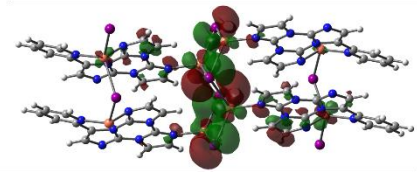
HOMO – 28 (MO 584)



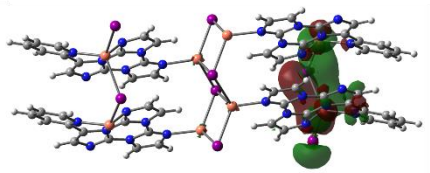
HOMO – 27 (MO 585)



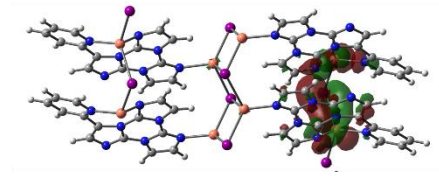
HOMO – 26 (MO 586)



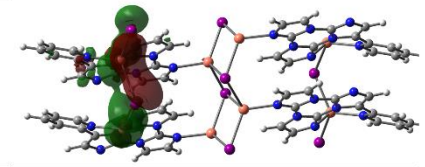
HOMO – 25 (MO 587)



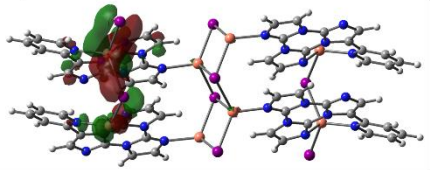
HOMO – 24 (MO 588)



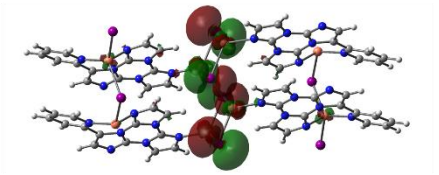
HOMO – 23 (MO 589)



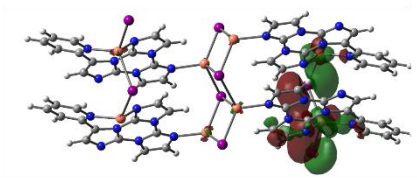
HOMO –22 (MO 590)



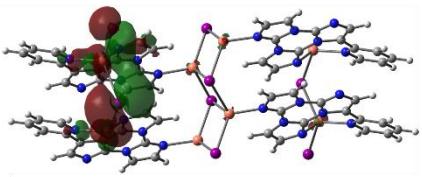
HOMO – 21 (MO 591)



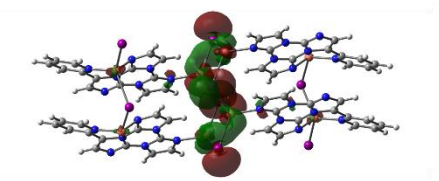
HOMO – 20 (MO 592)



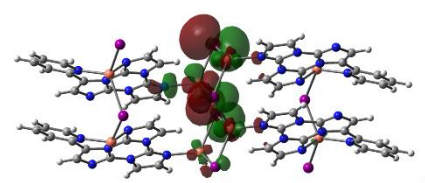
HOMO – 19 (MO 593)



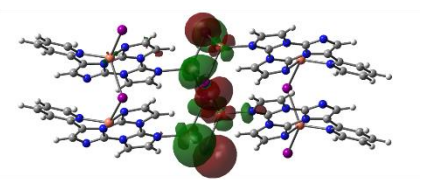
HOMO – 18 (MO 594)



HOMO – 17 (MO 595)



HOMO – 16 (MO 596)



HOMO – 15 (MO 597)

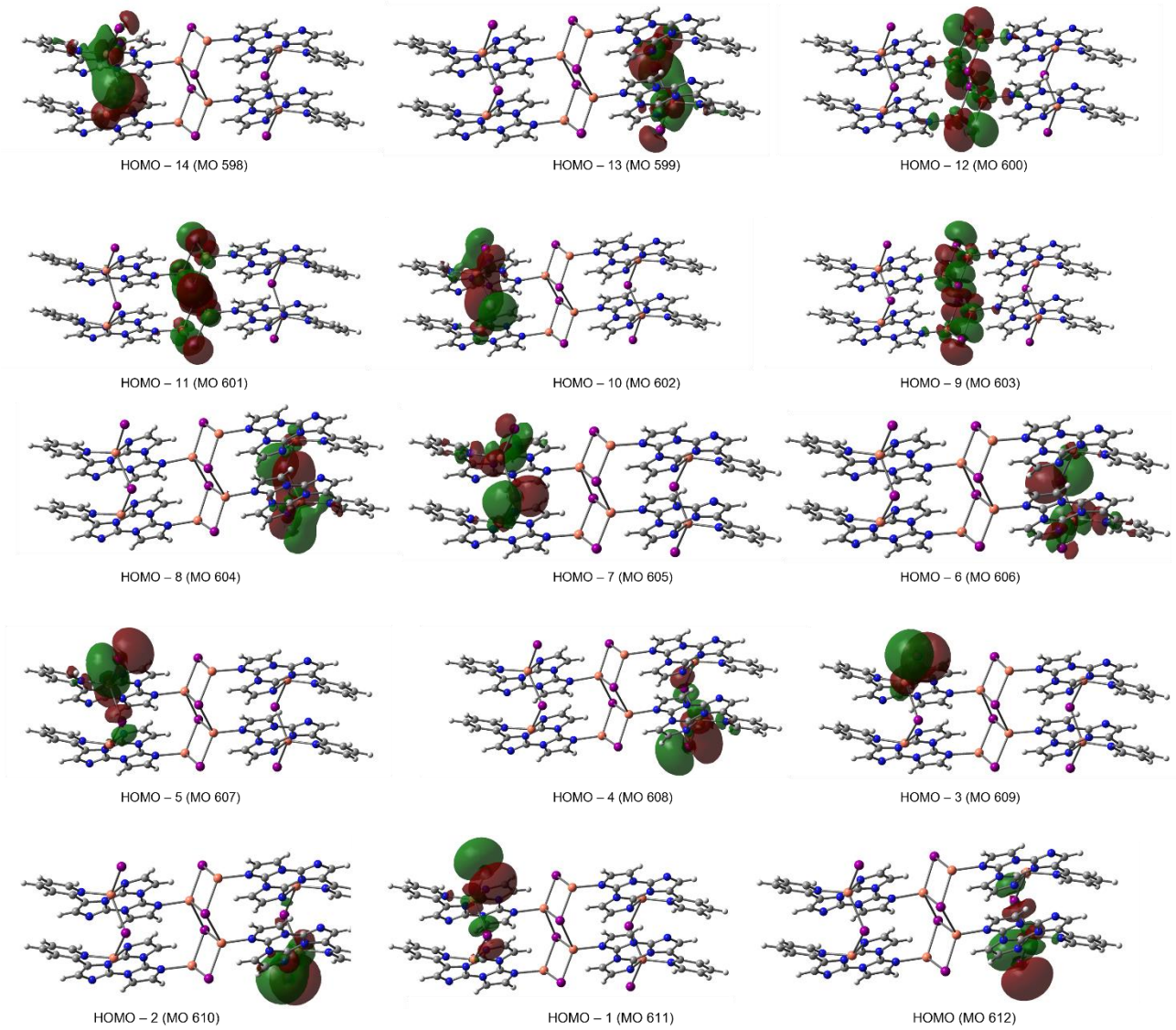


Figure S6. Plots of the ωB97X/6-311++G(d,p) HOMOs mainly involved in the lowest energy singlet transitions of the model compound of **[Cu_2I_2(TT-Py)]$_n$** (Isosurfaces value 0.02).

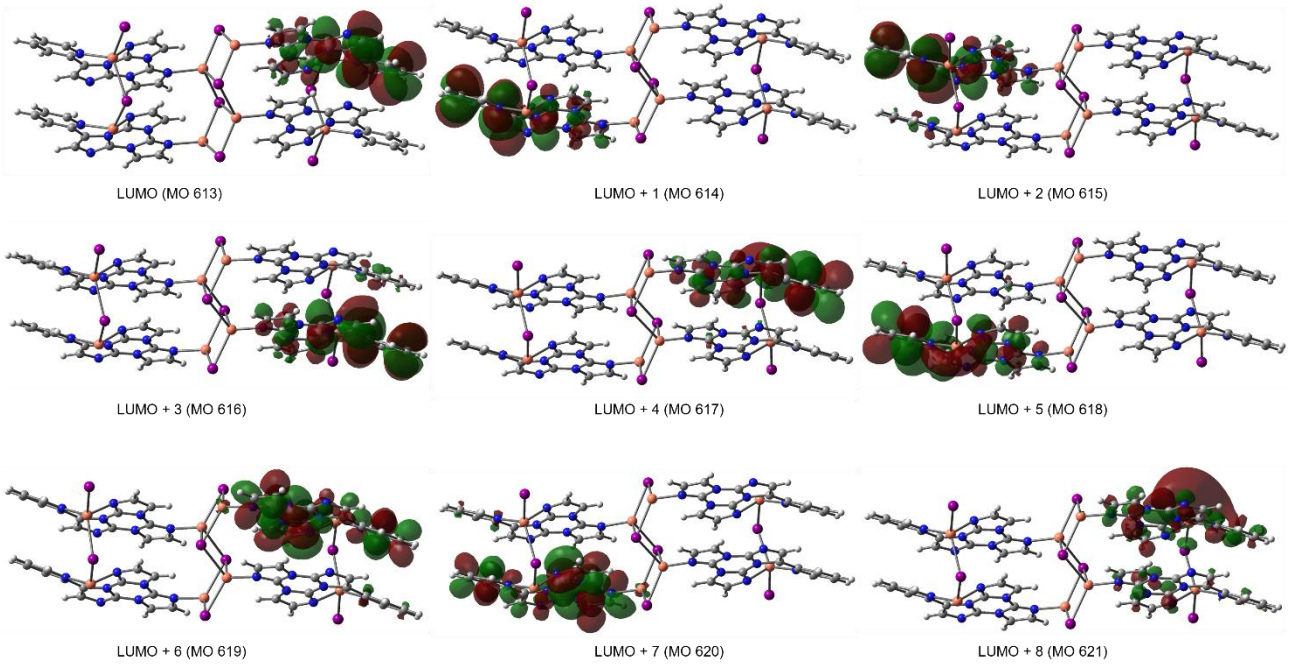


Figure S7. Plots of the ωB97X/6-311++G(d,p) HOMOs mainly involved in the lowest energy singlet transitions of the model compound of **[Cu_2I_2(TT-Py)]**$_n$ (Isosurfaces value 0.02).

Table S4 First TD-ωB97X/6-311++G(d,p) $S_0 \rightarrow S_n$ transitions computed for the optimized geometry of the model compound of **[Cu_2I_2(TT-Py)]**$_n$.

```
Excited State   1:      Singlet-A      3.3288 eV  372.46 nm  f=0.0073  <S**2>=0.000
     593 -> 616        0.13367
     604 -> 616        0.13546
     606 -> 616       -0.29873
     610 -> 616        0.30632
     612 -> 616        0.39031

 Excited State   2:      Singlet-A      3.3434 eV  370.83 nm  f=0.0042  <S**2>=0.000
     594 -> 615        0.13934
     598 -> 615       -0.14990
     605 -> 615        0.34113
     609 -> 615        0.39130
     611 -> 615        0.28786

 Excited State   3:      Singlet-A      3.3703 eV  367.88 nm  f=0.0063  <S**2>=0.000
     580 -> 617        0.13865
     580 -> 621        0.16013
     589 -> 613       -0.11317
     589 -> 617       -0.17740
     589 -> 621       -0.20684
     599 -> 617       -0.13567
     599 -> 621       -0.15665

 Excited State   4:      Singlet-A      3.4531 eV  359.05 nm  f=0.0071  <S**2>=0.000
     606 -> 616       -0.18922
     608 -> 613        0.10372
     608 -> 616        0.52345
     608 -> 627        0.13216
     610 -> 616       -0.24571

 Excited State   5:      Singlet-A      3.4698 eV  357.33 nm  f=0.0062  <S**2>=0.000
     581 -> 615        0.10149
     605 -> 615        0.11288
     607 -> 614        0.12502
     607 -> 615        0.48623
     609 -> 615       -0.21291
     611 -> 615        0.12400
```

```
Excited State   6:      Singlet-A      3.4852 eV  355.74 nm  f=0.0062  <S**2>=0.000
     591 -> 618       -0.11019
     591 -> 622        0.10372
     598 -> 614        0.12973
     598 -> 618        0.15453
     598 -> 622       -0.14646
     598 -> 646       -0.10664
     605 -> 614        0.11088
     605 -> 618        0.10820
     605 -> 622       -0.10355
     607 -> 615        0.22944
     609 -> 615       -0.13479

Excited State   7:      Singlet-A      3.5756 eV  346.75 nm  f=0.0042  <S**2>=0.000
     604 -> 616        0.20274
     606 -> 616        0.26658
     610 -> 616       -0.32439
     612 -> 613        0.11269
     612 -> 616        0.42209

Excited State   8:      Singlet-A      3.6267 eV  341.87 nm  f=0.0021  <S**2>=0.000
     545 -> 621       -0.13155
     580 -> 621        0.11901
     588 -> 617       -0.12984
     588 -> 621       -0.15788
     593 -> 617       -0.11330
     593 -> 621       -0.13397
     604 -> 613        0.11040
     604 -> 617        0.13262
     604 -> 621        0.14756

Excited State   9:      Singlet-A      3.6420 eV  340.43 nm  f=0.0034  <S**2>=0.000
     602 -> 615       -0.16889
     605 -> 615       -0.20476
     607 -> 615       -0.18295
     609 -> 615       -0.20111
     611 -> 614        0.13015
     611 -> 615        0.49425

Excited State  10:      Singlet-A      3.7911 eV  327.04 nm  f=0.0008  <S**2>=0.000
     590 -> 618        0.11673
     590 -> 622       -0.11928
     594 -> 614       -0.16082
     594 -> 618       -0.15422
     594 -> 622        0.14658
     594 -> 646        0.10365
     602 -> 614       -0.16140
     602 -> 618       -0.15403
     602 -> 622        0.13892
     605 -> 614        0.11083

Excited State  11:      Singlet-A      3.8067 eV  325.70 nm  f=0.0027  <S**2>=0.000
     599 -> 613       -0.11847
     608 -> 613       -0.25119
     610 -> 613        0.23715
     612 -> 613        0.46846
     612 -> 616       -0.10046
     612 -> 617        0.10071

Excited State  12:      Singlet-A      3.9087 eV  317.20 nm  f=0.0042  <S**2>=0.000
     583 -> 614        0.12142
     591 -> 614       -0.12509
     598 -> 614        0.17506
     605 -> 614        0.12074
     607 -> 614       -0.29027
     609 -> 614        0.24697
     611 -> 614        0.34073
```

Table S5 First TD-ωB97X/6-311++G(d,p) $T_0 \rightarrow T_n$ transitions computed for the optimized geometry of the model compound of **[Cu_2I_2(TT-Py)]$_n$**.

```
Excited State   1:      Triplet-A      3.0016 eV  413.06 nm  f=nd      <S**2>=2.000
     568 -> 614       -0.11137
```

```
    571 -> 614        0.10473
    572 -> 614       -0.17011
    573 -> 614        0.14872
    574 -> 614       -0.21666
    575 -> 614       -0.35222
    575 -> 618        0.11428
    583 -> 614       -0.13154
    586 -> 614        0.11015

Excited State   2:      Triplet-A      3.0150 eV  411.23 nm  f=nd      <S**2>=2.000
    566 -> 613        0.12472
    571 -> 613        0.22845
    573 -> 613        0.15975
    574 -> 613        0.35952
    574 -> 617       -0.11000
    575 -> 613       -0.11232
    582 -> 613       -0.11841
    586 -> 613        0.15458

Excited State   3:      Triplet-A      3.0192 eV  410.66 nm  f=nd      <S**2>=2.000
    537 -> 616        0.10263
    574 -> 613       -0.12194
    582 -> 616       -0.24607
    584 -> 616        0.12564
    585 -> 616        0.15461
    586 -> 616        0.28273
    588 -> 616        0.11689
    589 -> 616        0.10920
    610 -> 616       -0.17245
    612 -> 616       -0.15059

Excited State   4:      Triplet-A      3.0248 eV  409.90 nm  f=nd      <S**2>=2.000
    535 -> 615       -0.10149
    575 -> 615        0.11459
    581 -> 615       -0.19928
    583 -> 615       -0.27521
    585 -> 615       -0.25189
    586 -> 615        0.18266
    590 -> 615       -0.13231
    591 -> 615        0.12075
    607 -> 615        0.10706
    609 -> 615       -0.16188

Excited State   5:      Triplet-A      3.1485 eV  393.79 nm  f=nd      <S**2>=2.000
    580 -> 617        0.15110
    580 -> 621        0.17639
    589 -> 613       -0.10336
    589 -> 617       -0.17836
    589 -> 621       -0.21405
    599 -> 617       -0.13033
    599 -> 621       -0.15727

Excited State   6:      Triplet-A      3.2160 eV  385.52 nm  f=nd      <S**2>=2.000
    588 -> 616       -0.10346
    593 -> 616       -0.14773
    599 -> 616       -0.10262
    604 -> 616       -0.14239
    606 -> 616        0.38230
    606 -> 627        0.12552
    608 -> 616       -0.16776
    610 -> 616       -0.19374
    612 -> 616       -0.29060

Excited State   7:      Triplet-A      3.2179 eV  385.30 nm  f=nd      <S**2>=2.000
    594 -> 615        0.14896
    598 -> 615       -0.16289
    602 -> 615       -0.10127
    605 -> 615        0.37977
    605 -> 623        0.10492
    607 -> 615        0.12084
    609 -> 615        0.29411
    611 -> 615        0.25294

Excited State   8:      Triplet-A      3.2829 eV  377.66 nm  f=nd      <S**2>=2.000
    583 -> 618        0.10858
    583 -> 622       -0.10029
    585 -> 618       -0.10381
    591 -> 618       -0.12073
```

```
    591 -> 622        0.11822
    598 -> 614        0.11754
    598 -> 618        0.15859
    598 -> 622       -0.15929
    598 -> 646       -0.12079
    605 -> 618        0.10436

Excited State   9:      Triplet-A      3.3305 eV  372.27 nm  f=nd      <S**2>=2.000
    545 -> 621       -0.11898
    580 -> 617        0.11133
    580 -> 621        0.13164
    588 -> 617       -0.12902
    588 -> 621       -0.16098
    593 -> 617       -0.11014
    593 -> 621       -0.13400
    599 -> 621        0.10724
    604 -> 617        0.12617
    604 -> 621        0.14762

Excited State  10:      Triplet-A      3.3676 eV  368.17 nm  f=nd      <S**2>=2.000
    582 -> 616        0.23275
    606 -> 616       -0.13803
    608 -> 616        0.42544
    608 -> 627        0.11386
    610 -> 616       -0.22398
    612 -> 616       -0.22141

Excited State  11:      Triplet-A      3.4061 eV  364.01 nm  f=nd      <S**2>=2.000
    581 -> 615        0.22372
    607 -> 615        0.49178
    609 -> 615       -0.29702

Excited State  12:      Triplet-A      3.4975 eV  354.49 nm  f=nd      <S**2>=2.000
    599 -> 616        0.11172
    604 -> 616       -0.24057
    606 -> 616       -0.20118
    608 -> 616       -0.14884
    610 -> 616        0.35716
    612 -> 616       -0.32550

Excited State  13:      Triplet-A      3.5156 eV  352.67 nm  f=nd      <S**2>=2.000
    590 -> 618        0.11410
    590 -> 622       -0.12414
    594 -> 614       -0.12014
    594 -> 618       -0.14914
    594 -> 622        0.14664
    594 -> 646        0.11302
    602 -> 614       -0.11840
    602 -> 618       -0.14666
    602 -> 622        0.14137
    602 -> 646        0.10343

Excited State  14:      Triplet-A      3.5597 eV  348.30 nm  f=nd      <S**2>=2.000
    598 -> 615        0.11395
    602 -> 615       -0.23060
    605 -> 615       -0.17158
    609 -> 615       -0.20071
    611 -> 614        0.10029
    611 -> 615        0.44232

Excited State  15:      Triplet-A      3.7083 eV  334.35 nm  f=nd      <S**2>=2.000
    555 -> 617       -0.10357
    555 -> 621       -0.12349
    573 -> 617        0.10662
    580 -> 613        0.14654
    589 -> 613       -0.11302
    606 -> 621        0.10781
    608 -> 613       -0.11052
    612 -> 613        0.24268
```