Electronic Supplementary Information for

From Blue to White to Yellow Emitter: A Hexanuclear Copper Iodide Nanocluster

Ke Xu, Bu-Lin Chen, Rui Zhang, Li Liu*, Xin-Xin Zhong*, Lei Wang*, Feng-Yan Li*, Guang-Hua Li, Khalid A. Alamry, Fa-Bao Li, Wai-Yeung Wong*, Hai-Mei Qin

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Experimental Details

1. NMR Experiments

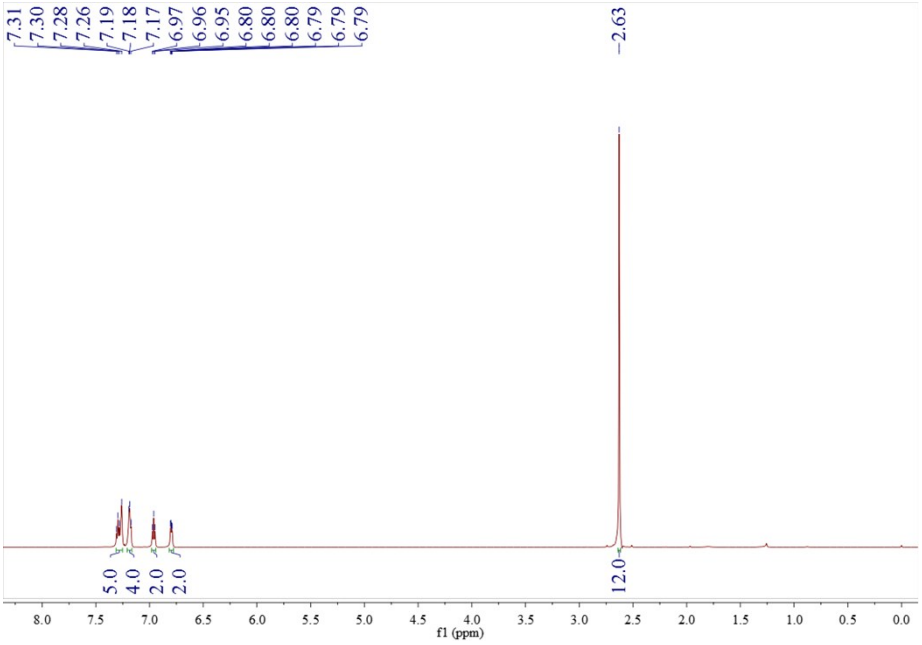


Fig. S1. ^{1}H NMR spectrum of ppda in $CDCl_3$.

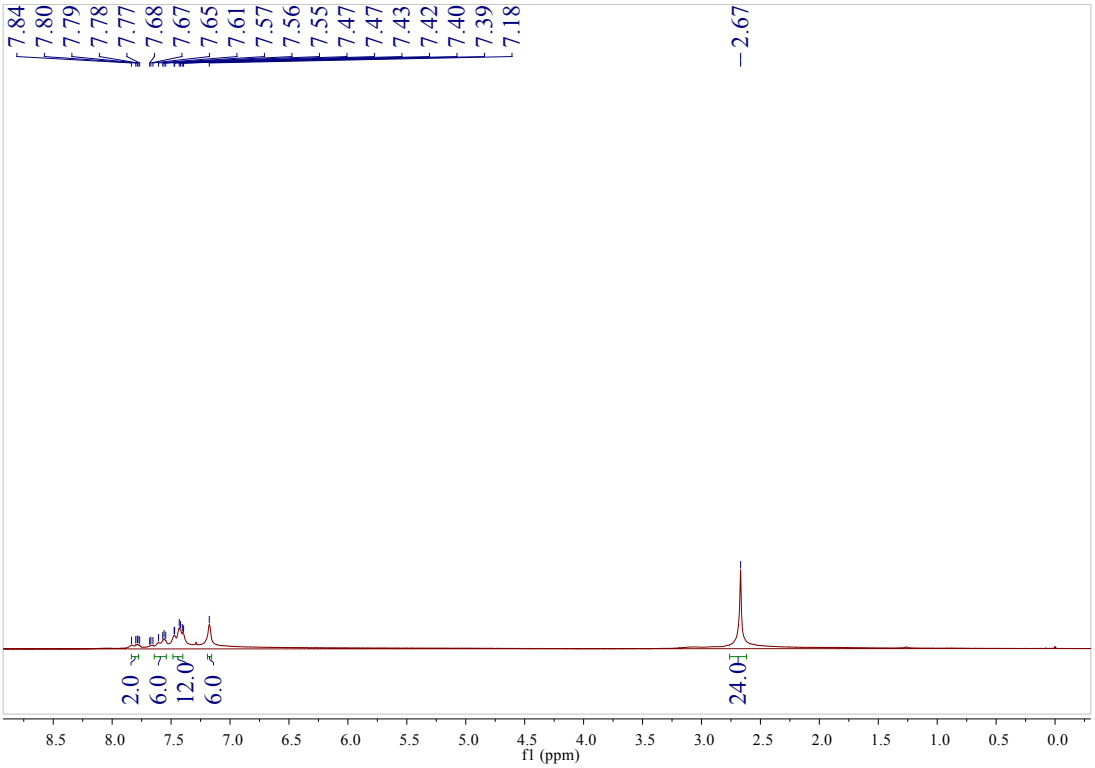


Fig. S2. ^{1}H NMR spectrum of $Cu_6I_6(ppda)_2$ in $CDCl_3$.

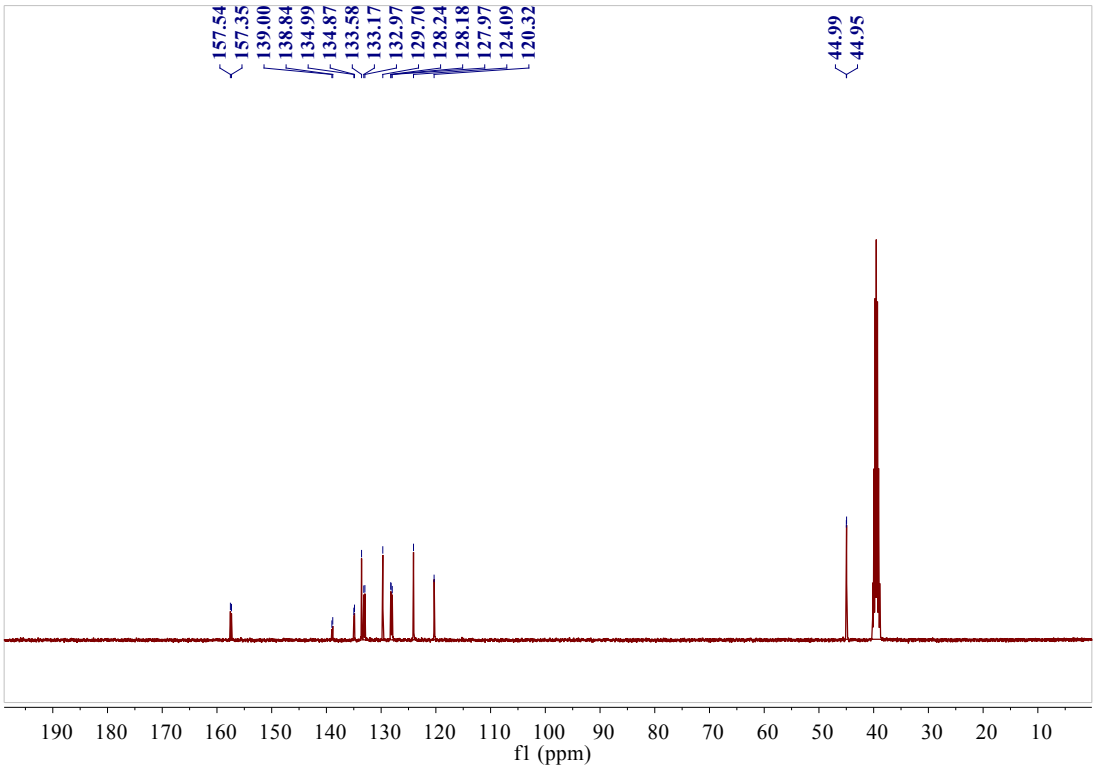


Fig. S3. ^{13}C NMR spectrum of ppda in d_6-DMSO.

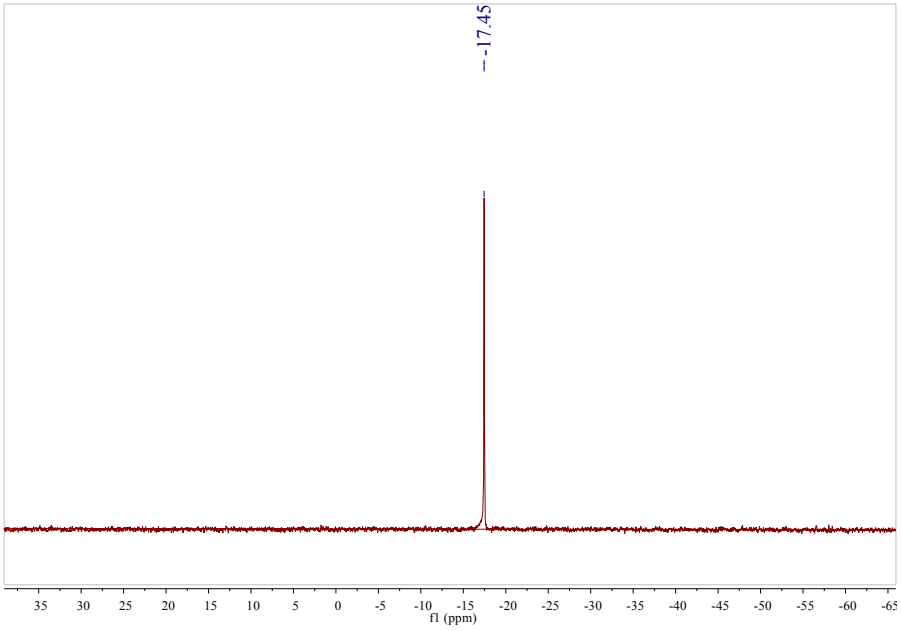


Fig. S4. ^{31}P NMR spectrum of ppda in $CDCl_3$.

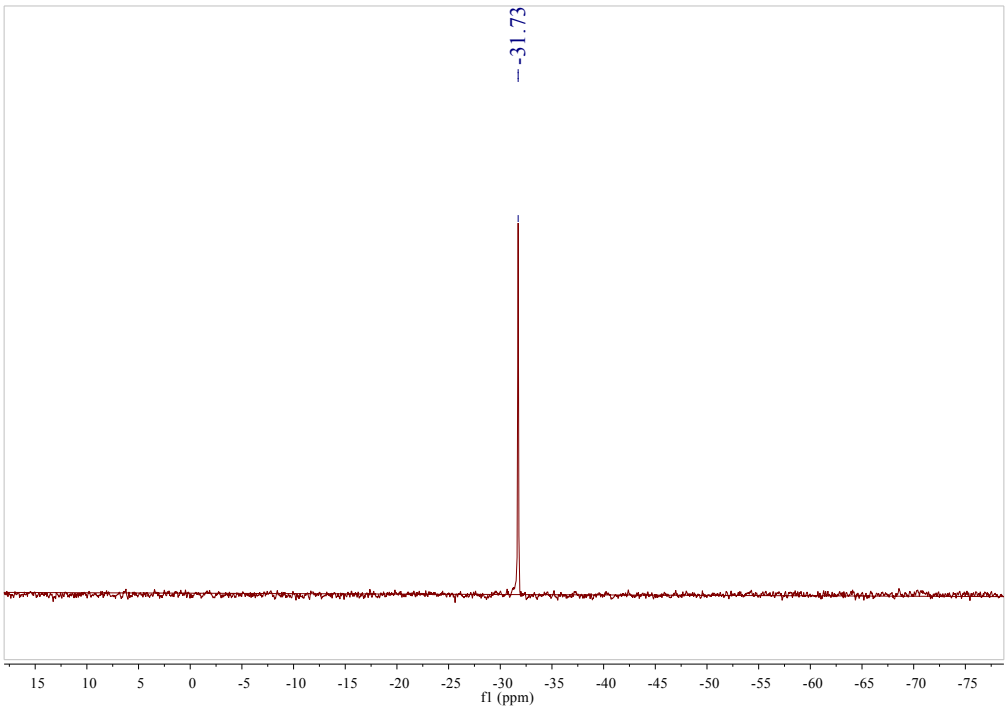


Fig. S5. ^{31}P NMR spectrum of $Cu_6I_6(ppda)_2$ in $CDCl_3$.

2. Molecular structures

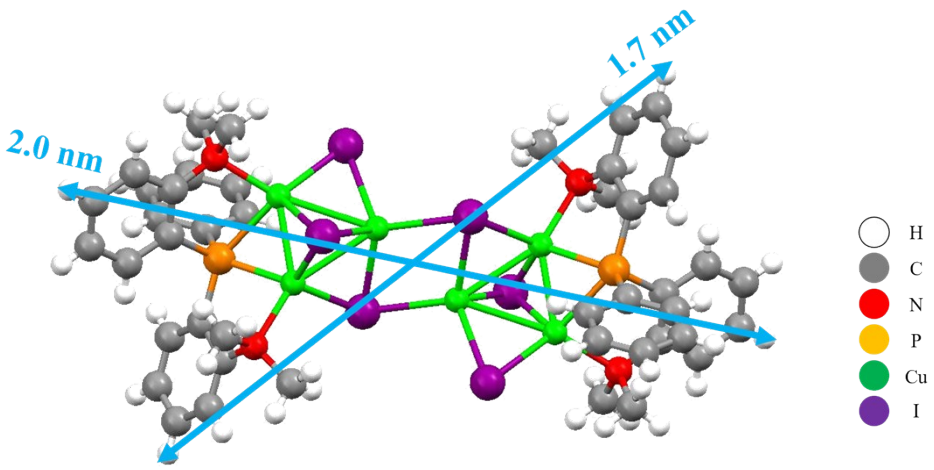


Fig. S6. ORTEP diagram of complex $[Cu_6I_6(ppda)_2]$.

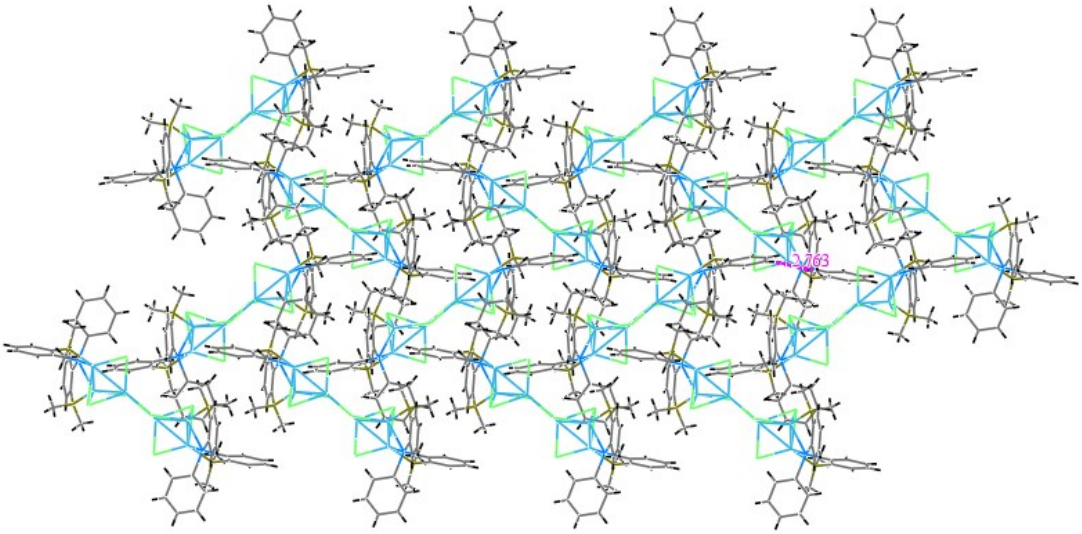


Fig. S7. 2-D sheet in the *ab* plane and C–H···π interactions in $[Cu_6I_6(ppda)_2]$.

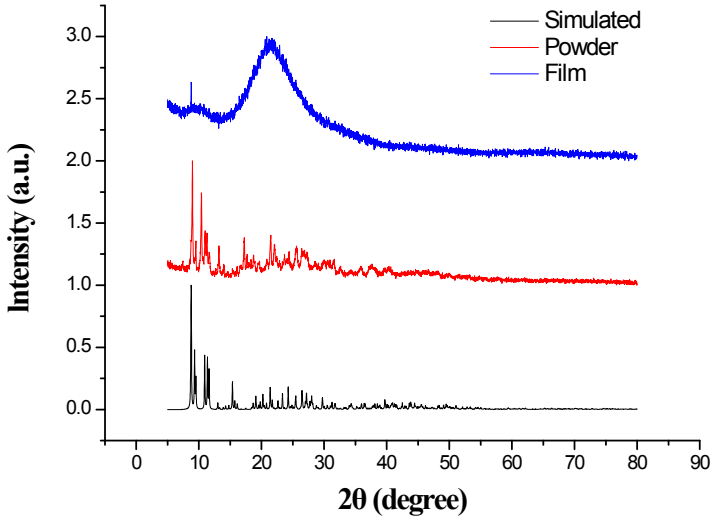


Fig. S8. PXRD profiles of powder and film samples of $[Cu_6I_6(ppda)_2]$ at 297 K.

3. Photophysical properties

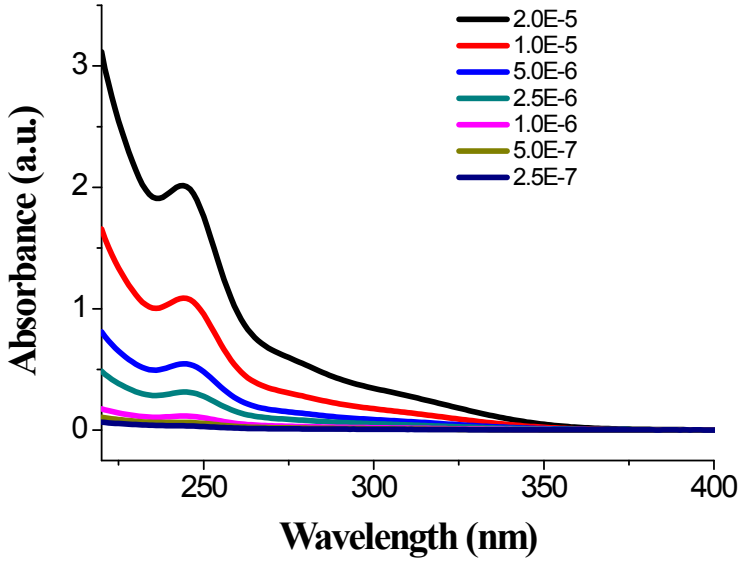
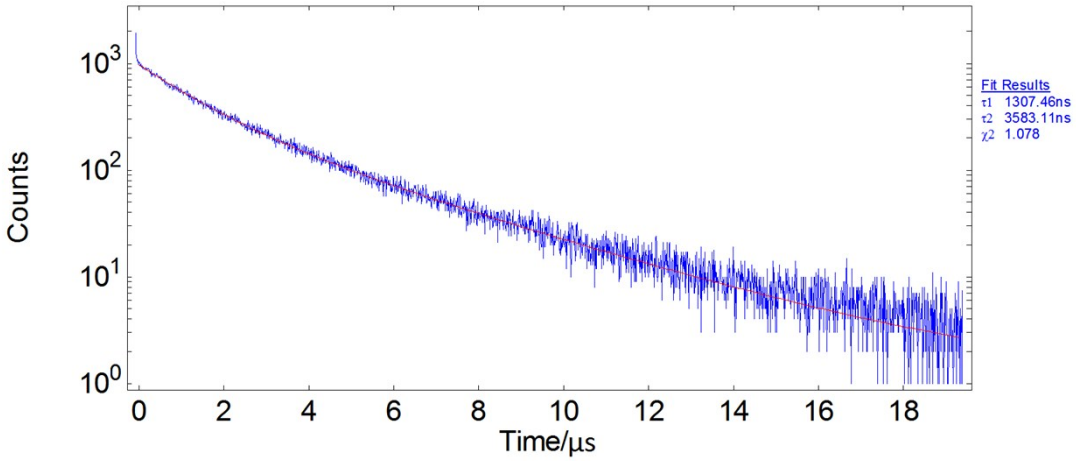


Fig. S9. The concentration dependence of the UV-Vis absorption spectra of complex $[Cu_6I_6(ppda)_2]$ in CH_3CN.



	Fix	Value / ns	Std. Dev / ns		Fix	Value	Std. Dev	Rel %
τ_1	☐	1307.4577	32.58369	B_1	☐	630.652	15.2575	40.16
τ_2	☐	3583.1076	75.07286	B_2	☐	342.860	16.8032	59.84
τ_3	☐			B_3	☐			
τ_4	☐			B_4	☐			
				A	☐	1.162		

χ^2 : 1.078

Fig. S10. Time profiles of luminescence decay and exponential fit spectrum of $[Cu_6I_6(ppda)_2]$ at 297 K with λ_{em}= 476 nm in crystal state.

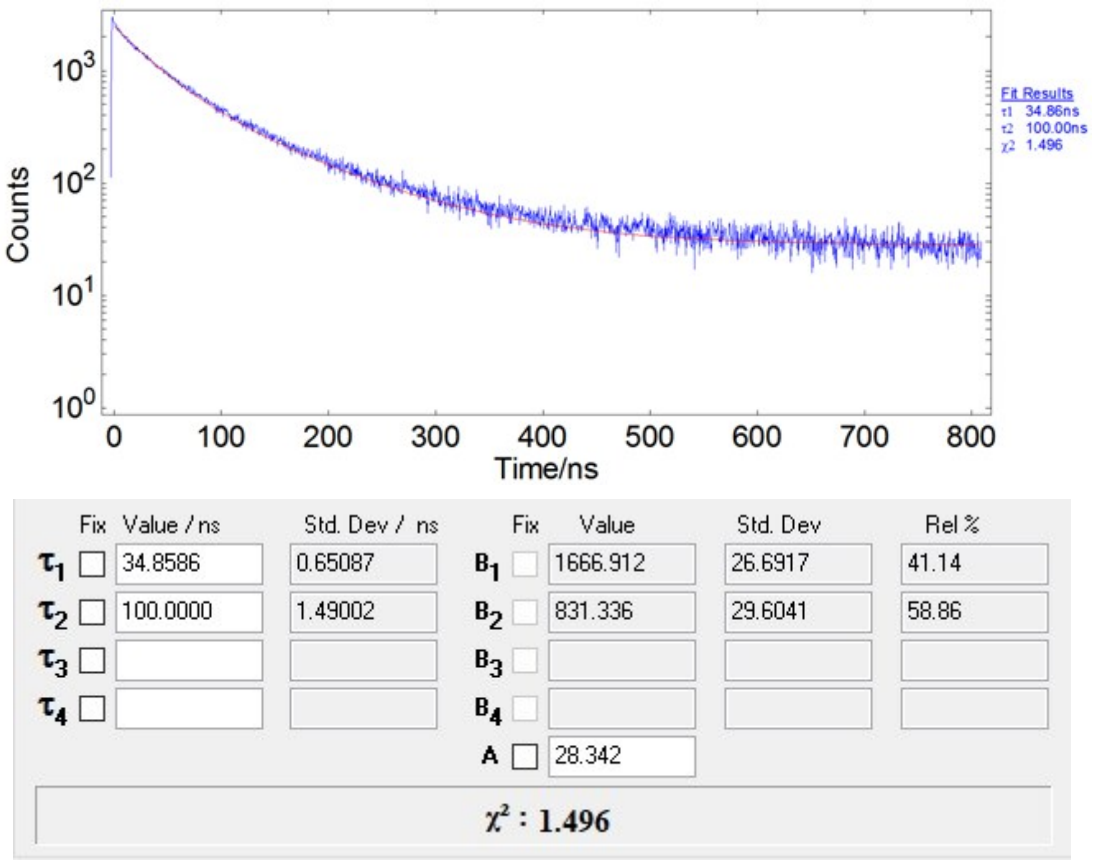
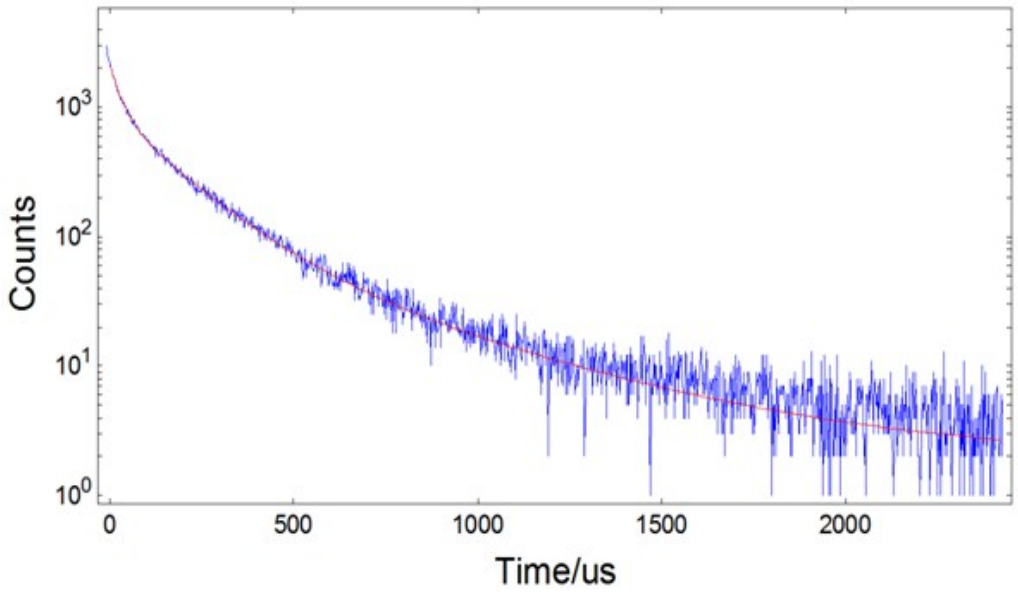


Fig. S11. Time profiles of luminescence decay and exponential fit spectrum of $[Cu_6I_6(ppda)_2]$ at 297 K with λ_{em}= 716 nm in crystal state.

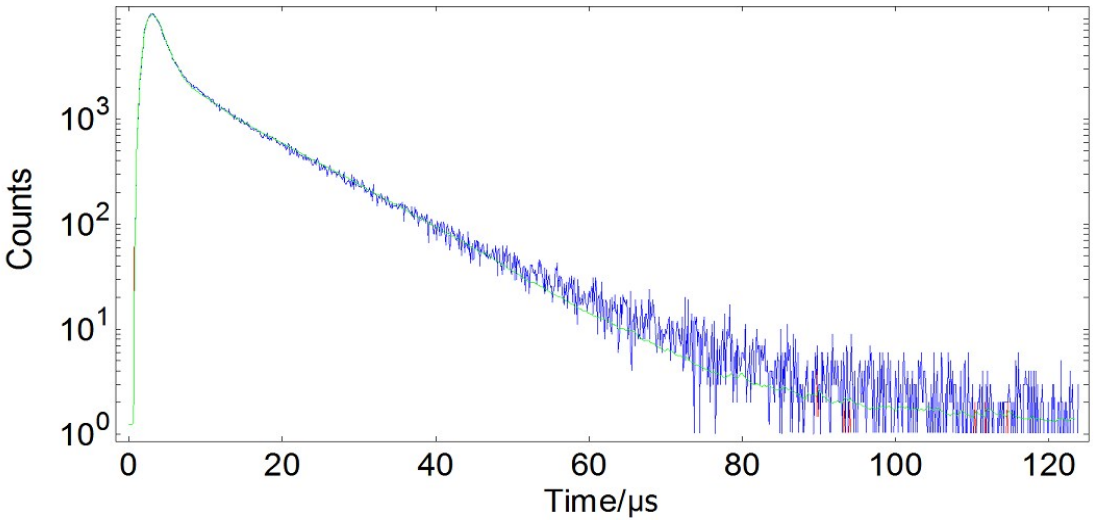


Fit = A + B1.exp(-t/T1) + B2.exp(-t/T2) + B3.exp(-t/T3)

	Value	Std Dev		Value	Std Dev	Rel %
T1	2.828E-5	1.053E-6	B1	1.300E+3	2.735E+1	16.84

T2	1.573E-4	5.384E-6	B2	8.150E+2	1.627E+1	58.72
T3	4.767E-4	3.292E-5	B3	1.119E+2	1.732E+1	24.43
	Chisq	1.295E+0		A	2.011E+0	

Fig. S12. Time profiles of luminescence decay and exponential fit spectrum of $[Cu_6I_6(ppda)_2]$ at 77 K with λ_{em}= 470 nm in crystal state.



	Fix	Value / ns	Std. Dev / ns		Fix	Value	Std. Dev	Rel %
τ_1	☐	1004.8705	7.46091	B_1	☐	0.117	0.0008	61.63
τ_2	☐	9940.2863	43.53249	B_2	☐	0.007	0.0001	38.37
τ_3	☐			B_3	☐			
τ_4	☐			B_4	☐			
δt	☐	-30.1418	3.1676	A	☐	1.233		

χ^2 : 1.812

Fig. S13. Time profiles of luminescence decay and exponential fit spectrum of $[Cu_6I_6(ppda)_2]$ at 297 K with λ_{em}= 535 nm in powder state.

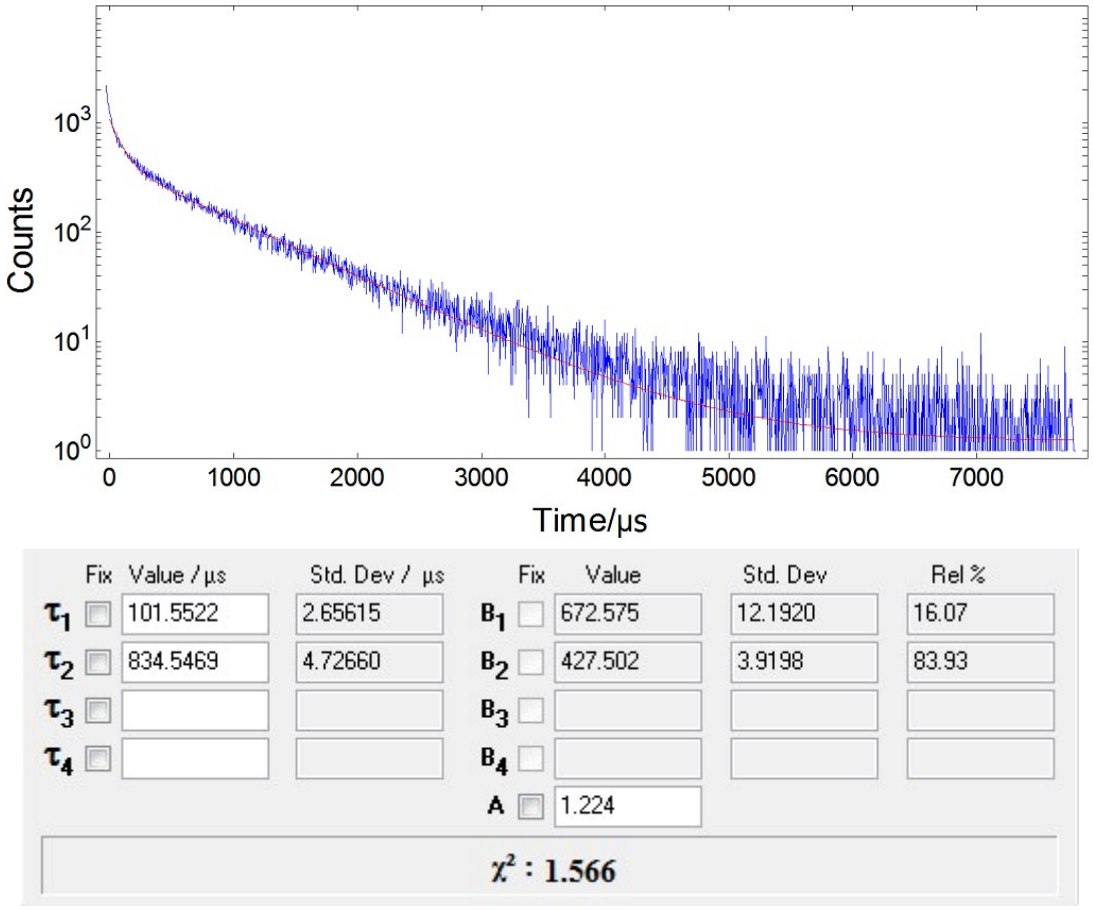


Fig. S14. Time profiles of luminescence decay and exponential fit spectrum of $[Cu_6I_6(ppda)_2]$ at 77 K with λ_{em}= 470 nm in powder state.

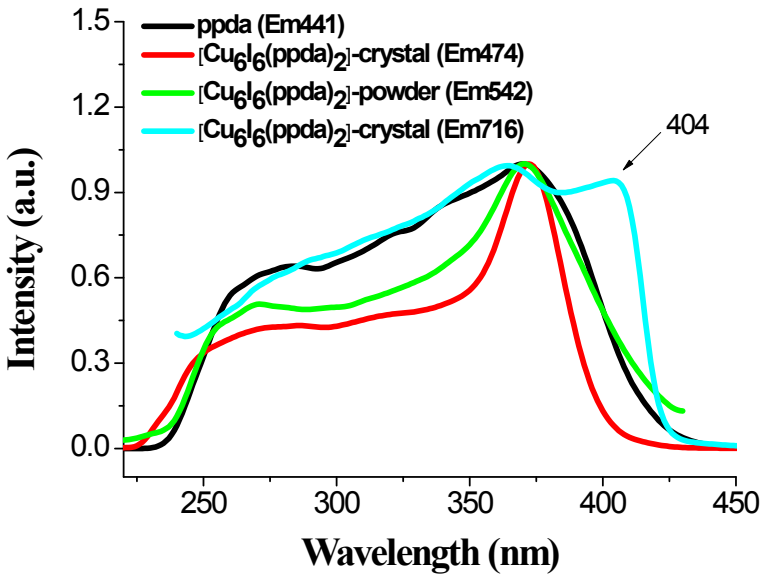


Fig. S15. Excitation spectra of ligand ppda and complex $[Cu_6I_6(ppda)_2]$ in crystal and powder states at 297 K.

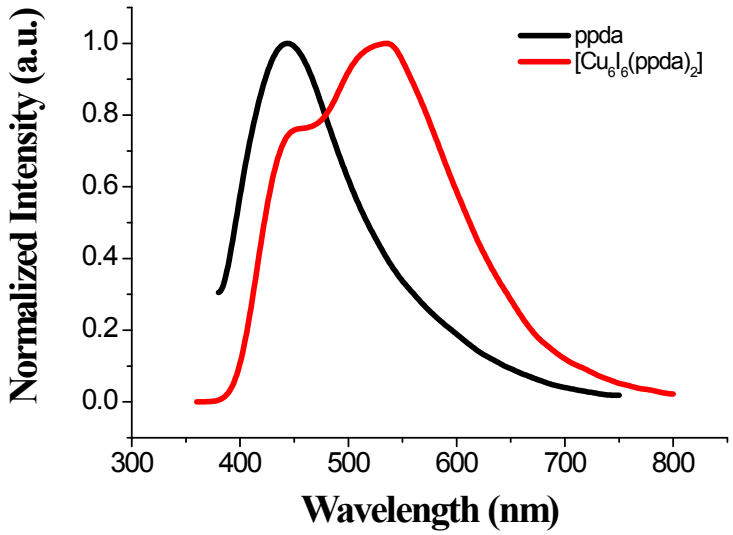


Fig. S16. Normalized emission spectra of ligand ppda and complex $[Cu_6I_6(ppda)_2]$ in powder state at 297 K (λ_{ex} = 370 nm).

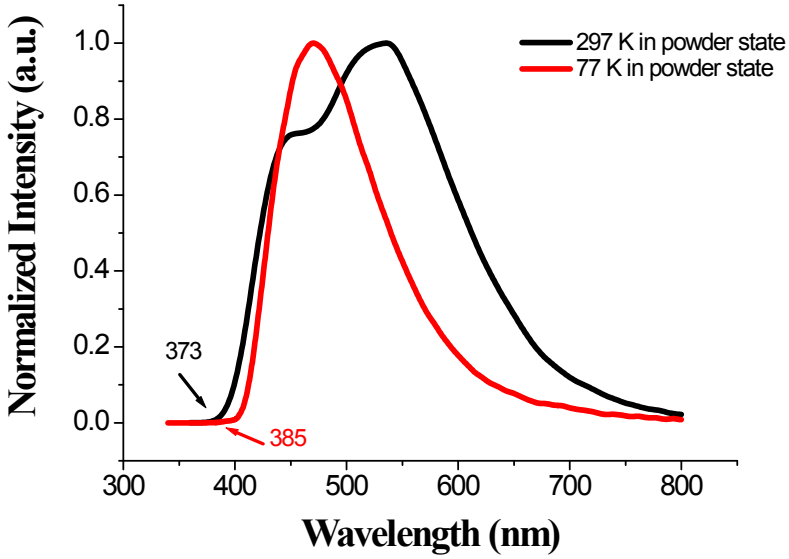


Fig. S17. Normalized emission spectra of $[Cu_6I_6(ppda)_2]$ in powder state at 297 K (λ_{ex} = 350 nm) and 77 K (λ_{ex} = 320 nm).

4. Computational details

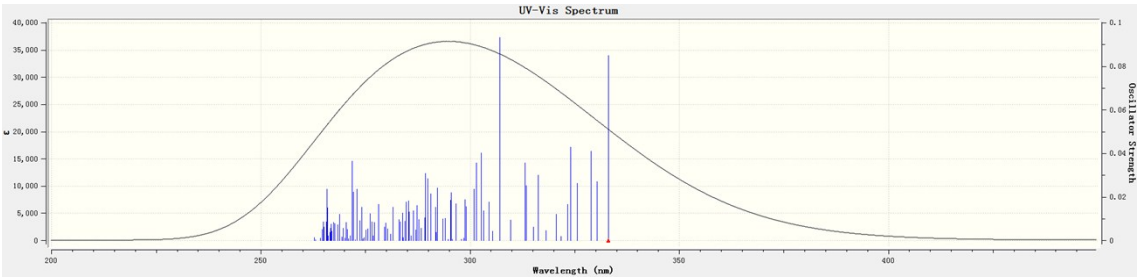
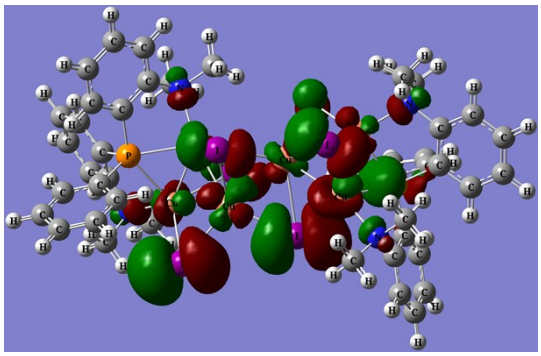
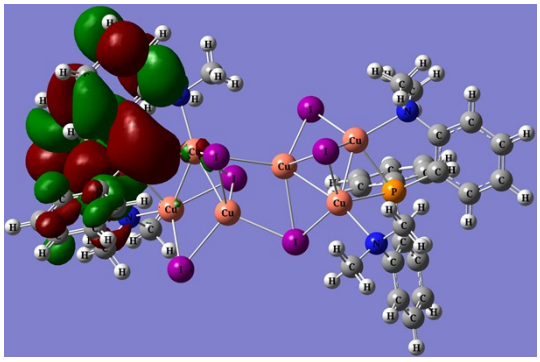


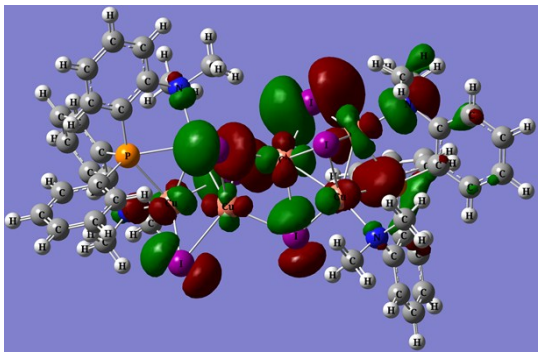
Fig. S18. The absorption spectrum of complex $[Cu_6I_6(ppda)_2]$ in CH_3CN.



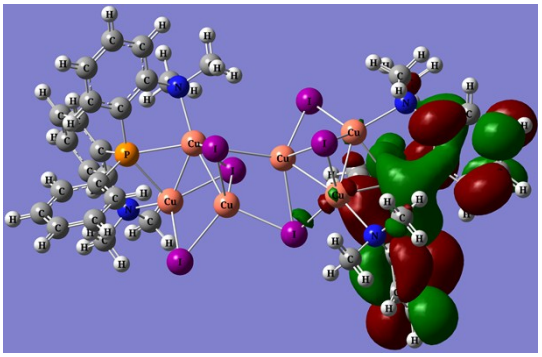
HOMO



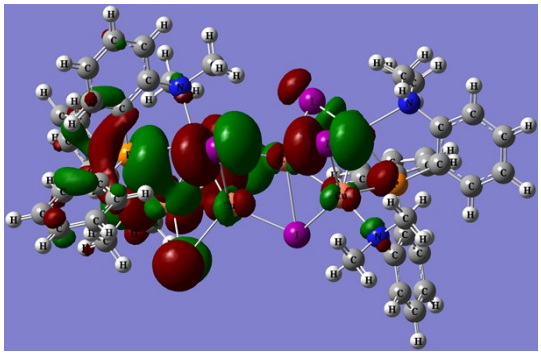
LUMO



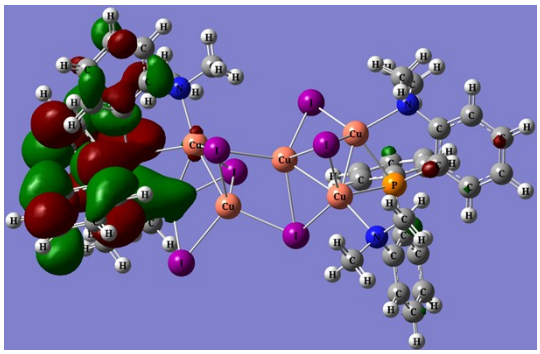
HOMO−1



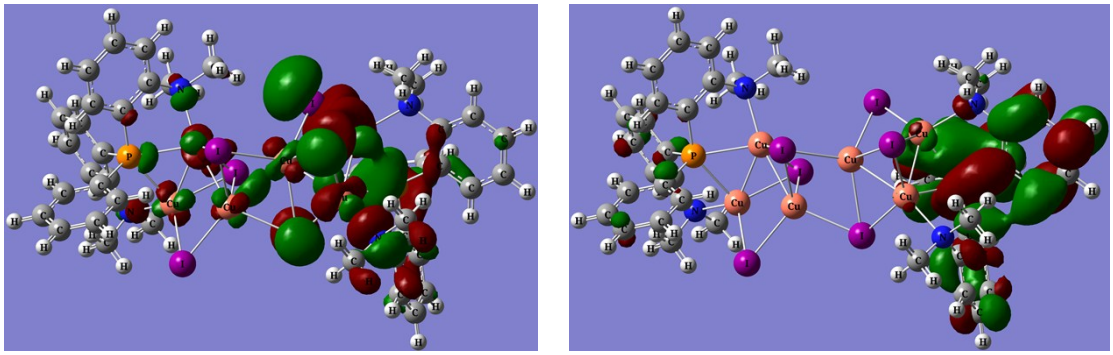
LUMO+1



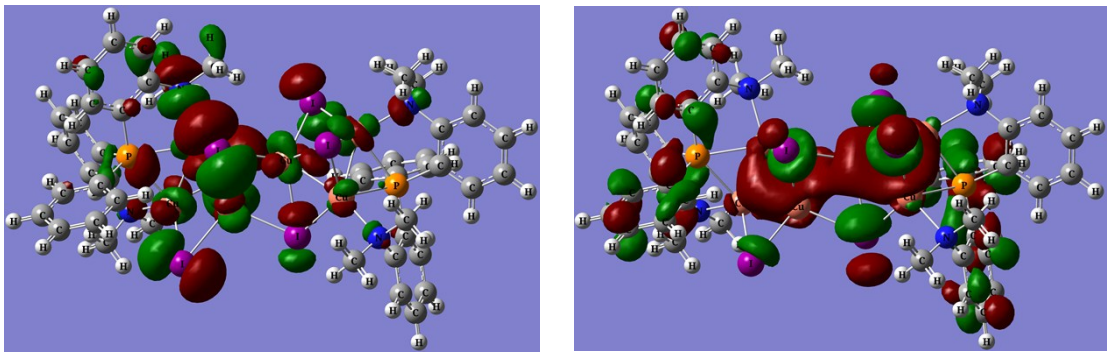
HOMO−2



LUMO+2

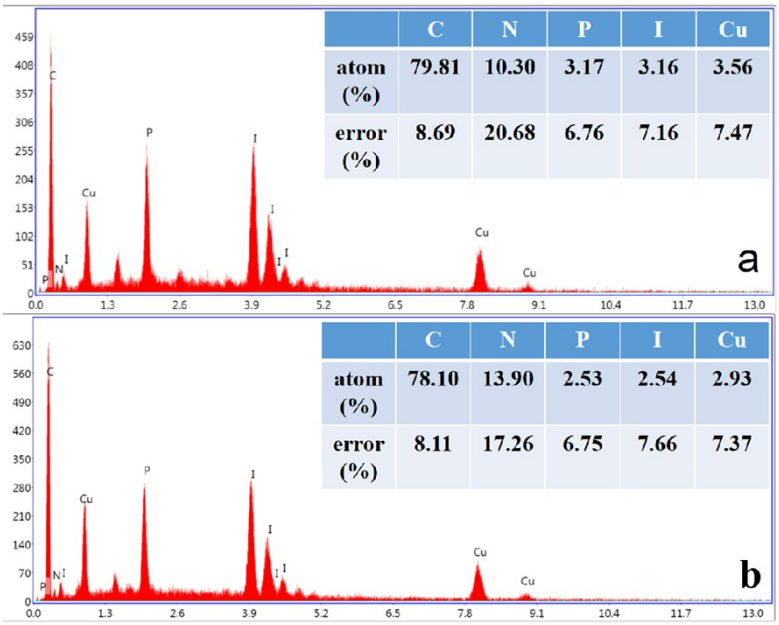


HOMO−3 LUMO+3



HOMO−4 LUMO+4

Fig. S19. Contour plots of frontier molecular orbitals of complex $[Cu_6I_6(ppda)_2]$ in CH_3CN.



	C	N	P	I	Cu
atom (%)	79.81	10.30	3.17	3.16	3.56
error (%)	8.69	20.68	6.76	7.16	7.47

	C	N	P	I	Cu
atom (%)	78.10	13.90	2.53	2.54	2.93
error (%)	8.11	17.26	6.75	7.66	7.37

Fig. S20. SEM-EDS for the Cu_6I_6 cluster (a) before and (b) after the photocatalysis.

Table S1. Selected bond lengths (Å) and angles (°) in the optimized S_0 and S_1 geometries for complex $[Cu_6I_6(ppda)_2]$.

Complex	Geometry	
$[Cu_6I_6(ppda)_2]$	S_0	S_1
Cu–I	2.7370, 2.6277, 2.6413, 2.6318 3.2665, 2.6656, 2.8291, 2.7151	2.8354, 2.6392, 2.6599, 2.6476 2.7818, 2.6247, 3.7673, 2.6110
Cu–P	2.5119, 2.4611	2.4254, 2.5127
Cu–N	2.17670, 2.1784	2.1582, 2.2043
Cu···Cu	2.44630, 2.6282, 2.7718	2.4684, 2.6368, 2.7618
I–Cu–I	114.91, 131.82, 98.86, 104.09 127.96, 92.81, 115.95, 108.88	110.59, 137.76, 112.73, 97.08 113.99, 110.43, 128.13, 87.30
Cu–I–Cu	54.07, 54.13, 51.51, 63.15, 57.40, 59.84, 113.29	53.27, 55.98, 60.95, 60.12, 47.12, 57.12, 104.08
I–Cu–N	112.84, 110.00, 108.62, 104.12	112.85, 108.50, 104.94, 98.65
I–Cu–P	114.05, 117.46, 115.69, 102.68	112.67, 124.51, 115.88, 101.60
P–Cu–N	83.42, 82.46	84.70, 81.98
Cu–P–Cu	58.92	59.95

Table S2. Computed excitation states for complex $[Cu_6I_6(ppda)_2]$ in CH_3CN.

State	λ(nm)/*E*(eV)	Configurations	*f*
1	333.1 (3.72)	H-4→L+1 (2); H-3→L+1 (4); H-1→L+1 (25); H→L+1 (62)	0.0850
3	328.9 (3.77)	H-4→L+3 (2); H-2→L (6); H-1→L+3 (27); H→L+2 (6); H→L+3 (41); H→L+4 (3)	0.0411
5	324.0 (3.83)	H-4→L (8); H-3→L (7); H-2→L (31); H-2→L+2 (6); H→L (29); H→L+2 (4); H→L+4 (3)	0.0429
15	307.1 (4.04)	H-4→L (2); H-3→L+7 (2); H-2→L+4 (30); H-1→L (3); H-1→L+3 (7); H-1→L+4 (7); H→L+3 (3); H→L+4 (5); H→L+5 (2); H→L+7 (5)	0.0932
19	302.6 (4.10)	H-6→L+2 (6); H-5→L+1 (5); H-4→L+1 (5); H-4→L+4 (26); H-4→L+6 (3); H-4→L+7 (6); H-3→L+4 (3); H-2→L+1 (7); H-1→L+2 (7); H-1→L+4 (6); H-1→L+7 (3)	0.0402

Table S3. Calculated photophysical data of $[Cu_6I_6(ppda)_2]$ from the crystal data.

Number of molecules	λ(nm)	
	297 K	77 K
One	346.14	354.28
Two	436.01	437.92
three	471.01	471.01