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Electronic Supplementary Information

Moiré superlattices of two-dimensional copper nanocluster assemblies with tuneable twin emissions from hierarchical components leading to white light emission

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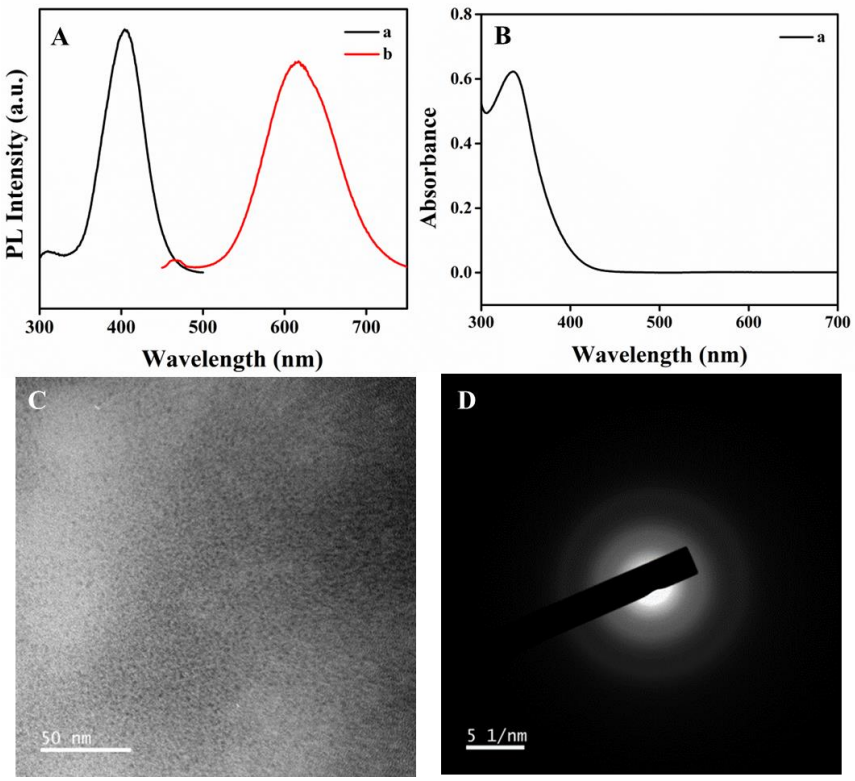

Fig. S1. (**A**) (**a**) Excitation spectrum (emission wavelength was set at 615 nm) and (**b**) emission spectrum (excitation wavelength was set at 405 nm) of the as-synthesized Cu nanoclusters (CuNCs). (**B**) UV-Vis spectrum of the CuNCs. (**C**) Transmission electron microscopy (TEM) image of the as synthesized CuNCs and (**D**) selected area electron diffraction (SAED) pattern acquired on a typical area shown in image C.

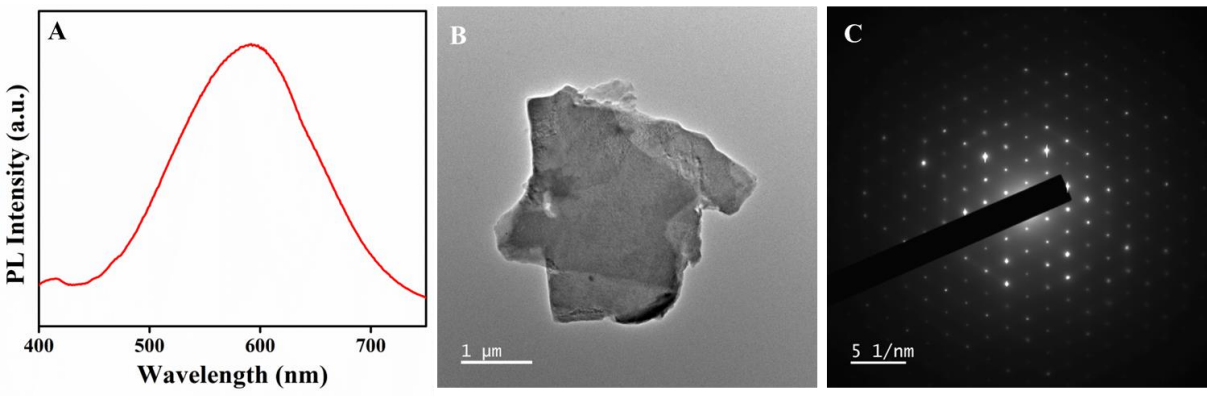

Fig. S2. (**A**) Photoluminescence emission spectrum of Zn-CuNCs (excitation maximum was set at 365 nm). (**B**) Transmission electron microscopy (TEM) image of Zn-CuNC nanosheet and (**C**) corresponding selected area electron diffraction (SAED) pattern image.

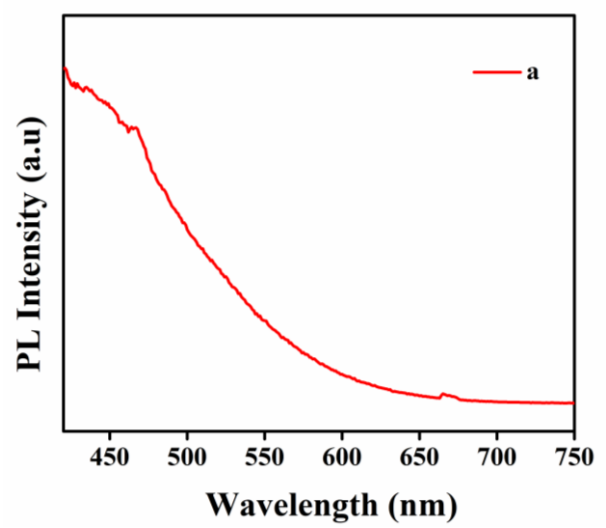

Fig. S3. (a) Photoluminescence emission spectrum of triphenylphosphine (TPP) added zinc acetate solution (excitation wavelength was set at 365 nm).

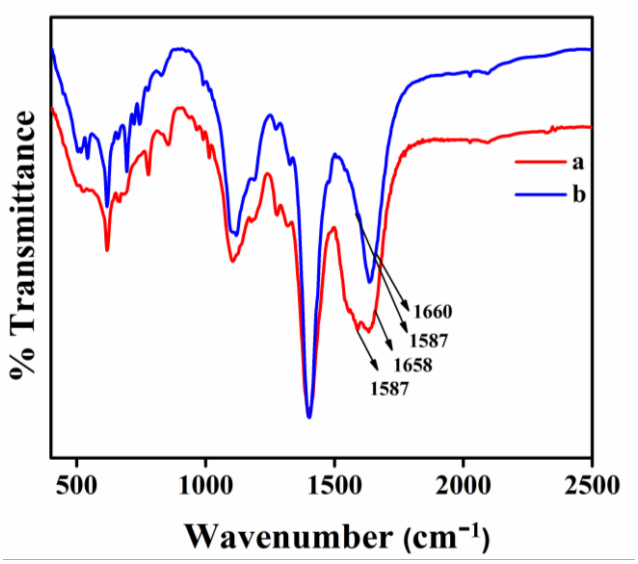

Fig. S4. Fourier-transform infrared spectra of (a) Zn-CuNCs and (b) 0.9mM TPP added Zn-CuNCs.

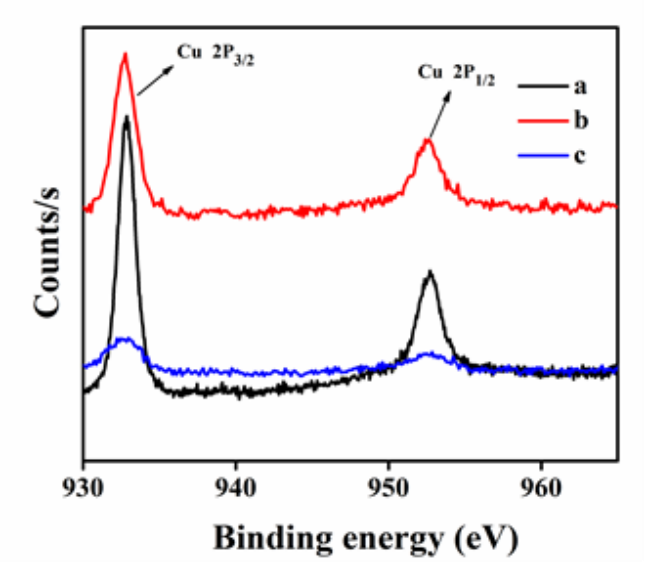

Fig. S5. X-ray photoelectron spectra of (a) as synthesized CuNCs, (b) Zn-CuNCs, and (c) . TPP added multi-twited Zn-CuNCs.

Calculation of association constant for supramolecular stacking process:

The degree of stacking-assembly was calculated with the following equation

$$\alpha = (I_C - I_H) / (I_S - I_H) \quad \text{.....Equation S1}$$

where, I_C = Photoluminescence intensity of the medium containing Zn-CuNCs at any given concentration of TPP,

I_H = Photoluminescence intensity of the medium containing component hexagonal Zn-CuNCs only (without any twisted stacking assembly), and

I_S = Photoluminescence intensity of the medium containing completely twisted-stacked nanosheets at the highest concentration of TPP.

Plot of α vs concentration of TPP resulted in the curve below with sigmoidal nature (characteristic of an isodesmic supramolecular reaction). [S1] The fitting of the curve with Hill equation using Origin software gave the association constant value of $(5.8 \pm 2.0) \times 10^4\ M^{-1}$.

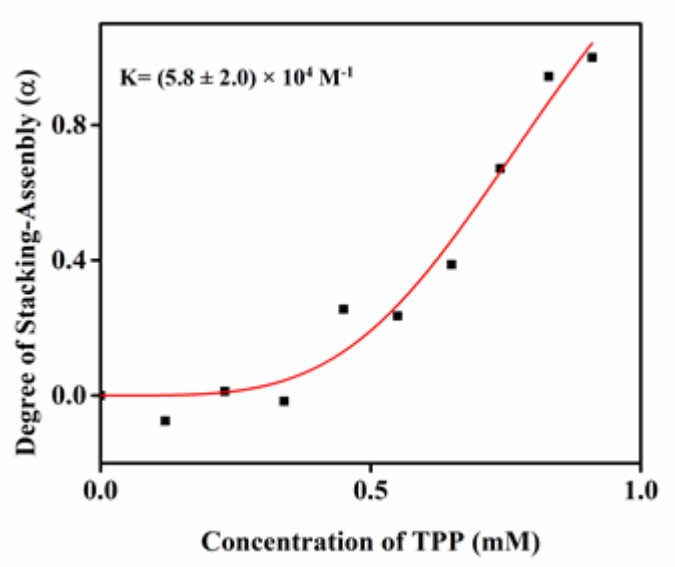

Fig. S6. Plot of degree of stacking assembly versus concentration of TPP.

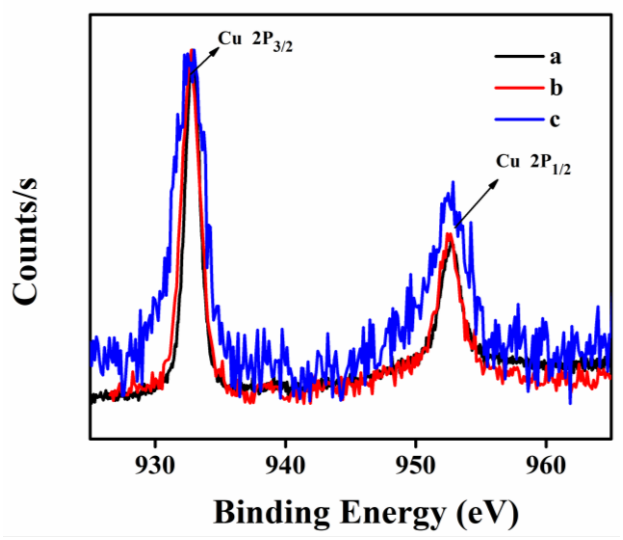

Fig S7. Normalized x-ray photoelectron spectra of (a) as synthesized CuNCs, (b) Zn-CuNCs, and (c) TPP added multi-twisted Zn-CuNCs.

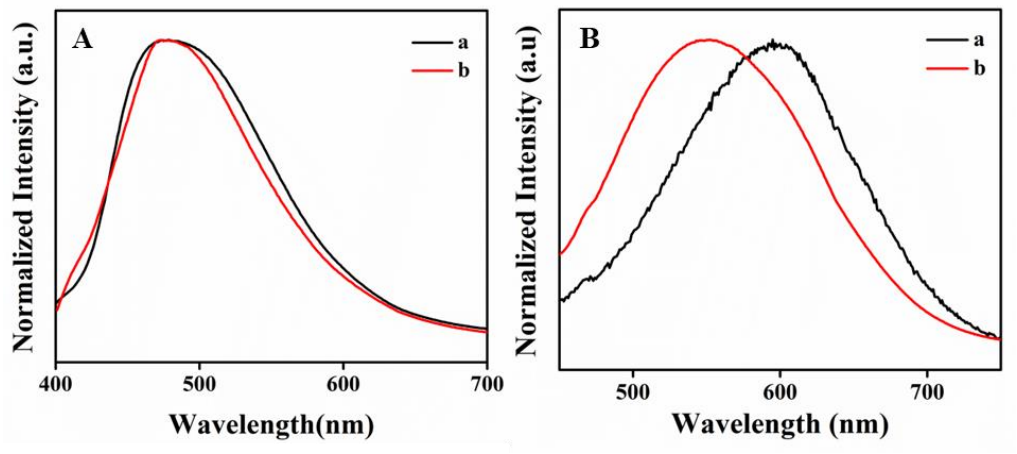

Fig. S8: (**A**) Photoluminescence spectra of 0.9mM TPP added Zn-CuNCs in (**a**) the dispersion medium and (**b**) solid state. (**B**) Photoluminescence spectra of hexagonal Zn-CuNCs in (**a**) the dispersion medium and (**b**) solid state.

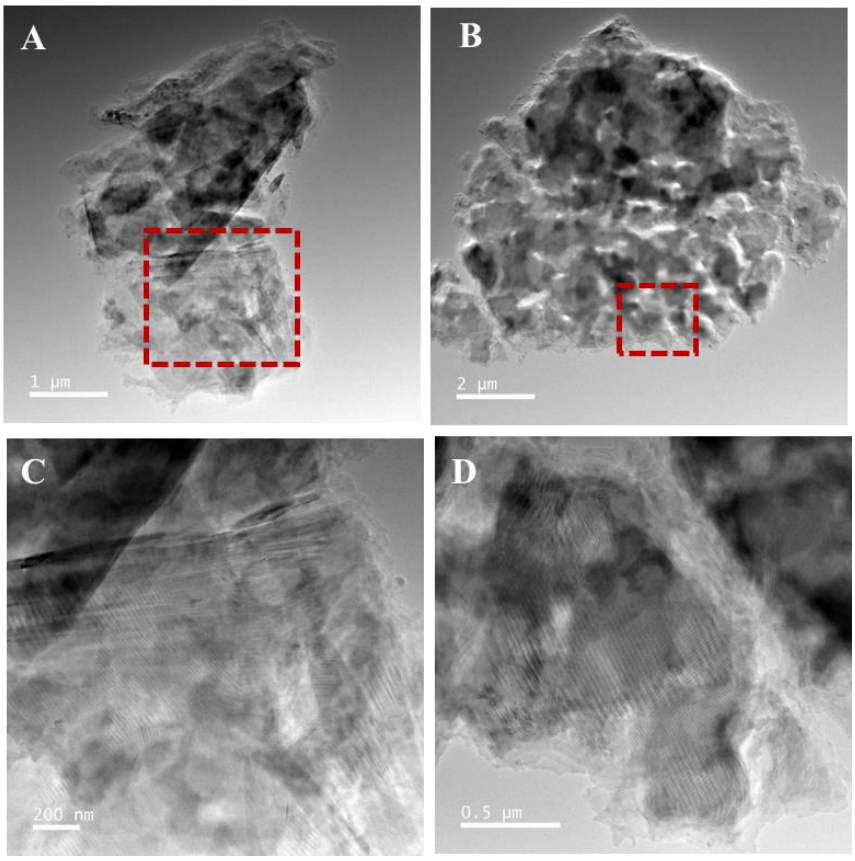

Fig. S9. (A, B) Transmission electron microscopy (TEM) images of TPP added Zn-CuNC moiré nanosheets and (**C, D**) enlarged views of the marked areas showing moiré lattices in the images A and C, respectively.

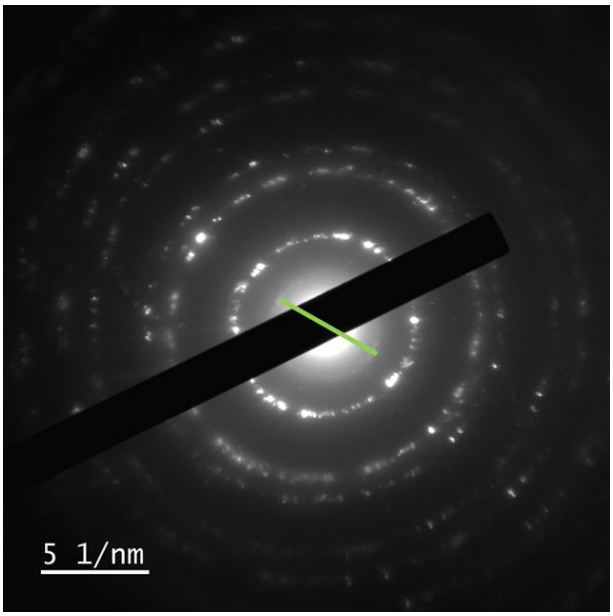

Fig. S10. Selected area electron diffraction (SAED) pattern image of the TPP added Zn-CuNC nanosheet given in Fig. S9C recorded through rotation of the sample holder at an angle of 17° (having marked the plane with lattice parameter of 4.2 Å).

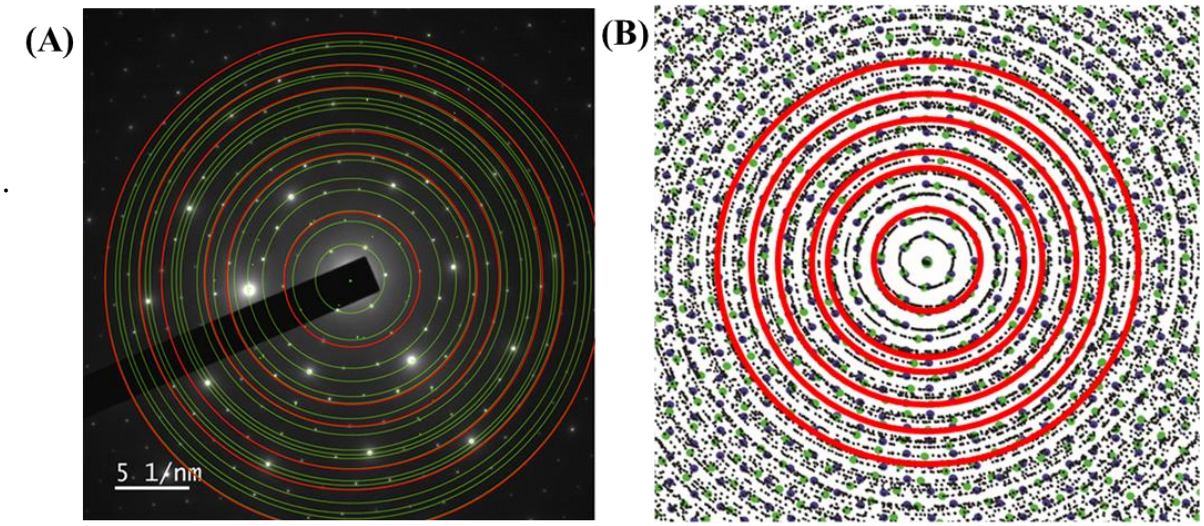

Fig. S11. (**A**) Experimentally obtained selected area electron diffraction (SAED) pattern image of a typical Zn-CuNC nanosheet with hexagonal diffraction lattices marking all the planes in green and the observed planes in the moiré nanosheet in red. (**B**) Simulated image of multiple twisted hexagonal lattices (with twist angles measured from **Fig.** 2C) with the experimentally obtained diffraction planes in red circles.

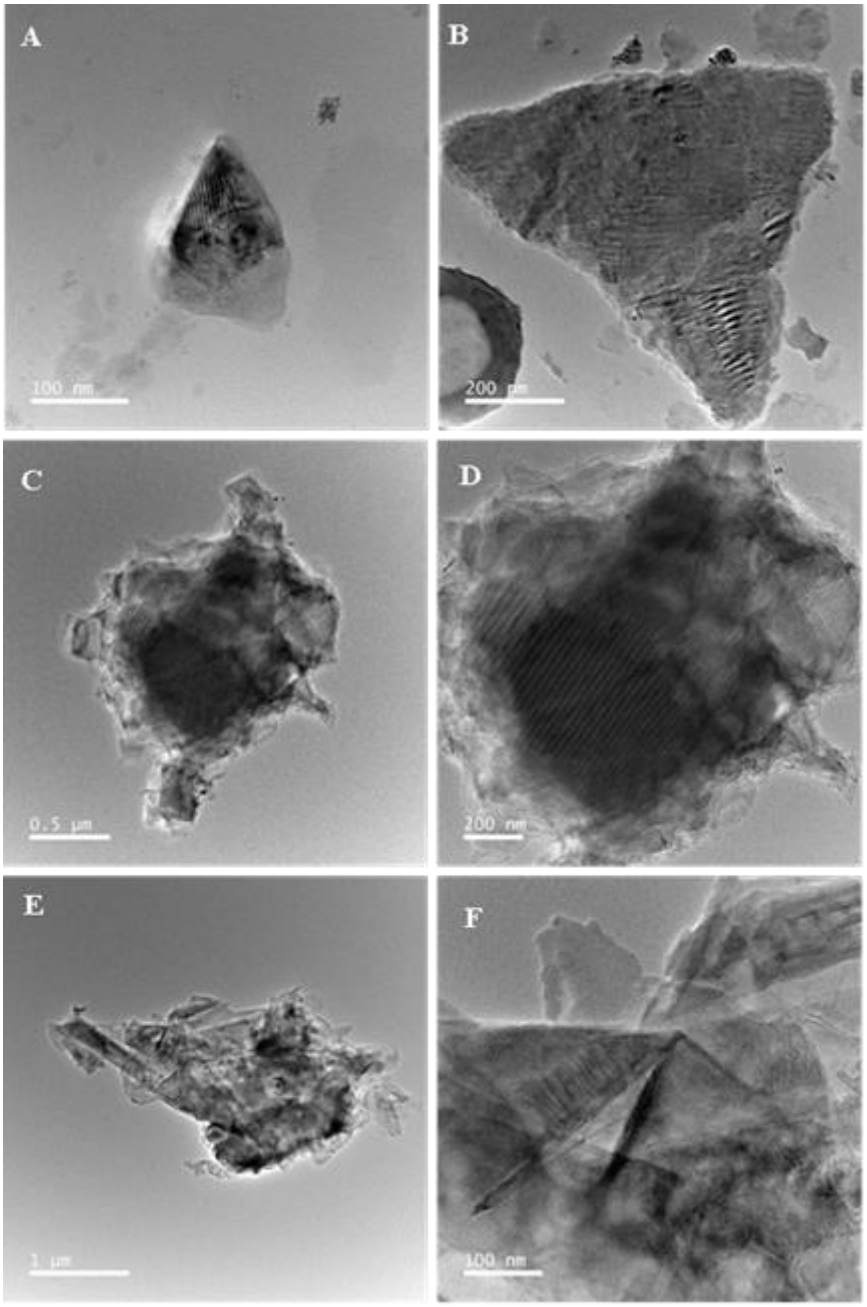

Fig. S12. (**A, B, C, E**) Additional transmission electron microscopy (TEM) images of moiré-Zn-CuNC nanosheets and (**D** and **F**) TEM images at different scales of those in C and E, respectively.

Table S1. All the relative twisted angles measured from the SAED image in the **Fig.** 2C and the calculated values of the corresponding moiré periods.

	Angle notation	Angles, **θ** (Degree)	Moire Period, **D** (nm)
1	<a0b, <j0k	2.3	**11.7**
2	<b0c, <o0p	1.6	16.8
3	<c0d	4	**6.7**
4	<d0e, <t0u	2.1	**12.8**
5	<e0f, <m0n, <p0q	0.5	53.8
6	<f0g, <i0j	1	26.9
7	<g0h	2.6	10.4
8	<h0i, <k0l	3.3	8.1
9	<l0m	0.6	44.8
10	<q0r, <s0t	0.9	29.9
11	<r0s	5	**5.4**
12	<t0u, <w0x	2	13.4
13	<u0v, <x0y	1.3	20.7
14	<v0w	1.2	**22.4**
15	<y0z	0.8	33.6
16	<z0z1, <z10z2	1.8	14.9
17	<n0o	3	**8.9**

Quantum yield calculation (based on relative method):

Photoluminescence quantum yield was measured with respect to quinine sulphate in 0.1 M H_2SO_4 with reported quantum yield of 54% using the following equation-

$$\varphi_S = \varphi_R \times \frac{I_S}{I_R} \times \frac{A_R}{A_S} \times \frac{\eta_S^2}{\eta_R^2} \quad \text{……. Equation S2}$$

Here, φ_S = quantum yield of the sample; φ_R = quantum yield of the reference; I_S = area under the emission spectrum of the sample; I_R = area under the emission spectrum of reference; A_R = absorbance of reference; A_S = absorbance of the sample; η_S = refractive index of the sample solution; η_R = refractive index of reference. Refractive index of water = 1.33, QY of quinine sulphate=0.54

Table S2. Parameters for quantum yield measurements (based on relative method).

Sample	Experi-ment No	Area under the PL curve of QS excited at 365 nm (a.u.) (I_R)	Area under the PL curve of sample excited at 365 nm (a.u.) (I_S)	Absorbance of QS at 365 nm (A_R)	Absorbance of the sample at 365 nm (A_S)	Quantum yield (Q.Y.) (%)	Average quantum yield with error bar (%)
Hexagonal Zn-CuNCs	1	4.4×10^8	1.37×10^6	0.1074	0.1254	0.14	0.10±0.03
	2	5.5×10^8	1.12×10^6	0.1003	0.1367	0.08	
	3	5.5×10^8	1.04×10^6	0.1003	0.1131	0.09	
Moiré Zn-CuNCs	1	4.4×10^8	5.07×10^6	0.1074	0.1241	0.54	0.54±0.04
	2	4.4×10^8	3.87×10^6	0.1074	0.1037	0.49	
	3	4.4×10^8	4.66×10^6	0.1074	0.1054	0.58	

Table S3. Absolute quantum yield values (using an integrating sphere) of hexagonal Zn-CuNCs and moiré Zn-CuNCs in the dispersed medium and solid state.

Sample		Dispersed medium		Solid state (thin film)	
	Experiment No.	Absolute quantum yield (%)	Average absolute quantum yield (%)	Absolute quantum yield (%)	Average absolute quantum yield (%)
Hexagonal Zn-CuNCs	1	0.50	1.35±0.6	1.90	2.28±0.29
	2	1.60		2.62	
	3	1.95		2.34	
Moiré Zn-CuNCs	1	10.84	12.04±1.36	3.68	4.57±0.64
	2	11.34		4.85	
	3	13.95		5.19	

Table S4. Calculated parameters as-obtained from time resolved delayed photoluminescence decay study of Zn-CuNCs and TPP added moiré Zn-CuNCs in sub-millisecond range.

Sample	Hexagonal Zn-CuNCs			Moiré Zn-CuNCs		
Experiment no	1	2	3	1	2	3
χ^2	0.99	0.99	0.99	0.99	0.99	0.99
First component α_1 (%)	6.37×10^5	6.52×10^5	4.71×10^5	9.33×10^7	1.54×10^7	1.95×10^7
First component lifetime τ_1 (ms)	0.027	0.023	0.070	0.040	0.036	0.033
Second component α_2 (%)	3.76×10^6	5.12×10^5	4.29×10^6	8.31×10^7	1.46×10^7	1.49×10^7
Second component lifetime τ_2 (ms)	7.0×10^{-4}	0.003	0.016	0.152	0.131	0.129
Average lifetime τ_{av} (ms)	0.024	0.021	0.033	0.1265	0.1096	0.1133
Average lifetime with error bar τ_{av} (μs)	26.0 ± 6.2			116.4 ± 7.2		

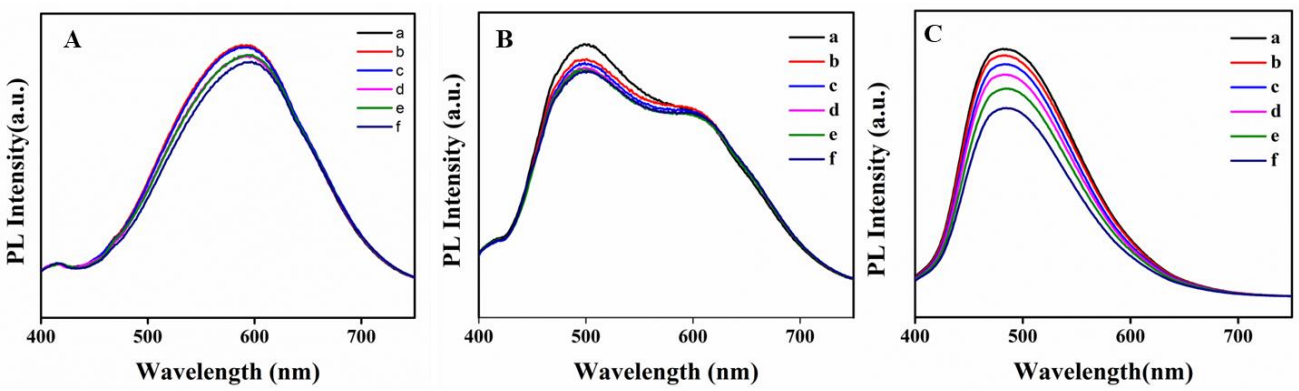

Fig. S13. (**A-C**) Photoluminescence spectra recorded in (**a**) 0min, (**b**) 30 min, (**c**) 60 min, (**d**) 90 min, (**e**) 120 min and (**f**) 270 min of three compounds having red, white and blue luminescence respectively, digital images of which are shown in the Fig. 3E of the manuscript.

Reference:

S1. Hartlieb, M.; Mansfield, E. D. H.; Perrier, S., A guide to supramolecular polymerizations. *Polymer Chemistry* **2020,** *11* (6), 1083-1110.