

# ADVANCED MATERIALS

## Supporting Information

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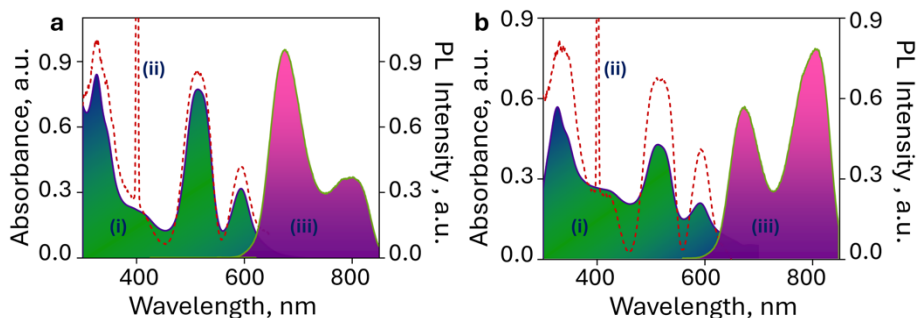
Bimetallic Nanocluster-Based Light-Emitting Diodes With High External Quantum Efficiency and Saturated Red Emission

*Jose V. Rival, Savita Chand, Arijit Jana, Nonappa, Vasudevanpillai Biju, Thalappil Pradeep, Pachaiyappan Rajamalli\* and Edakkattuparambil Sidharth Shibu\**

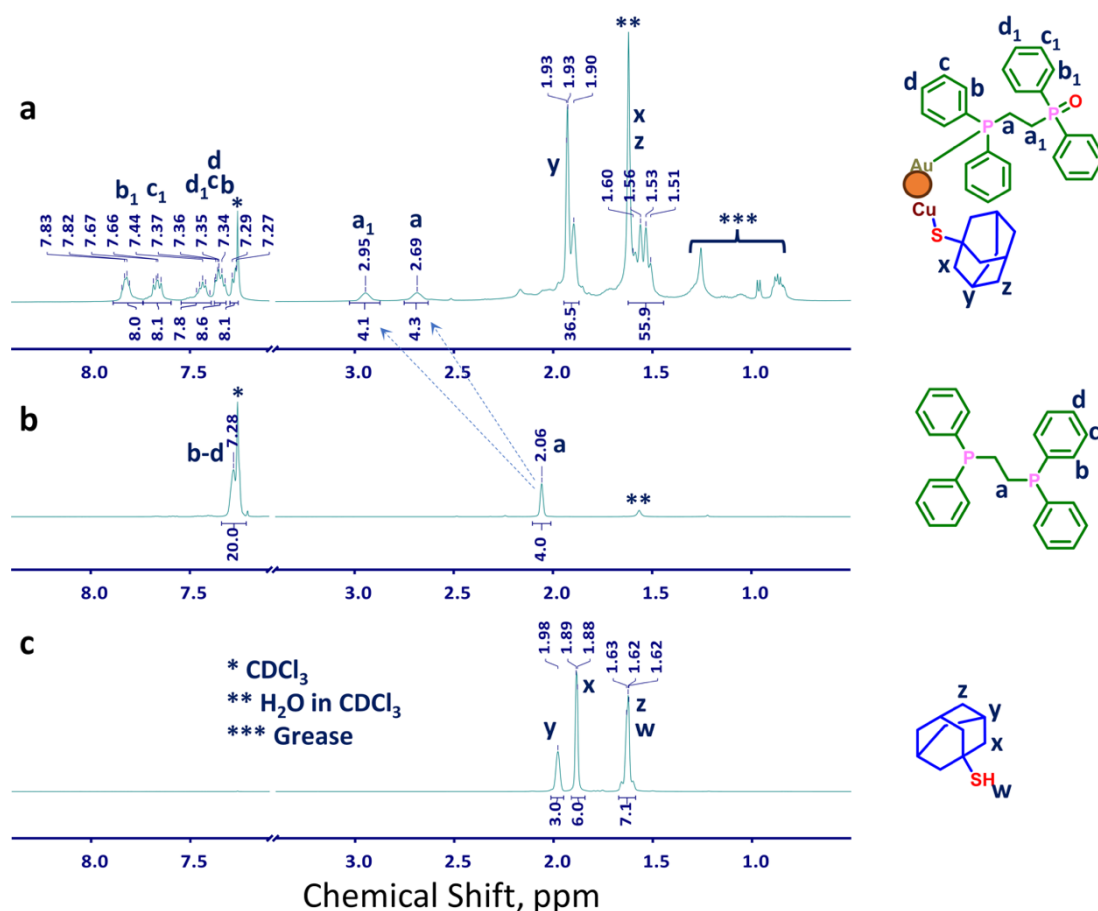
## Supporting Information

## Bimetallic Nanocluster-based Light-Emitting Diodes with High External Quantum Efficiency and Saturated Red Emission

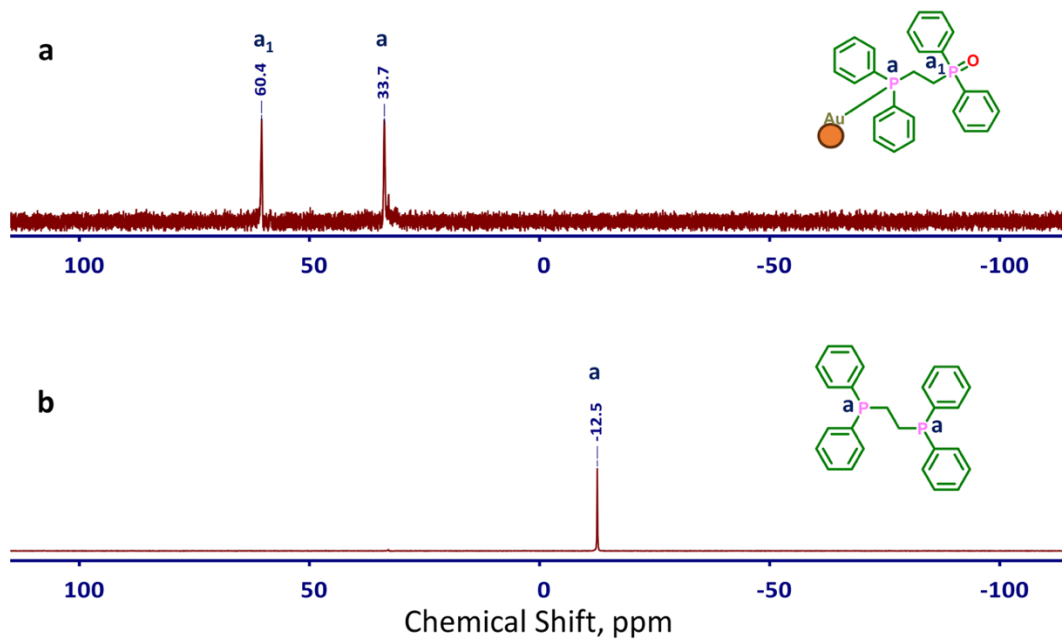
Jose V. Rival,<sup>a</sup> Savita Chand,<sup>b</sup> Arijit Jana,<sup>c</sup> Nonappa,<sup>d</sup> Vasudevanpillai Biju,<sup>e</sup> Thalappil Pradeep,<sup>c</sup> Pachaiyappan Rajamalli,<sup>b\*</sup> Edakkattuparambil Sidharth Shibu<sup>a\*</sup>



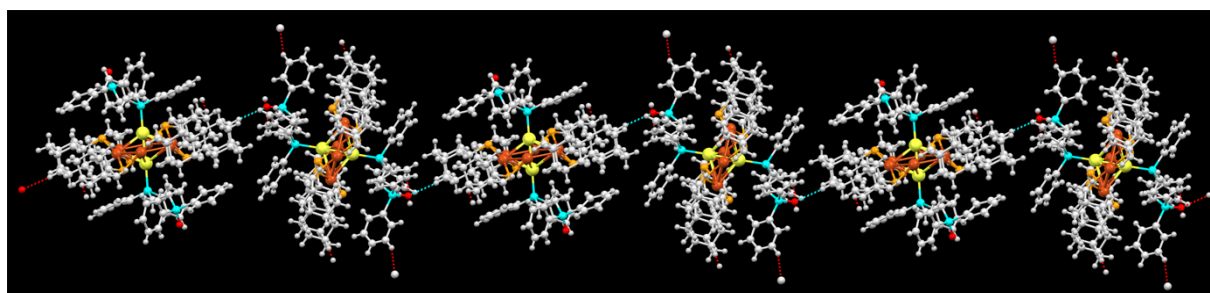
**Figure S1.** (i) UV/Vis absorption, (ii) excitation (corresponding to the emissions at 798 and 806 nm from  $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$  and  $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{TPP})_2]$  NCs, respectively) and PL (iii) spectra of (a)  $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$  and (b)  $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{TPP})_2]$  NCs.



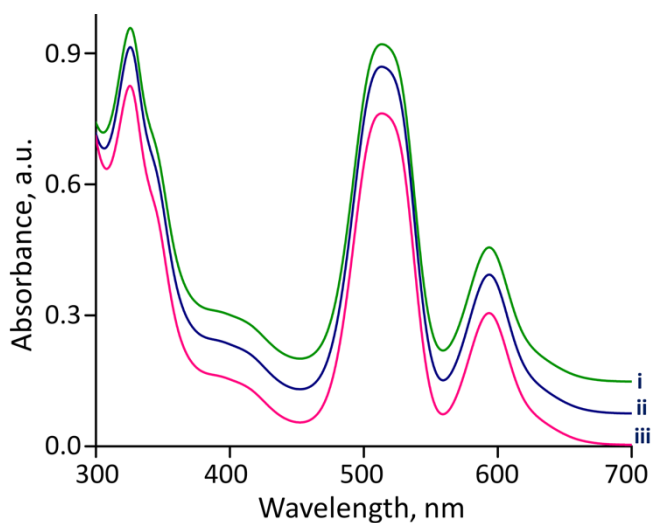
**Figure S2.**  $^1\text{H}$  NMR spectra of (a)  $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$  NC, (b) DPPE, and (c) HSadm.



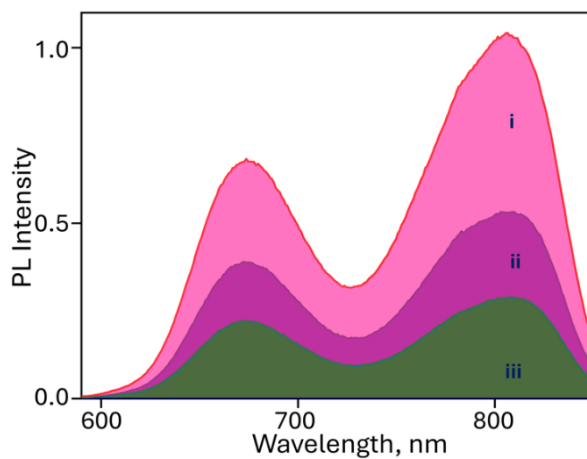
**Figure S3.**  $^{31}\text{P}$  NMR spectra of (a)  $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$  NC and (b) DPPE ligand in  $\text{CDCl}_3$ .



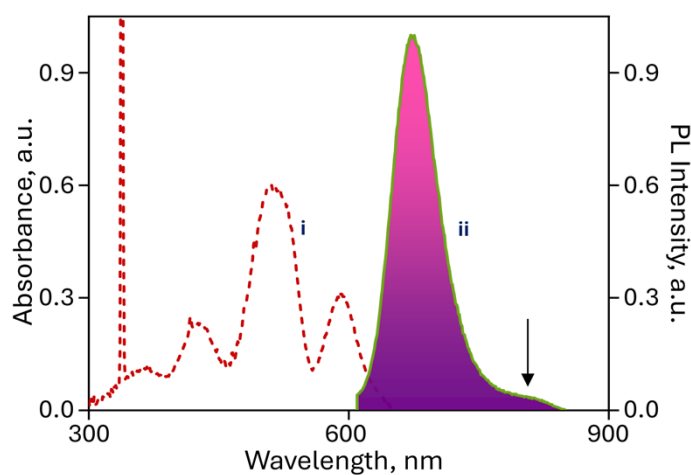
**Figure S4.** The C-H...O interactions between the neighboring NCs in the crystal resulted in a zig-zag tape arrangement of NCs.



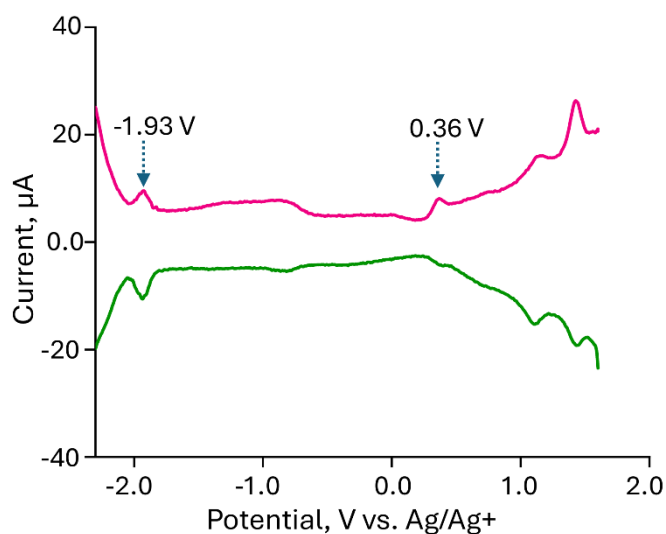
**Figure S5.** UV/Vis absorption spectra of NC solution recorded under (i) argon, (ii) ambient, and (iii) oxygen atmospheres (for clarity, spectra were vertically translated).



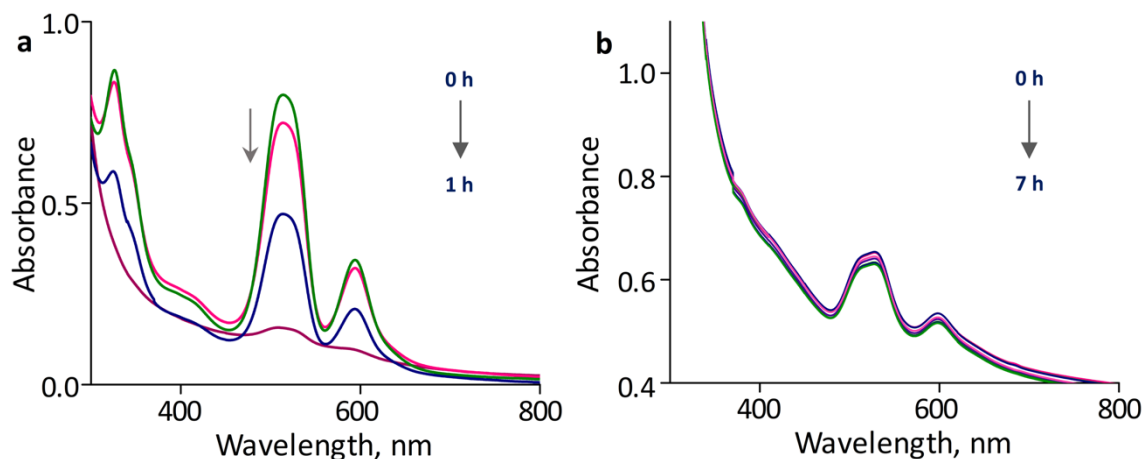
**Figure S6.** PL spectra of  $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{TPP})_2]$  NC solution recorded under (i) argon, (ii) ambient, and (iii) oxygen atmospheres.



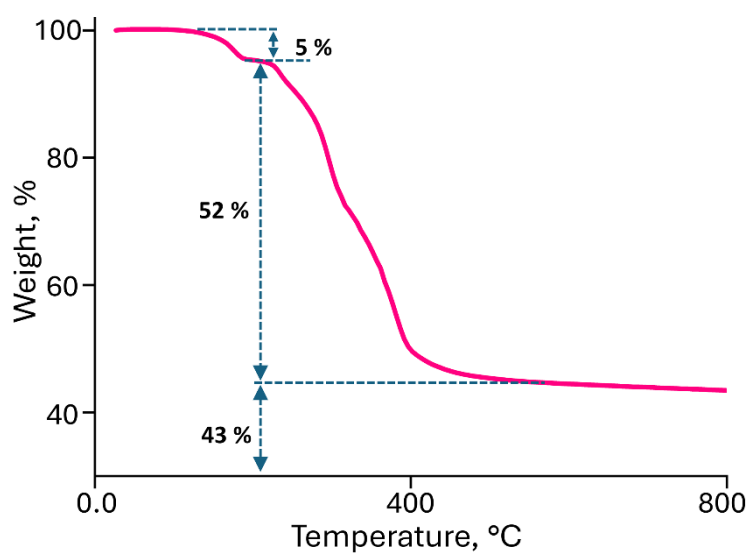
**Figure S7.** Excitation (i) and emission (ii) spectra of  $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{TPP})_2]$  NC.



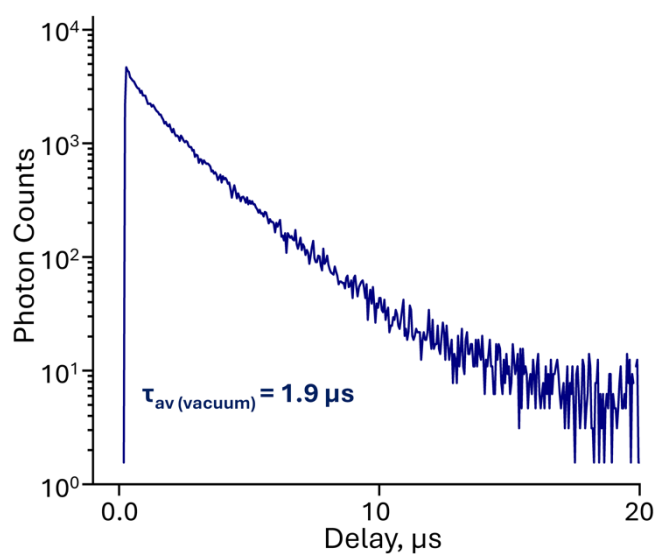
**Figure S8.** Differential pulse voltammetry (DPV) of  $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$  ( $20\ \mu\text{M}$ ) in acetonitrile/toluene mixture (1:1).



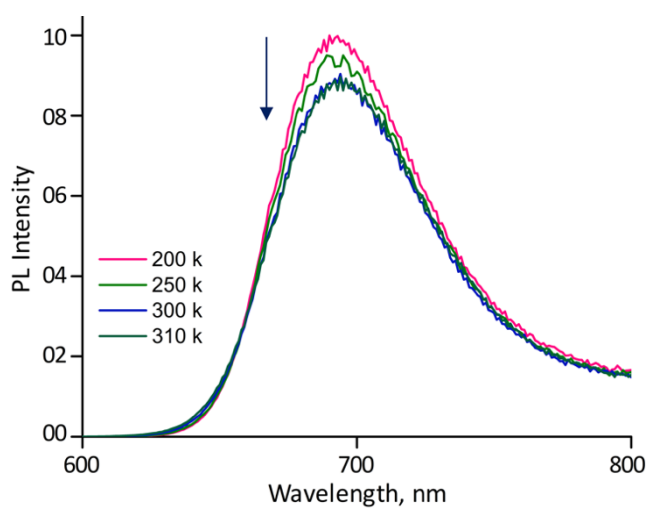
**Figure S9.** Temporal UV/Vis absorption spectra recorded from (a) NC solution and (b) NC film under UV illumination.



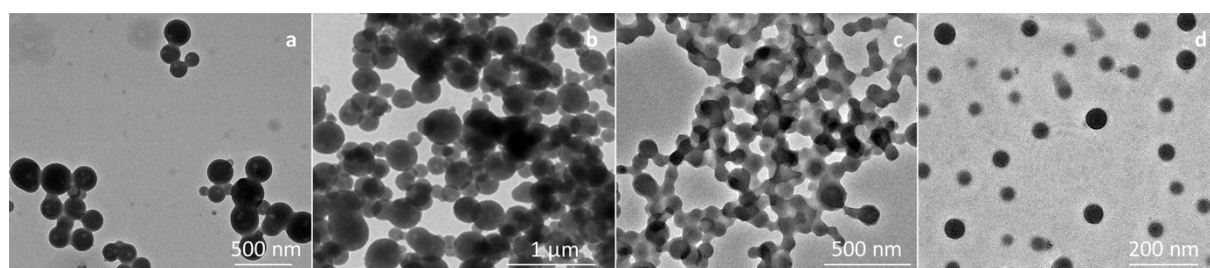
**Figure S10.** TGA curve of  $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$  NC.



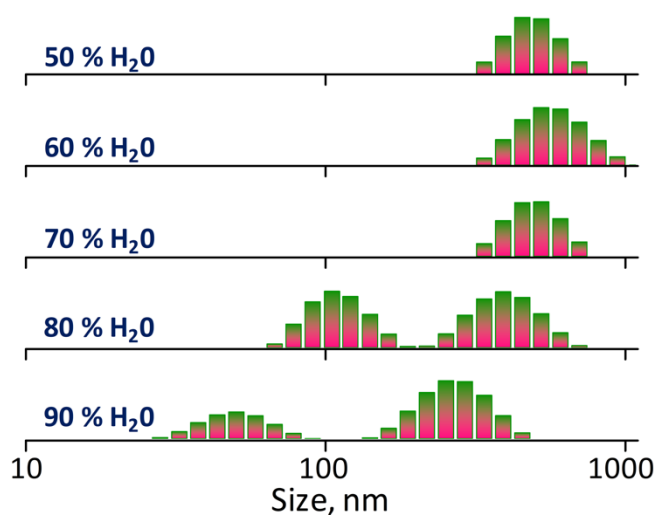
**Figure S11.** The PL decay profile of NC solid under vacuum.



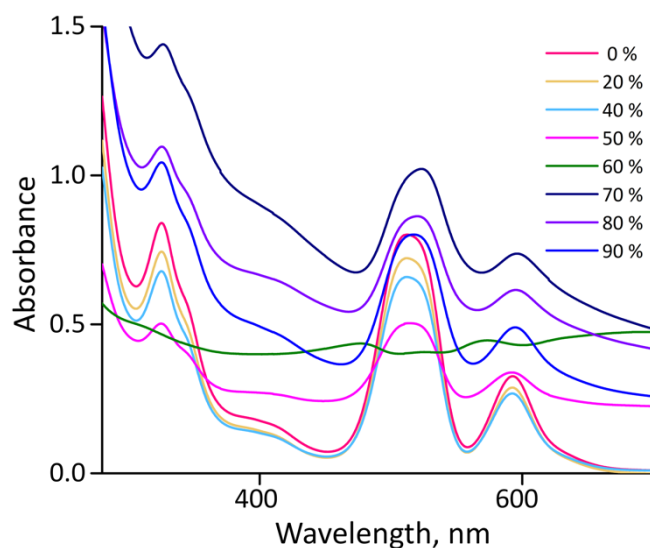
**Figure S12.** The temperature-dependent PL spectra recorded from NC solid.



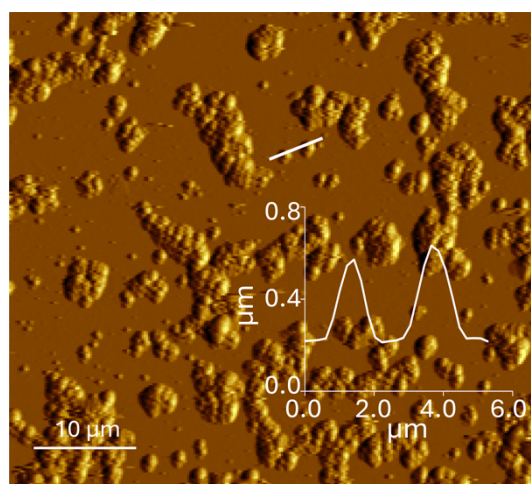
**Figure S13.** TEM micrographs of assembled-NCs at (a) 50%, (b) 60%, (c) 70%, and (d) 90%  $f_w$ .



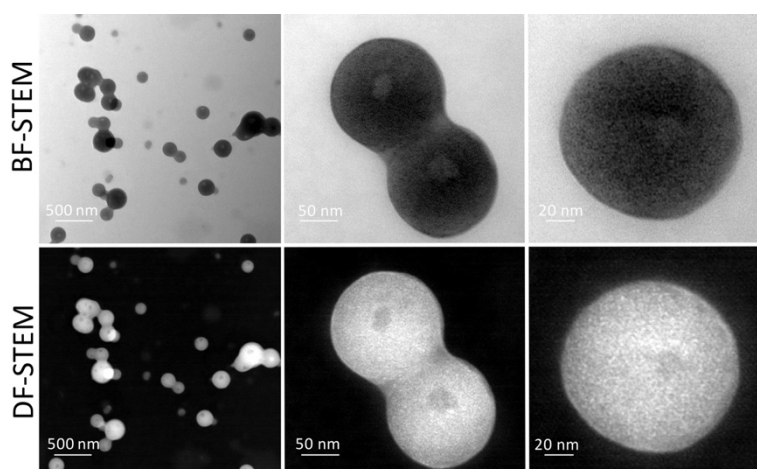
**Figure S14.** DLS spectra of  $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$  NCs in THF at different  $f_w$ .



**Figure S15.** The UV/Vis absorption spectra of NC solution at different  $f_w$ .

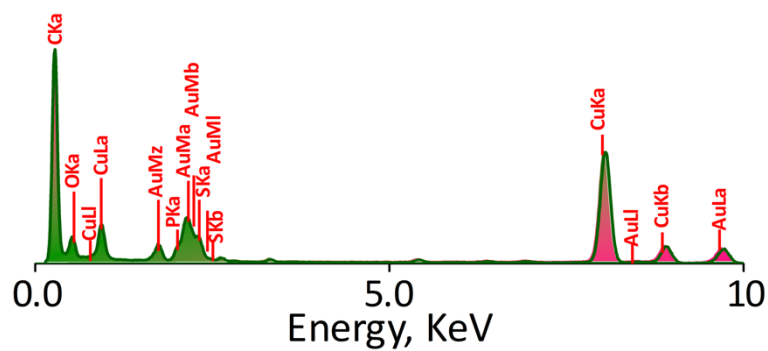


**Figure S16.** A large area AFM image of assembled-NCs (60%  $f_w$ ). The height profile is shown in the inset.

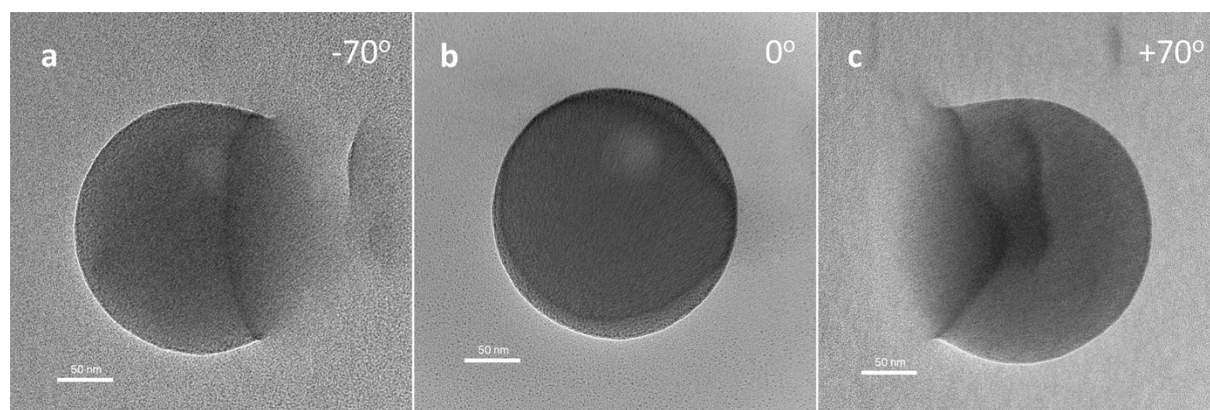


**Figure S17.** BF- and DF-STEM images show large area assembly, and assembled dimer and monomer.

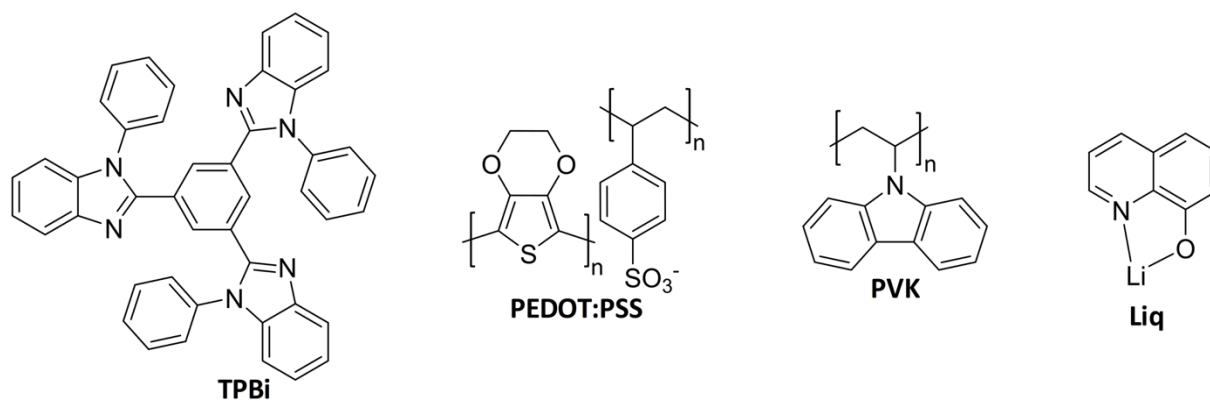




**Figure S18.** The EDS spectrum of assembled superstructures ( $f_w = 60\%$ ). Respective elements are labeled.

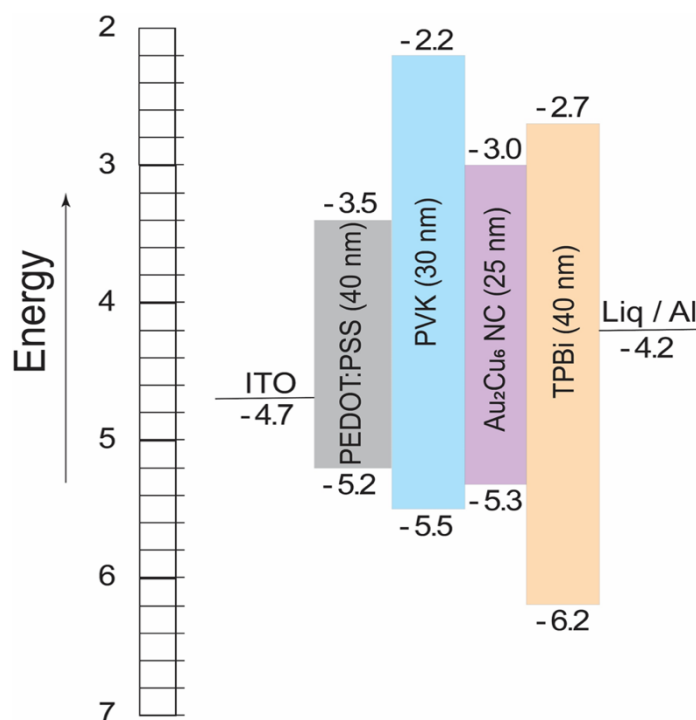


**Figure S19.** BF-TEM micrographs of  $[\text{Au}_2\text{Cu}_6(\text{Sadm})_6(\text{DPPEO})_2]$  NC assembly ( $f_w = 60\%$ ) at different tilt angles.

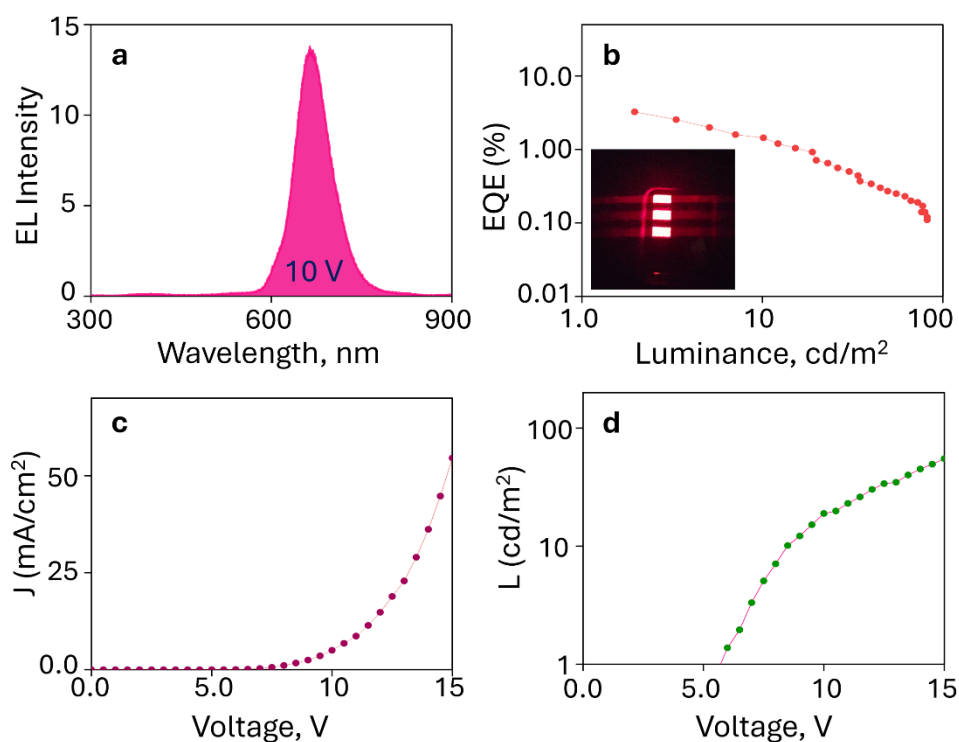


**Figure S20.** The chemical structure of different organic materials used for LED fabrication.





**Figure S21.** The energy level alignment in the device.



**Figure S22.** (a) EL spectra of [Au<sub>2</sub>Cu<sub>6</sub>(Sadm)<sub>6</sub>(TPP)<sub>2</sub>] NC-based device at 10V. (b) EQE vs luminance curve. The inset shows a photograph of the fabricated LED device. (c) Current density-voltage curve of the device. (d) Luminance-voltage curve of the device.

| Light emitting<br>NC Layer                                                                     | PLQY<br>(%) | $L_{\max}$<br>(cd m <sup>-2</sup> ) | Wavelength<br>(nm) | EQE <sub>max</sub><br>(%)       | CIE<br>Coordinates<br>(x, y)   | Ref.            |
|------------------------------------------------------------------------------------------------|-------------|-------------------------------------|--------------------|---------------------------------|--------------------------------|-----------------|
| Au <sub>25</sub> or Ag <sub>25</sub>                                                           | –           | –                                   | 750                | 0.013                           | –                              | 1               |
| Au@GSH                                                                                         | 15          | 40                                  | 625                | 0.12                            | (0.57–0.59,<br>0.40–0.41)      | 2               |
| Au@TOP                                                                                         | 4.99        | 100                                 | White light        | 0.08                            | (0.27,0.33)                    | 3               |
| (Au <sub>4</sub> L <sub>4</sub> ) <sub>n</sub> /(Au <sub>4</sub> D <sub>4</sub> ) <sub>n</sub> | 41.4        | –                                   | 503                | 1.5                             | –                              | 4               |
| TOAB/Arg/ATT@Au                                                                                | 73.4        | 1104                                | 544                | 5.1                             | (0.31,0.65)                    | 5               |
| Au <sub>4</sub> Ag <sub>2</sub>                                                                | 77.2        | 8804                                | 539                | 7.0 (d)                         | –                              | 6               |
| Ag <sub>6</sub> Cu                                                                             | 78          | 184                                 | 573                | 13.9 (d)                        | –                              | 7               |
| PtAu <sub>3</sub>                                                                              | 90          | 1000                                | 588                | 18.1 (d)                        | (0.33,0.61)                    | 8               |
| PtAu <sub>3</sub>                                                                              | 90.1        | 6539                                | 556                | 16.6 (d)                        | (0.30,0.61)                    | 9               |
| Au <sub>3</sub> Ag                                                                             | 25          | 5211                                | 440                | 2.06 (d)                        | (0.16,0.09)                    | 10              |
| Ag <sub>8</sub> Au <sub>10</sub>                                                               | 77          | 14,859                              | 567                | 15.7 (d)                        | (0.4714,0.520<br>0)            | 11              |
| Ag <sub>3</sub> Cu <sub>5</sub>                                                                | 75          | 8554                                | 585                | 14.7 (d)                        | (0.51,0.48)                    | 12              |
| R/S-Cu <sub>2</sub> Au <sub>2</sub>                                                            | 94/ 89      | 2010/1670                           | 564                | 36.5% (d)<br>23.5/20.<br>8 (nd) | (0.395,0.572)<br>(0.394,0.574) | 13              |
| [Au <sub>2</sub> Cu <sub>6</sub> (Sadm) <sub>6</sub> (DPPEO) <sub>2</sub> ]                    | 62          | 1246                                | 668                | 12.6 (nd)                       | (0.70,0.30)                    | Current<br>Work |
| [Au <sub>2</sub> Cu <sub>6</sub> (Sadm) <sub>6</sub> (TPP) <sub>2</sub> ]                      | 17.8        | 55.17                               | 666                | 3.24 (nd)                       | (0.67,0.31)                    | Current<br>Work |
| [DBFDP] <sub>2</sub> Cu <sub>4</sub> I <sub>4</sub>                                            | 5           | 1500                                | White light        | 0.73 (d)                        | (0.37,0.45)                    | 14              |
| [DtBCzDBFDP] <sub>2</sub> Cu <sub>4</sub> I <sub>4</sub>                                       | 65          | 7000                                | 491                | 7.9 (d)                         | (0.22,0.43)                    | 15              |
| [DPACDBFDP] <sub>2</sub> Cu <sub>4</sub> I <sub>4</sub>                                        | 81          | 4000                                | 500                | 19.5 (d)                        | (0.21±0.1,0.45<br>± 0.1)       | 16              |
| [TMeOPP] <sub>4</sub> Cu <sub>4</sub> I <sub>4</sub>                                           | 99          | 10710                               | 550                | 15.6 (d)                        | (0.40±0.05,<br>0.53±0.04)      | 17              |
| Cu <sub>2</sub> I <sub>2</sub> [P-m-(Tol) <sub>3</sub> ] <sub>2</sub> Pyrphos                  | 90          | 1426                                | 560                | 19.1 (d)                        |                                | 18              |
| Cu <sub>6</sub> I <sub>6</sub> (ppda) <sub>2</sub>                                             | 36          | –                                   | 564                | 0.31 (d)                        | (0.43,0.51)                    | 19              |
| Cu <sub>2</sub> I <sub>2</sub> (BINAP) <sub>2</sub>                                            | 4.7         | 1200                                | 515                | 0.54                            | –                              | 20              |
| [DDMACDBFDP] <sub>2</sub> Cu <sub>4</sub> I <sub>4</sub>                                       | 99          | 5502                                | 504                | 29.4 (d)<br>9.5 (nd)            | (0.21,0.50)                    | 21              |

**Table S1.** The comparison table shows the details of reported NCs in the device fabrication (d- doped and nd- non-doped).

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