# Supporting Information

## Efficient Deep-Blue Crystalline OLED via Hot Exciton Nanoaggregate Sensitizing TTA Emitter

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## 1. Atomic force microscopy (AFM) image

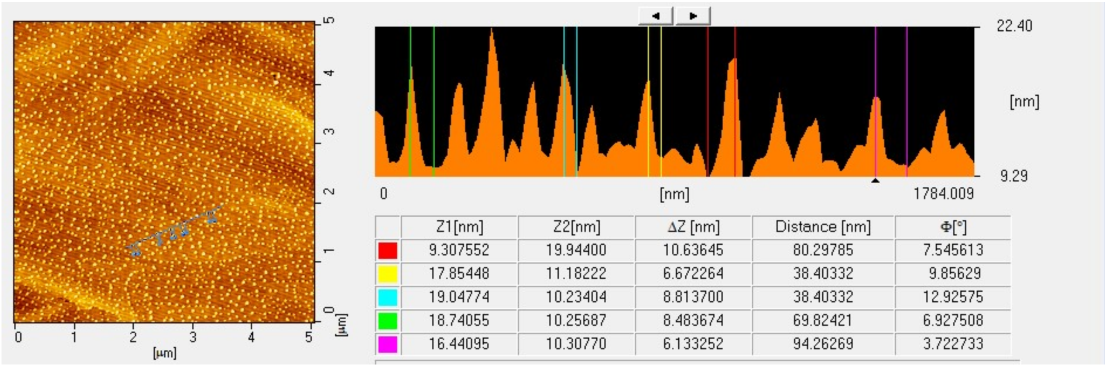



**Fig. S1** Average height of nanoaggregates (6–11 nm).

## 2. EL performance of Crystalline OLED

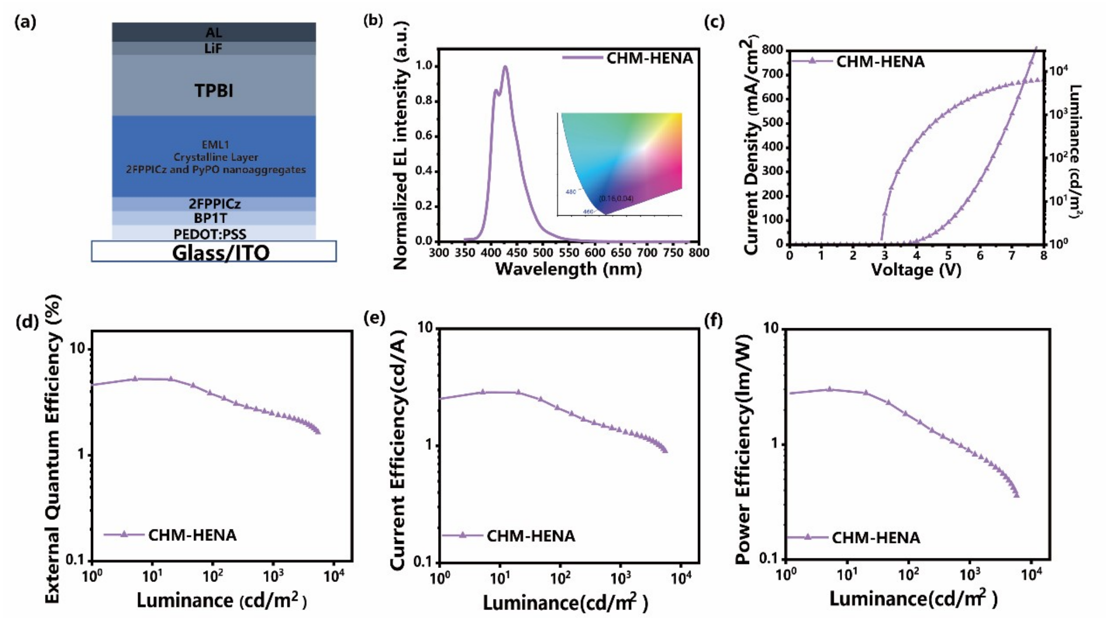
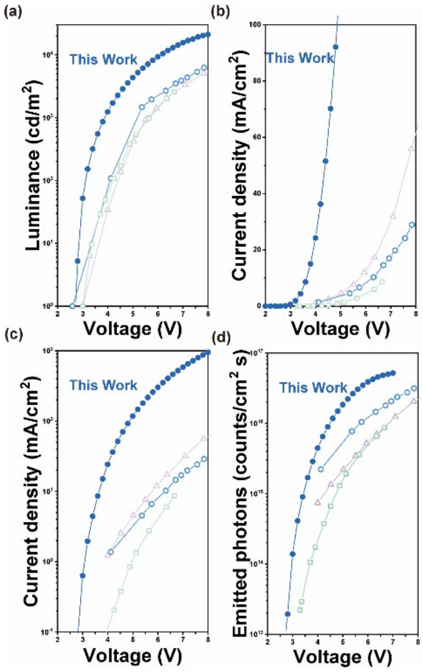



**Fig. S2** Device Performance of CHM-HENA OLED. (a) The device structure of CHM-HENA OLED. (b) EL spectrum at luminance of 1000cd/$m^2$ and the corresponding CIE of the device. (c) Voltage-dependent current density and luminance. (d) Luminance-dependent external quantum efficiency characteristics. (e) Luminance-dependent current efficiency characteristics. (f) Luminance-dependent power efficiency characteristics.

## 3. Comparisons of CHM-HENA-TTAD OLED with amorphous high EQE OLEDs




| | CIE (x,y) | $V_{on}/V_{1000}/\Delta V$ (V) | $EQE_{max}$ (%) |
|---|---|---|---|
| This Work | (0.15,0.10) | 2.8V/3.9V/1.1V | 8.16 |
| TTA(DPASP) | (0.14,0.17) | 3.0V/5.0V/2.0V | 12 |
| TADF(IDCz-DBS) | (0.14,0.16) | 2.6V/4.6V/2.0V | 31 |
| Phos.(FIrpic) | (0.14,0.29) | 3.0V/5.7V/2.7V | 34 |

| | Slope 1 | Slope 2/3 | Slope 4/5 |
|---|---|---|---|
| This Work | 45.71 | 1.6/1.0 | 4.73/0.98 |
| TTA(DPASP) | 9.97 | 0.5/0.9 | 0.46/0.41 |
| TADF(IDCz-DBS) | 3.04 | 0.3/0.4 | 0.43/0.39 |
| Phos.(FIrpic) | 3.72 | 0.8/0.4 | 0.95/0.45 |

**Fig. S3** Comparisons of CHM-HENA-TTAD OLED with amorphous high EQE OLEDs. (a) Comparison of voltage (*V*)-dependent luminance (*L*) curves. (b) Comparison of voltage (*V*)-dependent current density (*J*) characteristics. (c)Comparison of voltage (*V*) with dependent semi-log current density (*J*) characteristics. (d)Comparison of voltage (*V*) with semi-log emitted photons (*N*) between CHM-HENA-TTAD OLED and reported high EQE OLEDs based on TTA, TADF, phosphorescent materials. Reference data for comparison are taken from the relevant literature.

## 4. Summary of PLQYs of thin films

**Table S1** Summary of PLQYs of films.

| The film | $\Phi_{pl}$ |
|---|---|
| 2FPPICz neat crystalline film | 0.29[S1] |
| PyPO neat film | 0.76[S2] |
| DPASP neat film | 0.99[S3] |
| CHM-HENA film | 0.69 |
| CHM-HENA-TTAD film | 0.85 |

## 5. Comparison of CHM-HENA-TTAD OLED with high-EQE amorphous OLEDs

**Table S2** Comparison of CHM-HENA-TTAD OLED with high-EQE amorphous OLEDs.

| Device | $CE/PE/EQE_{max}$ [a)] [cd $A^{-1}$/lm $W^{-1}$/%] | Input power[b)] [mW $cm^{-2}$] | differential resistance[b)] [kΩ·$cm^2$] | Joule heat[b)] [mW $cm^{-2}$] | Ratio[b)] [%] | Ref. |
|---|---|---|---|---|---|---|
| **CHM-HENA-TTAD** | 8.20/8.59/8.16 | 70.20 | 0.020 | 7.0 | 10.06 | **This work** |
| **DPASP** | 18.5/16.5/12.0 | 42.15 | 0.100 | 7.2 | 17.00 | [S3] |
| **IDCz-DBS** | -/29.8/31.1 | 24.32 | 0.329 | 5.2 | 21.19 | [S4] |
| **FIrpic** | 61.7/56.2/34.6 | 15.58 | 0.269 | 2.0 | 13.10 | [S5] |

[a)] Maximum CE, PE and EQE values; [b)] The areal Joule heat loss of the CHM-HENA-TTAD compared with that of other typical amorphous blue-emission OLEDs at a luminance of approximately 1000 cd/$m^2$. All reference data for comparison are extracted from the corresponding literature.

## 6. References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S2. Z. Cheng, C. Du, S. Ge, Y. Wang, F. Liu, Y. Chang, Y. Lv and P. Lu, *Chem. Eng. J.*, 2023, **474**.

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S5. D. Li, J. Li, D. Liu, W. Li, C.-L. Ko, W.-Y. Hung and C. Duan, *ACS Appl. Mater. Interfaces*, 2021, **13**, 13459-13469.