Electronic supplementary information for

A Chemopalette Strategy for White Light by Modulating Monomeric and Excimeric Phosphorescence of a Simple Cu(I) Cyclic Trinuclear Unit

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Experimental Section

Materials. Chemicals and solvents were purchased and used as received without further purification.

Methods. UV-Vis absorption spectra were recorded on a Bio-Logic MOS-500 multifunctional circular dichroism spectrometer. Infrared spectra were obtained in KBr disks on a Thermo Scientific FTIR Nicolet iS10 spectrometer in the range of 4000~400 cm$^{-1}$, and abbreviations used for the IR bands are: w = weak, m = medium, b = broad, s = strong, vs = very strong. Elemental analyses were carried out with an Elementar vario MICRO CUBE equipment. Powder X-ray diffraction (PXRD) experiments were performed on an Rigaku Ultima IV X-ray diffractometer (Cu Kα, λ = 1.5418 Å) in the step of 0.02° under the conditions 40 KV and 40 mA. Steady state photoluminescence spectra were recorded by a single-photon counting spectrometer on a Fluorolog Horiba spectrofluorometer at room temperature. PTI Quanta Master Model QM/TM scanning spectrofluorometer recorded the variable temperature solid-state emission spectra. Absolute quantum yield was recorded by Hamamatsu C11347-01 absolute PL quantum yield spectrometer under room temperature. The different concentrations of Cl-α were achieved by adding different amounts of samples into KBr for solid-state emission measurements. Thermogravimetric analysis curve was recorded by TGA Q50 V20.6 with a heating rate of 10 °C/min from 40 to 800 °C in a N$_2$ atmosphere.

Synthesis and characterization

Cl-α

Cu(NO$_3$)$_2$•3H$_2$O (60.4 mg) and 4-chloropyrazole (51.26 mg) were dissolved in ethanol, then diluted with ethanol into 25.00 mL, so that the concentration of the Cu$^{2+}$ ion and 4-chloropyrazolate are 0.01 mol/L and 0.02 mol/L, respectively. 2.00 ml of above solution was added into a clean and heavy-wall glass tube, followed by the addition of 1.00 mL of chlorobenzene. After flame sealed, these tubes were heated at 140 °C in an oven for 12 h and cooled to room temperature at a rate of 5 °C/h. The yield is 83.3% for Cl-α based on Cu(NO$_3$)$_2$•3H$_2$O.
**Cl-β**

Cu(NO₃)₂•3H₂O (241.60 mg) and 4-chloropyrazole (102.52 mg) were dissolved in ethanol, then diluted with ethanol into 100 mL, so that the concentration of the Cu²⁺ ion and 4-chloropyrazolate are 0.01 mol/L and 0.01 mol/L, respectively. 2.00 mL of above solution was added into a clean and dry heavy-wall glass tube, followed by the addition of 1.00 mL of chlorobenzene. After flame sealed, these tubes were heated at 140 °C in an oven for 24 h and cooled to room temperature at a rate of 5 °C/h. Colorless needle crystals were collected and air-dried, although sometimes mixed with Cl-α, suggested by their different emission colors (blue for Cl-α and orange for Cl-β) under 365 nm UV light. The yield is 54.5% for Cl-β based on Cu(NO₃)₂•3H₂O.

**FT-IR and Elemental analyses**

**Cl-α**

FT-IR (KBr pellet, cm⁻¹): 3122(m), 1643(m), 1392(s), 1302(s), 1223(w), 1197(s), 1160(s), 1054(s), 1012(m), 970(s), 832(s), 613(s). Elemental analyses (Cu₃C₉H₆N₆Cl₃), calculated (%): C 21.83, H 1.22, N 16.97; found (%): C 22.25, H 1.28, N 16.56.

**Cl-β**

FT-IR (KBr pellet, cm⁻¹): 3118(m), 1644(m), 1388(s), 1298(s), 1223(w), 1198(s), 1157(s), 1056(s), 1010(w), 968(s), 833(s), 820(s), 611(s). Elemental analyses (Cu₃C₉H₆N₆Cl₃), calculated (%): C 21.83, H 1.22, N 16.97; found (%): C 22.05, H 1.31, N 16.59.

*Caution!* In the solvothermal crystallization processes, the volume of solution should not exceed one third of the volume of the glass tubes. Be careful and avoid potential empyrosis and incised wound when flame-sealing and opening the glass tubes.
**Fig. S1** Comparison of the experimental and simulated PXRD patterns of polymorphs. Note that the simulated patterns are extracted from the corresponding single-crystal X-ray data obtained at 300 K.

**Fig. S2** Thermogravimetric analyses curves of CI-α and CI-β.
Crystal Data

Suitable single crystals of Cl-α/Cl-β were mounted with glue at the end of a glass fiber. Data collection was performed on an Oxford Diffraction XtalAB [Rigaku(Cu) X-ray dual wavelength source, Kα, λ = 1.5418 Å] equipped with a monochromator and CCD plate detector (CrysAlisPro CCD, Oxford Diffraction Ltd) at 150 K, 300 K. Structures were solved by direct methods by ShelXS in Olex2 1.2 and refined on $F^2$ using full-matrix least-squares (SHELXL-2016/6 in Olex2 1.2). All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Crystal data and structure refinement parameters are summarized in Table S1. The crystals of the Cl-α form in Pbcn have crystallographically-imposed twofold symmetry and that in the Cl-β form in Pbca with no crystallographically imposed symmetry. CCDC Nos. 1889441-1889444.

<table>
<thead>
<tr>
<th>Table S1 Summary of the structure refinement and crystallographic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>C$_9$H$_6$Cu$_3$Cl$_3$N$_6$</td>
</tr>
<tr>
<td>Formula weight</td>
</tr>
<tr>
<td>Temperature (K)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
</tr>
<tr>
<td>Crystal system</td>
</tr>
<tr>
<td>space group</td>
</tr>
<tr>
<td>a (Å)</td>
</tr>
<tr>
<td>b (Å)</td>
</tr>
<tr>
<td>c (Å)</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>$\rho_{calc}$ (g/cm$^3$)</td>
</tr>
<tr>
<td>F(000)</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>Theta range for data collection (°)</td>
</tr>
<tr>
<td>Total reflections</td>
</tr>
<tr>
<td>Unique reflections</td>
</tr>
<tr>
<td>( R_{int} )</td>
</tr>
<tr>
<td>Completeness (%)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
</tr>
<tr>
<td>Goodness-of-fit on ( F^2 )</td>
</tr>
<tr>
<td>( R_I ) [I&gt;2sigma(I)]</td>
</tr>
<tr>
<td>( wR^2 ) (all data)</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e/Å³)</td>
</tr>
</tbody>
</table>

\[ aR_I = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \quad wR^2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum [w(F_o^2)^2]} \quad w = 1/ [\sigma^2(F_o^2) + (aP)^2 + bP], \text{ where} \\
\text{P = [max}(F_o^2,0) + 2F_c^2)/3 \text{ for all data.} \]

### Table S2 Selected bond lengths (Å) and angles (°)

<table>
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<tr>
<th>Cl-α (150 K)</th>
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<tbody>
<tr>
<td>Cu(1)-N(1)</td>
<td>1.865(4)</td>
</tr>
<tr>
<td>Cu(2)-N(3)</td>
<td>1.859(4)</td>
</tr>
<tr>
<td>N(2)-Cu(1)-N(1)</td>
<td>179.03(19)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cl-α (300 K)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-N(1)</td>
<td>1.870(8)</td>
</tr>
<tr>
<td>Cu(2)-N(3)</td>
<td>1.859(10)</td>
</tr>
<tr>
<td>N(2)-Cu(1)-N(1)</td>
<td>178.6(5)</td>
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</table>

<table>
<thead>
<tr>
<th>Cl-β (150 K)</th>
<th></th>
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<tbody>
<tr>
<td>Cu(1)-Cu(2)#1</td>
<td>2.9150(11)</td>
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<tr>
<td>Cu(1)-N(2)</td>
<td>1.860(4)</td>
</tr>
<tr>
<td>Cu(2)-N(5)</td>
<td>1.861(5)</td>
</tr>
<tr>
<td>Cu(3)-N(6)</td>
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<td>N(2)-Cu(1)-N(3)</td>
<td>175.8(2)</td>
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</table>
N(5)-Cu(2)-N(4)  175.7(2)  --  --

<table>
<thead>
<tr>
<th>Crystal</th>
<th>d(Cu···Cu, intra) a (Å)</th>
<th>d(Cu···Cu, inter) a (Å)</th>
<th>d(C–Cl) b (Å)</th>
<th>d(C···Cl) c (Å)</th>
<th>Angle (°)</th>
<th>Torsion Angle d (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-α</td>
<td>3.24443(7)</td>
<td>~3.26519(7)</td>
<td>3.37382(9)</td>
<td>~3.45494(6)</td>
<td>129.8696(12)</td>
<td>~3.55708(7)</td>
</tr>
<tr>
<td></td>
<td>~3.52981(8)</td>
<td>~3.75789(7)</td>
<td>3.63562(6)</td>
<td>~3.82579(4)</td>
<td>~132.7983(4)</td>
<td>~4.06732(8)</td>
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<tr>
<td>Cl-β</td>
<td>3.17891(8)</td>
<td>~3.27406(6)</td>
<td>3.16889(6)</td>
<td>~3.43789(7)</td>
<td>115.013(2)</td>
<td>~5.27221(10)</td>
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<tr>
<td></td>
<td>~2.9150(11)</td>
<td>~3.95366(9)</td>
<td>3.50231(10)</td>
<td>~129.3707(11)</td>
<td>~14.80595(15)</td>
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Intra-and inter-molecular Cu···Cu distance; Cu···Cl distance between molecules; D···A distance and D–H···A angle for C–H···Cl hydrogen bonding, where D = C and A = Cl; Torsion angle between Cu(I) trinuclear plane and pyrazole plane.

**Table S3** Structural parameters related to supramolecular interactions (150 K)

<table>
<thead>
<tr>
<th>Crystal</th>
<th>d(Cu···Cu,intra) a (Å)</th>
<th>d(Cu···Cu, inter) a (Å)</th>
<th>d(C–Cl) b (Å)</th>
<th>d(C···Cl) c (Å)</th>
<th>Angle (C–H···Cl) c (°)</th>
<th>Torsion Angle d (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-α</td>
<td>3.2343(3)</td>
<td>~3.2380(3)</td>
<td>3.4199(3)</td>
<td>~3.5479(3)</td>
<td>132.086(5)</td>
<td>~133.021(2)</td>
</tr>
<tr>
<td></td>
<td>~3.5414(5)</td>
<td>~3.8257(4)</td>
<td>3.6850(2)</td>
<td>~3.96594(17)</td>
<td>~130.381(2)</td>
<td>~14.4330(3)</td>
</tr>
<tr>
<td>Cl-β</td>
<td>3.17315(15)</td>
<td>~3.2625(12)</td>
<td>3.21854(12)</td>
<td>~3.48095(16)</td>
<td>116.513(3)</td>
<td>~4.82003(18)</td>
</tr>
<tr>
<td></td>
<td>~2.9706(12)</td>
<td>~3.96594(17)</td>
<td>3.54907(18)</td>
<td>~130.381(2)</td>
<td>~4.82003(18)</td>
<td>~14.4330(3)</td>
</tr>
</tbody>
</table>

Intra-and inter-molecular Cu···Cu distance; Cu···Cl distance between molecules; D···A distance and D–H···A angle for C–H···Cl hydrogen bonding, where D = C and A = Cl; Torsion angle between Cu(I) trinuclear plane and pyrazole plane.

**Table S4** Structural parameters related to supramolecular interactions (300 K)

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<tr>
<th>Crystal</th>
<th>d(Cu···Cu,intra) a (Å)</th>
<th>d(Cu···Cu, inter) a (Å)</th>
<th>d(C–Cl) b (Å)</th>
<th>d(C···Cl) c (Å)</th>
<th>Angle (C–H···Cl) c (°)</th>
<th>Torsion Angle d (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-α</td>
<td>3.2343(3)</td>
<td>~3.2380(3)</td>
<td>3.4199(3)</td>
<td>~3.5479(3)</td>
<td>132.086(5)</td>
<td>~133.021(2)</td>
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<td></td>
<td>~3.5414(5)</td>
<td>~3.8257(4)</td>
<td>3.6850(2)</td>
<td>~3.96594(17)</td>
<td>~130.381(2)</td>
<td>~14.4330(3)</td>
</tr>
<tr>
<td>Cl-β</td>
<td>3.17315(15)</td>
<td>~3.2625(12)</td>
<td>3.21854(12)</td>
<td>~3.48095(16)</td>
<td>116.513(3)</td>
<td>~4.82003(18)</td>
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<td>~2.9706(12)</td>
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<td>3.54907(18)</td>
<td>~130.381(2)</td>
<td>~4.82003(18)</td>
<td>~14.4330(3)</td>
</tr>
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</table>

Intra-and inter-molecular Cu···Cu distance; Cu···Cl distance between molecules; D···A distance and D–H···A angle for C–H···Cl hydrogen bonding, where D = C and A = Cl; Torsion angle between Cu(I) trinuclear plane and pyrazole plane.

**Fig. S3** The asymmetric units of Cl-α shown by ORTEP diagrams of 50% probability.
Fig. S4 The asymmetric units of Cl-β shown by ORTEP diagrams of 50% probability.

Fig. S5 Packing modes of Cl-α (300 K), showing the wave layer structure constructed by intralayer Cl-related non-covalent interactions.

Fig. S6 Packing modes of Cl-β (300 K), showing the three-dimensional supramolecular framework along (a) the b axis and (b) the c axis.
**Photoluminescence data**

**Fig. S7** The solid-state excitation spectra of (a) Cl-α; (b) Cl-β at 300 K.

**Table S5** The average emission lifetime ($\mu$s) of polymorphs in 77 K and 300 K

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>$\lambda_{ex}$</th>
<th>$\lambda_{em}$</th>
<th>77 K</th>
<th>300 K</th>
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<tbody>
<tr>
<td>Cl-α</td>
<td>290</td>
<td>480</td>
<td>55.98</td>
<td>19.84</td>
</tr>
<tr>
<td></td>
<td>290</td>
<td>564</td>
<td>40.80</td>
<td>42.18</td>
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<tr>
<td></td>
<td>310</td>
<td>480</td>
<td>47.99</td>
<td>21.56</td>
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<td></td>
<td>310</td>
<td>564</td>
<td>54.28</td>
<td>33.36</td>
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<tr>
<td>Cl-β</td>
<td>330</td>
<td>650</td>
<td>40.97</td>
<td>29.96</td>
</tr>
</tbody>
</table>

**Fig. S8** The solid-state emission spectra for (a) low concentration (LC) and high concentration (HC) of Cl-α in KBr at 270 nm excitation, pure sample in Cl-α at 290 nm and 310 nm excitation (normalized); (b) LC at different excitation wavelength, dash rectangle indicates KBr sample peak; (c) HC at different excitation wavelength. Pure KBr was used as background and its spectra (yellow curve) were amplified 20 times in (b), 40 times in (c).
Fig. S9  Photographs of LEDs: (a) a 260 nm reference UV LED (commercially available); LED coated with a thin layer of (b) Cl-α, (c) Cl-β; (d) the not coated LED showing a purple light; (e) the LED coated with Cl-α illuminating bright yellow light; (f) the LED coated with Cl-β illuminating bright orange light.

Fig. S10  Photographs of deposited polymorphs crystals on quartz glass (300 K): (a) Cl-α excited at 365 nm; (b) Cl-α excited at 254 nm, (c) Cl-α excited at 310 nm; (d) Cl-β excited at 330 nm.
**Computational Detail**

**Non-covalent Interaction Analysis**

Reduced density gradient (RDG) analysis is a convenient and cost-effective method for exploring supramolecular interactions, developed by Wei-Tao Yang et al\(^3\) and Tian Lu\(^4\). Color-filled RDG isosurface between two interacting atoms or molecules indicate strong attraction (e.g. hydrogen bond), weak attraction (e.g. van der Waals interaction), weak repulsion, and strong repulsion by blue, green, brown, and red colors, respectively. Repulsion herein could be also expressed as steric hindrance.

The RDG analysis based on promolecular density embedded in Multiwfn 3.5\(^4\) allows our rapid non-covalent interaction analysis for large supramolecular unit taken from a crystal after inputting XYZ file of this supramolecular unit.

Herein, the supramolecular units containing a [Cu(ClPz)]\(_3\) molecule and its surrounding molecules not connected by Cu···Cu interaction are chosen for both polymorphs at 300 K, in order to explore the supramolecular interactions orthogonal to intermolecular Cu···Cu bonding. The color-filled RDG isosurfaces were created in the cubic space centered at the geometrical center of the central [Cu(ClPz)]\(_3\) molecule with extended distance for 23 Bohr in X, Y, Z direction, and the total grid numbers are 12167000 for both polymorphs.

**Photophysical process**

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed for clarifying photophysical process in both polymorphs.

All calculations were carried out using Gaussian 09 software package\(^\text{55}\) and some of the output files were used as input files of Multiwfn 3.5 software packages\(^4\) to perform wave function analysis.

PBE0 functional\(^6,^7\) was used throughout unless otherwise mentioned, and effective core potential (ECP) of LanL2dz basis set was used for Cu and 6-31G** basis set was used for other atoms, based on the following calculated models:

1. **M**: the optimized monomer of a [Cu(ClPz)]\(_3\).
2. **Cl-α-M**: the monomer taken from the X-ray structure of Cl-α at 150 K.
(3) **Cl-β-M**: the monomer taken from the X-ray structure of Cl-β at 150 K.

(4) **D**: the optimized geometry of chair dimer of [Cu(ClPz)]₃ from the Cl-α at 150 K, displaying intermolecular Cu···Cu interaction.

(5) **Cl-α-D**: the dimer taken from the X-ray structure of Cl-α at 150 K, displaying intermolecular Cu···Cu interaction.

(6) **Cl-β-D**: the dimer taken from the X-ray structure of Cl-β at 150 K, displaying intermolecular Cu···Cu interaction.

(7) **Cl-α-D(Cl)**: the dimer of [Cu(ClPz)]₃ taken from the X-ray structure of Cl-α at 150 K, displaying the Cu···Cl, Cl···H-C interaction. The TDDFT results for this additional model (Table S20) shows that both the lowest-energy singlet and triplet excited states (S₁ and T₁) locate in only one [Cu(ClPz)]₃ molecule, confirming that the low-energy excimeric phosphorescence arise from the excimer formed by intermolecular Cu···Cu bonding but Cl-involved interactions.

Electron density difference (EDD) maps (isovalue = 5.0×10⁻⁴ a.u.) were obtained to provide accurate assignments of excited states by calculating the first 20 singlet-singlet spin-allowed transitions and the first 40 singlet-triplet spin-forbidden transitions with IOp(9/40=4) and then the results were further treated by Multiwfn 3.5 software packages using the formatted checkpoint file (fchk files) as well as the Gaussian output file (log files) as input files.

Oscillator strengths are denoted as f. MMCT = metal-metal charge transfer; ILCT = intraligand charge transfer; MLCT = metal-to-ligand charge transfer; LMMCT = ligand-to-metal-metal-bonding charge transfer.

Note that the models without optimization are taken from X-ray data at 150 K rather than at 300 K for higher quality of crystal data, but the key structural parameters are very similar in both temperatures.

The key intramolecular structural parameters for both polymorphs at either 300 K or 150 K have been well-reproduced in optimized geometries, and the intermolecular Cu···Cu distances lie between those of Cl-α and Cl-β at either temperature (Table S6).

For confirming that TD-PBE0 functional is suitable for our systems, M06-2X and
ωB97XD\textsuperscript{59} functional, which are usually considered to be more suitable for charge-transfer excited states than PBE0, are used in TD-DFT calculations for calculating the lowest-lying spin-allowed and spin-forbidden transitions based on the monomer and chair dimer models for Cl-\textit{a} at 150 K. The results (Table S7) show that PBE0 functional seems more suitable for our systems, because the calculated lowest-lying transition energies PBE0 are the closest to experimental excitation wavelengths among the above three functionals. Moreover, the assignments of excited states indicated by EDD maps show neglectable difference for the same electronic states based on the same models between these functionals, except for the T\textsubscript{1} state of monomer show the largest contributions from ligands at ωB97XD level.

![Fig. S11](image)

**Fig. S11** Color-filled RDG isosurfaces for polymorphs (isovalue = 0.5 a.u.) at 300 K, showing the supramolecular interaction related to Cl, (a) Cl-\textit{a}; (b) Cl-\textit{β}, red circle means the Cu atoms interact with pyzaolate of adjacent molecule, while the blue circle means the interaction between the Cu atoms and Cl atoms. Green isosurfaces between molecules indicates Cu···Cl and C-H···Cl interactions in the level of van der Waals attraction, while brown isosurfaces indicates weak steric hindrance (ranging from -0.03 to 0.02 a.u.).
Table S6 The comparison between X-ray data and optimized geometries of polymorphs

<table>
<thead>
<tr>
<th></th>
<th>M</th>
<th>D</th>
<th>Cl-α (150 K)</th>
<th>Cl-β (150 K)</th>
<th>Cl-α (300 K)</th>
<th>Cl-β (300 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Cu····Cu,intra)</td>
<td>3.249</td>
<td>3.245</td>
<td>3.244</td>
<td>3.179</td>
<td>3.234</td>
<td>3.173</td>
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<tr>
<td>d(Cu···Cu,inter)</td>
<td></td>
<td>3.167</td>
<td>3.530,</td>
<td>2.915,</td>
<td>3.541,</td>
<td>2.970</td>
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<td>Å</td>
<td>--</td>
<td>3.167</td>
<td>3.530,</td>
<td>2.915,</td>
<td>3.541,</td>
<td>2.970</td>
</tr>
<tr>
<td>N-Cu-N(°)</td>
<td>179.5</td>
<td>172.6</td>
<td>179.0</td>
<td>175.7</td>
<td>178.6</td>
<td>176.0</td>
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<td>~179.6</td>
<td>~176.7</td>
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<td>Torsion Angle(°)</td>
<td>0</td>
<td>3.91</td>
<td>3.56</td>
<td>5.27</td>
<td>2.39</td>
<td>4.82</td>
</tr>
<tr>
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<td>0</td>
<td>7.42</td>
<td>3.56</td>
<td>14.58</td>
<td>2.39</td>
<td>13.47</td>
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<tr>
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<td>0</td>
<td>8.31</td>
<td>4.06</td>
<td>14.80</td>
<td>6.58</td>
<td>14.43</td>
</tr>
</tbody>
</table>

*Torsion angle between trinuclear plane and pyrazole plane

Fig. S12 The optimized geometry for the dimer (D), showing two kinds of intermolecular Cu···Cu contacts with the distances of 3.254 Å (d1) and 3.167 Å (d2), respectively.
Comment:

The HOMO in each model consists of the $\pi^*$ orbitals of the pyrazolates and the d orbitals of the Cu(I) ions, while the LUMO is the typical Cu···Cu bonding orbital. These features are similar to those of Cu$_3$Pz$_3$ without any aromatic substituents, although $p$--$\pi$ conjugation between Cl and the pyrazolyl ring increases ligand participation in the FMOs of [Cu(ClPz)$_3$].

<table>
<thead>
<tr>
<th>Table S7</th>
<th>Comparison for TDDFT results with various functionals based on the monomer and dimer models taken from X-ray data for Cl-α at 150 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Monomer</td>
</tr>
<tr>
<td>PBE0</td>
<td>$S_1$</td>
</tr>
<tr>
<td></td>
<td>$E = 4.697$ eV, $\lambda = 264.1$ nm, $f = 0.00$</td>
</tr>
<tr>
<td></td>
<td>$E = 4.106$ eV, $\lambda = 302.2$ nm</td>
</tr>
<tr>
<td>Method</td>
<td>State</td>
</tr>
<tr>
<td>------------</td>
<td>-------</td>
</tr>
<tr>
<td>M06-2X</td>
<td>S₁</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T₁</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>ωB97XD</td>
<td>S₁</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T₁</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table S8 Comparison of maximum oscillator strengths between the [Cu(ClPz)]₃ and [Cu(EBP)]₃ among the first 10 singlet-singlet spin-allowed transitions at TD-PBE0/(LanL2dz for Cu and 6-31G** for other atoms) level

<table>
<thead>
<tr>
<th></th>
<th>Monomer</th>
<th>Dimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(ClPz)]₃ (optimized)</td>
<td>0.04</td>
<td>0.07</td>
</tr>
<tr>
<td>Cl-α</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>Cl-β</td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td>[Cu(EBP)]₃</td>
<td>1.05</td>
<td>0.96</td>
</tr>
</tbody>
</table>

a reference S10. EBP = ethyl-4′-benzoate-3,5-dimethylpyrazolate. [Cu(EBP)]₃ is complex 1 in reference S10. b Taken from SCXRD data at 150 K. c Chair dimers.

Fig S14 The experimental UV-Vis absorption (black curve) and excitation spectra (blue and red curves) in comparison with the simulated UV-Vis absorption spectra of (a) showing only S₀→S₁ transitions for a monomer and a dimer denoted only their wavelengths but oscillator strengths by two magenta columns, and (b) all our simulated singlet-singlet transitions for a monomer and a chair dimer for Cl-α. (c) The experimental UV-Vis absorption (black curve) and excitation spectra (red curve) in comparison with the simulated UV-Vis absorption spectra (blue columns) of a chair dimer for Cl-β, and the magenta column denotes the wavelength of S₀→S₁ transition but oscillator strength.

Comment:

Compared with our previously reported [Cu(EBP)]₃, the oscillator strengths for [Cu(ClPz)]₃ are much smaller among the first 10 singlet excited states (Table S7). Besides, the experimental optimal excitation wavelengths for triggering yellow, white, or blue light for Cl-α and orange light for Cl-β, lie in the weak absorption regions in their UV-Vis absorption spectra (Fig. S14), indicating these optimal excitations are weak allowed transitions. As a result, it seems reasonable to propose that the excitations at 270 nm and 310 nm for Cl-α corresponds to S₀→S₁ transitions of a dimer and a monomer, respectively, although their oscillator strengths are quite close to 0. Moreover, since the 330 nm excitation for blue light is weaker than 310 nm for white light, the 330
nm is more likely a spin-forbidden monomeric \(S_0 \rightarrow T_1\) excitation. Previously, Omary and Dias have figured out that the bright orange light for \{Cu[3,5-(CF_3)_2-Pz]\}_3 arise from a spin-forbidden excitation, based on their comprehensive spectroscopic evidences.511 The optimal excitation (\(\lambda_{ex} = 330\) nm) for orange light of \(\text{Cl-}\beta\) should arise from the \(S_0 \rightarrow S_1\) transitions of a dimer. Indeed, the calculated wavelengths for \(S_0(M) \rightarrow T_1(M)\) transitions are 260 nm for \(\text{Cl-}\alpha\) and 293 nm for \(\text{Cl-}\beta\), consistent with the order of experimental excitations (270 nm for \(\text{Cl-}\alpha\) and 330 nm for \(\text{Cl-}\beta\)).

Table S9 The comparison between X-ray data at 300 K and optimized geometries (\(S_0\) and \(T_1\)) of polymorphs

<table>
<thead>
<tr>
<th></th>
<th>(\text{Cl-}\alpha)</th>
<th>(\text{Cl-}\beta)</th>
<th>(S_0)</th>
<th>(T_1^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{(\text{Cu-}\cdots\text{Cu, intra})}) (Å)</td>
<td>3.234, ~3.238</td>
<td>3.172, ~3.263</td>
<td>3.245, ~3.266</td>
<td>2.653, ~3.089</td>
</tr>
<tr>
<td>(d_{(\text{Cu-}\cdots\text{Cu, inter})}) (Å)</td>
<td>3.541, 3.541</td>
<td>2.970, 2.970</td>
<td>3.167, 3.167, 3.254, 3.254</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)The geometry of the chair dimer in \(T_1\) state was optimized at unrestricted PBE0 level, resulting in the typical Cu-\cdots Cu bonding excimer, suggested by the significant shorter Cu-\cdots Cu distances compared with those in the optimized \(S_0\) state.

Table S10 TDDFT results of selected \(S_0 \rightarrow S_n\) transitions for \(M\)

<table>
<thead>
<tr>
<th>No.</th>
<th>(\lambda) (nm)</th>
<th>(E) (eV)</th>
<th>(f)</th>
<th>EDD</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>268.3</td>
<td>4.625</td>
<td>0.00</td>
<td></td>
<td>(^1)LMMCT/(^1)ILCT/</td>
</tr>
<tr>
<td>3</td>
<td>255.9</td>
<td>4.849</td>
<td>0.04</td>
<td></td>
<td>(^1)MMCT/(^1)MLCT/(^1)ILCT</td>
</tr>
</tbody>
</table>
Table S11 TDDFT results of selected S₀→Tₙ transitions for M

<table>
<thead>
<tr>
<th>No.</th>
<th>λ (nm)</th>
<th>E (eV)</th>
<th>EDD</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>313.2</td>
<td>3.961</td>
<td></td>
<td>³MMCT/³MLCT</td>
</tr>
<tr>
<td>2</td>
<td>313.1</td>
<td>3.962</td>
<td></td>
<td>³MMLCT</td>
</tr>
<tr>
<td>11</td>
<td>268.9</td>
<td>4.615</td>
<td></td>
<td>³MLCT</td>
</tr>
<tr>
<td>12</td>
<td>260.4</td>
<td>4.765</td>
<td></td>
<td>³LMMCT</td>
</tr>
</tbody>
</table>

Table S12 TDDFT results of selected S₀→Sₙ transitions for D

<table>
<thead>
<tr>
<th>No.</th>
<th>λ (nm)</th>
<th>E (eV)</th>
<th>f</th>
<th>EDD</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Side view</td>
<td>Top view</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>305.2</td>
<td>4.065</td>
<td>0.00</td>
<td></td>
<td>³MMCT</td>
</tr>
<tr>
<td>3</td>
<td>298.8</td>
<td>4.153</td>
<td>0.01</td>
<td></td>
<td>³MMCT</td>
</tr>
<tr>
<td>No.</td>
<td>( \lambda ) (nm)</td>
<td>E (eV)</td>
<td>EDD</td>
<td>Assignment</td>
<td></td>
</tr>
<tr>
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<td>--------</td>
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<td>------------</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>362.8</td>
<td>3.420</td>
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<td>( ^3 )MMCT</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>301.0</td>
<td>4.122</td>
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<td>( ^3 )LMMCT</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>289.5</td>
<td>4.286</td>
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<td>( ^3 )MMCT</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>282.1</td>
<td>4.398</td>
<td><img src="image7" alt="Side view" /> <img src="image8" alt="Top view" /></td>
<td>( ^3 )LMMCT</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>273.6</td>
<td>4.535</td>
<td><img src="image9" alt="Side view" /> <img src="image10" alt="Top view" /></td>
<td>( ^3 )ILCT</td>
<td></td>
</tr>
</tbody>
</table>

**Table S13** TDDFT results of selected \( S_0 \rightarrow T_n \) transitions for **D**

<table>
<thead>
<tr>
<th>No.</th>
<th>( \lambda ) (nm)</th>
<th>E (eV)</th>
<th>( f )</th>
<th>EDD</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>264.1</td>
<td>4.697</td>
<td>0.00</td>
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<td>( ^1 )LMMCT/ ( ^1 )ILCT</td>
</tr>
<tr>
<td>3</td>
<td>251.0</td>
<td>4.944</td>
<td>0.03</td>
<td><img src="image13" alt="Side view" /> <img src="image14" alt="Top view" /></td>
<td>( ^1 )MMCT/ ( ^1 )ILCT</td>
</tr>
</tbody>
</table>
Table S15 TDDFT results of selected $S_0 \rightarrow T_n$ transitions for Cl-$\alpha$-M

<table>
<thead>
<tr>
<th>No.</th>
<th>$\lambda$ (nm)</th>
<th>E (eV)</th>
<th>EDD</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>302.2</td>
<td>4.106</td>
<td>3</td>
<td>$^3$MMCT/$^3$MLCT</td>
</tr>
<tr>
<td>11</td>
<td>268.3</td>
<td>4.624</td>
<td>3</td>
<td>$^3$LMMCT/$^3$ILCT</td>
</tr>
<tr>
<td>12</td>
<td>252.3</td>
<td>4.919</td>
<td></td>
<td>$^3$LMMCT</td>
</tr>
<tr>
<td>27</td>
<td>224.2</td>
<td>5.534</td>
<td></td>
<td>$^3$LMMCT/$^3$ILCT</td>
</tr>
</tbody>
</table>
**Table S16** TDDFT results of selected $S_0 \rightarrow S_n$ transitions for Cl-$\alpha$-D

<table>
<thead>
<tr>
<th>No.</th>
<th>$\lambda$ (nm)</th>
<th>$E$ (eV)</th>
<th>$f$</th>
<th>EDD</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Side view</td>
<td>Top view</td>
</tr>
<tr>
<td>1.</td>
<td>260.1</td>
<td>4.771</td>
<td>0.00</td>
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<td><img src="image2" alt="Diagram" /></td>
</tr>
<tr>
<td>3</td>
<td>258.7</td>
<td>4.797</td>
<td>0.04</td>
<td><img src="image3" alt="Diagram" /></td>
<td><img src="image4" alt="Diagram" /></td>
</tr>
<tr>
<td>8</td>
<td>249.6</td>
<td>4.972</td>
<td>0.03</td>
<td><img src="image5" alt="Diagram" /></td>
<td><img src="image6" alt="Diagram" /></td>
</tr>
</tbody>
</table>

**Table S17** TDDFT results of selected $S_0 \rightarrow T_n$ transitions for Cl-$\alpha$-D

<table>
<thead>
<tr>
<th>No.</th>
<th>$\lambda$ (nm)</th>
<th>$E$ (eV)</th>
<th>$f$</th>
<th>EDD</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Side view</td>
<td>Top view</td>
</tr>
<tr>
<td>1</td>
<td>302.7</td>
<td>4.099</td>
<td></td>
<td><img src="image7" alt="Diagram" /></td>
<td><img src="image8" alt="Diagram" /></td>
</tr>
<tr>
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<td>4.102</td>
<td></td>
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<td><img src="image10" alt="Diagram" /></td>
</tr>
<tr>
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<td><img src="image12" alt="Diagram" /></td>
</tr>
<tr>
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<td><img src="image14" alt="Diagram" /></td>
</tr>
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<tr>
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<td>4.805</td>
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</tr>
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<td>24</td>
<td>252.0</td>
<td>4.924</td>
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</tr>
<tr>
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<td>4.976</td>
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</tr>
<tr>
<td>26</td>
<td>249.1</td>
<td>4.980</td>
<td></td>
<td><img src="image23" alt="Diagram" /></td>
<td><img src="image24" alt="Diagram" /></td>
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</table>
Table S18 TDDFT results of selected S\textsubscript{0}→S\textsubscript{n} transitions for Cl-\(\beta\)-M

<table>
<thead>
<tr>
<th>No.</th>
<th>(\lambda) (nm)</th>
<th>E (eV)</th>
<th>(f)</th>
<th>EDD</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>265.0</td>
<td>4.681</td>
<td>0.00</td>
<td></td>
<td>(^1)MMCT/(^1)ILCT</td>
</tr>
<tr>
<td>3</td>
<td>254.0</td>
<td>4.884</td>
<td>0.04</td>
<td></td>
<td>(^1)MMCT</td>
</tr>
<tr>
<td>4</td>
<td>252.2</td>
<td>4.919</td>
<td>0.04</td>
<td></td>
<td>(^1)MMLCT/(^1)ILCT</td>
</tr>
<tr>
<td>9</td>
<td>224.1</td>
<td>5.537</td>
<td>0.02</td>
<td></td>
<td>(^1)MLCT</td>
</tr>
</tbody>
</table>

Table S19 TDDFT results of selected S\textsubscript{0}→T\textsubscript{n} transitions for Cl-\(\beta\)-M

<table>
<thead>
<tr>
<th>No.</th>
<th>(\lambda) (nm)</th>
<th>E (eV)</th>
<th>EDD</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>308.5</td>
<td>4.021</td>
<td></td>
<td>(^3)MMCT</td>
</tr>
</tbody>
</table>
Table S20 TDDFT results of selected $S_0\rightarrow S_n$ transitions for Cl-$\beta$-D

<table>
<thead>
<tr>
<th>No.</th>
<th>$\lambda$ (nm)</th>
<th>E (eV)</th>
<th>$f$</th>
<th>EDD</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Side view</td>
<td>Top view</td>
</tr>
<tr>
<td>1</td>
<td>293.2</td>
<td>4.232</td>
<td>0.00</td>
<td><img src="image" alt="Side view" /> <img src="image" alt="Top view" /></td>
<td>$^1$MMCT/ $^1$ILCT</td>
</tr>
<tr>
<td>3</td>
<td>281.7</td>
<td>4.405</td>
<td>0.04</td>
<td><img src="image" alt="Side view" /> <img src="image" alt="Top view" /></td>
<td>$^1$LMMCT</td>
</tr>
<tr>
<td>6</td>
<td>272.4</td>
<td>4.556</td>
<td>0.01</td>
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<td>$^1$LMMCT</td>
</tr>
<tr>
<td>8</td>
<td>262.4</td>
<td>4.729</td>
<td>0.03</td>
<td><img src="image" alt="Side view" /> <img src="image" alt="Top view" /></td>
<td>$^1$MMCT</td>
</tr>
<tr>
<td>9</td>
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<td>0.07</td>
<td><img src="image" alt="Side view" /> <img src="image" alt="Top view" /></td>
<td>$^1$LMMCT</td>
</tr>
</tbody>
</table>

Table S21 TDDFT results of selected $S_0\rightarrow T_n$ transitions for Cl-$\beta$-D

<table>
<thead>
<tr>
<th>No.</th>
<th>$\lambda$ (nm)</th>
<th>E (eV)</th>
<th>EDD</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Side view</td>
<td>Top view</td>
</tr>
<tr>
<td>1</td>
<td>343.1</td>
<td>3.616</td>
<td><img src="image" alt="Side view" /> <img src="image" alt="Top view" /></td>
<td>$^3$MMCT</td>
</tr>
<tr>
<td>Selected state</td>
<td>$\lambda$ (nm)</td>
<td>$E$ (eV)</td>
<td>$f$</td>
<td>EDD</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------</td>
<td>-----------</td>
<td>----</td>
<td>-----</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_1$</td>
<td>264.0</td>
<td>4.700</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>$S_0 \rightarrow T_1$</td>
<td>303.0</td>
<td>4.095</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

**Table S22** Selected TDDFT results of Cl-$\alpha$-D(Cl), showing that the non-covalent interactions related to Cl does not take part in the lowest-lying transitions.
**Fig. S15** The lowest-lying singlet-singlet and singlet-triplet vertical transition energies for the monomers in the optimized geometry (M), the single crystal of Cl-α at 150 K (Cl-α-M) and the single crystal of Cl-β at 150 K (Cl-β-M), showing the relationship between the energies of excited states and the maximum and average torsion angle (denoted as maxTA and aveTA, respectively).

**Fig. S16** The lowest-lying singlet-singlet and singlet-triplet vertical transition energies for the dimers in the optimized geometry and its modified versions (D), the single crystal of Cl-α at 150 K (Cl-α-D) and the single crystal of Cl-β at 150 K (Cl-β-D), showing the increasing energies of excited states following by the increasing intermolecular Cu···Cu distances. Herein, the data points denoted as D in the blue box refer to the transition energies for the optimized geometry (d1 = 3.254 Å) and its modified versions by simply changing d1 to 3.200 Å and 3.400 Å, respectively. See Fig. S12 for d1. Although the distorted molecular conformations in Cl-β-D results in the higher-lying S1 and T1 states than those for D, its energies are still much lower than those for Cl-α-D.
Literature survey for Cu$_3$pyrazolate$_3$

Table S23 Summary of intra- and inter-molecular Cu···Cu distance of cyclic Cu$_3$pyrazolate$_3$ for polymorphs.

<table>
<thead>
<tr>
<th>The pyrazolate ligand</th>
<th>T(K)</th>
<th>d(Cu···Cu, intra) (Å)</th>
<th>d(Cu···Cu, inter) (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,5-dimethylpyrazolate</td>
<td>295</td>
<td>3.195~ 3.258</td>
<td>2.944(2), 2.947(2)</td>
<td>S12</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>3.1950(5)~ 3.2582(5)</td>
<td>2.9534(5), 2.9534(5)</td>
<td>S13</td>
</tr>
<tr>
<td>4-(4-bromophenyl)-3,5-dimethylpyrazolate (Br-α)</td>
<td>293</td>
<td>3.1617(14)~ 3.2570(14)</td>
<td>2.8622(15)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3.1523(9)~ 3.2741(9)</td>
<td>2.8174(9)</td>
<td></td>
</tr>
<tr>
<td>4-(4-bromophenyl)-3,5-dimethylpyrazolate (Br-β)</td>
<td>100</td>
<td>3.1435(47)~ 3.2784(50)</td>
<td>3.020(3), 3.038(4)</td>
<td></td>
</tr>
<tr>
<td>ethyl-4′-benzoate-3,5-dimethyl-pyrazolate (2a)</td>
<td>293</td>
<td>3.160(2)~ 3.230(2)</td>
<td>3.135(2), 3.141(2)</td>
<td></td>
</tr>
<tr>
<td>ethyl-4′-benzoate-3,5-dimethyl-pyrazolate (2b)</td>
<td>293</td>
<td>3.158(2)~ 3.245(3)</td>
<td>3.124(2), 3.124(2), 3.171(3), 3.171(3)</td>
<td></td>
</tr>
<tr>
<td>ethyl-4′-benzoate-3,5-dimethyl-pyrazolate (2c)</td>
<td>293</td>
<td>3.1781(6)~ 3.2244(6)</td>
<td>3.0885(6), 3.0885(6)</td>
<td></td>
</tr>
</tbody>
</table>

Table S24 Summary of luminescent data for halogen cyclic Cu$_3$pyrazolate$_3$

<table>
<thead>
<tr>
<th>The pyrazolate ligand</th>
<th>d(Cu-Cu) (Å)</th>
<th>T$_{cry}$ (K)</th>
<th>λ$_{em}$ (nm)</th>
<th>T$_{em}$ (K)</th>
<th>Drawback$^f$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-iodo-3,5-dimethylpyrazolate</td>
<td>3.631(4), 3.897(4)</td>
<td>293</td>
<td>621</td>
<td>293</td>
<td>630</td>
<td>77</td>
</tr>
<tr>
<td>4-(4-bromophenyl)-3,5-dimethylpyrazolate (Br-α)$^a$</td>
<td>2.8622(15)</td>
<td>293</td>
<td>670</td>
<td>RT</td>
<td></td>
<td>(2) S14</td>
</tr>
<tr>
<td>4-(4-bromophenyl)-3,5-dimethylpyrazolate (Br-β)$^a$</td>
<td>2.8174(9)</td>
<td>100</td>
<td>670</td>
<td>RT</td>
<td></td>
<td>(2) S14</td>
</tr>
<tr>
<td>4-bromo-3,5-</td>
<td>&gt; 5.0</td>
<td>296</td>
<td>574</td>
<td>RT</td>
<td></td>
<td>(3) S16</td>
</tr>
</tbody>
</table>

S26
A pair of genuine polymorphs; \(^a\)Intermolecular \(\text{Cu} \cdots \text{Cu}\) distance; \(^b\)Determination temperature for single-crystal X-ray diffraction; \(^c\)Emission maximum; \(^d\)Determination temperature for luminescent property; \(^e\)The disadvantage for producing comparable high-energy and low-energy emission bands as follows: (1) although the \(\text{Cu} \cdots \text{Cu}\) distances are too long to form \(\text{Cu} \cdots \text{Cu}\) interaction, the excimer formation is still quite favorable due to the lack of rigid restriction from supramolecular interaction, leaving only excimeric low-energy band, (2) the quite short or moderate \(\text{Cu} \cdots \text{Cu}\) distances facilitate the direct population for excited dimers, leaving only low-energy band, (3) the \(\text{Cu}-\text{Cu}\) distances are too long to form excimeric \(\text{Cu} \cdots \text{Cu}\) bonding, as suggested in reference S16, but a reasonable assignment for the low-energy bands have not yet been provided.

| Table S25 Photophysical data determined at around room temperature (RT) for solid-state samples of our Polymorphs and previously reported Cu\(\text{Pz}_3\)\(^a\) |
|---|---|---|---|---|---|---|
| Complex | \(T\) (K) | \(\lambda_{\text{ex}}\) (nm) | \(\lambda_{\text{em}}\) (nm) | \(\tau_{\text{av}}\) (\(\mu\)s) | \(QY\) (%) | \(k_r\) (10\(^2\) s\(^{-1}\)) | \(k_{nr}\) (10\(^2\) s\(^{-1}\)) | Ref. |
| Cl-\(\alpha\) | 300 | 290 | 564 | 42.18 | 76.6 | 181.60 | 55.95 | This work |
| Cl-\(\beta\) | 300 | 330 | 650 | 29.96 | 78.2 | 261.01 | 72.76 |
| \([\text{Cu(L1)}]_3\)\(^b\) | RT | 254 | 631 | 42.8 | 90 | 210.28 | 23.36 | S17 |
| \([\text{Cu(L2)}]_3\)\(^c\) | 293 | 280 | 570 | 30.5 | 84 | 275.40 | 52.46 | S15 |
| \([\text{Cu(L3)}]_3\)\(^d\) | 293 | 280 | 621 | 21.7 | 62 | 285.71 | 175.11 |

\(^a\)Only those providing both emission decay times (\(\tau\)) and absolute quantum yield (QY) are summarized in this table, so that both radiative rate (\(k_r\)) and non-radiative rate (\(k_{nr}\)) could be calculated to be discussed. \(^b\)HL\(_1\) = 4-hexyl-3,5-dimethylpyrazole. The photophysical data for \([\text{Cu(L1)}]_3\) are determined in poly(methyl methacrylate) (PMMA) doped films. \(^c\)HL\(_2\) = 3,5-dimethyl-4-bromopyrazole. \(^d\)HL\(_3\) = 3,5-dimethyl-4-iodopyrazole.

Comment:

Herein, we confirmed that, for both polymorphs, rigid supramolecular networks constructed by non-covalent interactions related to Cl could facilitate high QYs (near 80%) by reducing vibrational relaxation, resulting in small non-radiative rate (\(k_{nr}\)). By comparing the room-temperature phosphorescent data with other Cu\(\text{Pz}_3\), it was found that reducing \(k_{nr}\) may be somewhat more effective than raising radiative rate (\(k_r\)) for obtaining high QYs. For instance, \([\text{Cu(3,5-dimethyl-4-iodopyrazole)}]_3\) displays lower QY (62%) than our polymorphs herein (78.2% for the yellow light of Cl-\(\alpha\) and 76.6% for the orange light of Cl-\(\beta\)), because its \(k_{nr}\) (17511 s\(^{-1}\)) is much larger than our cases.
(5595 s\(^{-1}\) for Cl-\(\alpha\) and 7276 s\(^{-1}\) for Cl-\(\beta\)), although its \(k_r\) (28571 s\(^{-1}\)) is also larger (18160 s\(^{-1}\) for Cl-\(\alpha\) and 26101 s\(^{-1}\) for Cl-\(\beta\)). In contrast, the highest QY (90%) among Cu\(_3\)Pz\(_3\) was the one with 4-hexyl-3,5-dimethylpyrazolate doped in a poly(methylmethacrylate) (PMMA) film,\(^{S17}\) exhibiting the \(k_{nr}\) as low as 2336 s\(^{-1}\) due to a rigid environment, although its \(k_r\) (21028 s\(^{-1}\)) is close to that of Cl-\(\alpha\) and significantly smaller than that of Cl-\(\beta\). Besides, the rigid networks seem inhibit noticeable shortening of intermolecular Cu···Cu distances when cooling, resulting in neglectable shifting of emission bands. In contrast, significant red-shifting (e.g., up to 100 nm) are usually observed for Cu\(_3\)Pz\(_3\) when cooling from room temperature to 77 K, through enhancing Cu···Cu bonding during lattice contraction.\(^{S11}\)
1444-1449.