Supporting Information

Visualization of Nonemissive Triplet Species of Zn(II) Porphyrins through Cu(II) Porphyrin Emission *via* the Reservoir Mechanism in a Porphyrin Macroring

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Experimental Section

General procedure. All chemicals and solvents were of commercial reagent quality, and used without further purification unless otherwise stated. **C-(Zn-Cu-Zn)₃** was prepared according to the literature.[S1] Toluene was prepared by passing through an activated alumina column and dried over molecular sieves 4A, otherwise toluene was dealt with sulfuric acid following simple distillation, and then neutralized with dilute $NaHCO_3$ aqueous solution. After washing with water and drying over $CaCl_2$, it was distilled on CaH_2. Solutions of the porphyrins were sealed in glass or quartz cuvettes (10 mm path-length) degassed by freeze-thaw cycles or bubbled with Ar gas. UV-vis absorption spectra were collected on a JASCO V-650 spectrometer. Steady-state fluorescence and excitation spectra at room temperature were recorded on a Hitachi F-4500 spectrometer or a spectro-fluorometer model HORIBA FluoroMax 4. On the other hand, measurements at 77 K and time-resolved measurements were carried out by using a quartz tube (o.d. = 5 mm). For emission lifetime measurements, porphyrins were excited at 540 nm prepared from an OPO laser model Continuum OPO Plus which was excited by the third harmonics of a nanosecond Nd:YAG laser model Continuum Surelite I. Emission was dispersed by a Ritsu MC-12N monochrometer and then detected by a photomultiplier Hamamatsu R928. Signals were accumulated on a digital oscilloscope model LecRoy LT344 and transferred to a PC. Lifetimes were determined by fitting the decay curves with a double exponential function.

Emission spectral fitting. Double-mode Franck-Condon band shape analysis was used to fit the emission spectra. The spectral fittings were carried out according to equation (S1).[S2]

$$I(\tilde{v}) = \sum_{n_1=0}^{5} \sum_{n_2=0}^{5} \left(\frac{E_{00} - n_1\tilde{v}_1 - n_2\tilde{v}_2}{E_{00}} \right)^4 \left(\frac{S_1^{n_1}}{n_1!} \right) \left(\frac{S_2^{n_2}}{n_2!} \right) exp\left[-4log2 \left(\frac{\tilde{v} - E_{00} + n_1\tilde{v}_1 + n_2\tilde{v}_2}{\tilde{v}_{1/2}} \right)^2 \right] \qquad (S1)$$

$I(\tilde{v})$ is the relative emission intensity at frequency $\tilde{v}$. E_{00} is the energy gap between the zeroth vibrational levels in the ground and excited states, n_1 and n_2 are the vibrational quantum numbers of the high- and low-frequency vibrational modes, respectively, S_1 and S_2 are the Huang–Rhys factors, and $\tilde{v}_{1/2}$ is the half-width at half-maximum (fwhm) of the individual vibronic band. The 0–0 band energy gaps between the lowest excited state and the ground state were obtained from the emission spectral fitting.

Quenching experiments. The Stern-Volmer relationship (eq. S2) was obtained by the plots of the relative emission intensity (I_0/I) versus the concentration of O_2:

$$I_0/I = 1 + K_{SV}[O_2] = 1 + k_q\tau[O_2] \qquad (S2)$$

where I_0 and I represent the intensity at 820 nm in the absence and the presence of O$_2$, respectively, and Ksv, k_q, τ are the Stern-Volmer constant, the quenching rate constant, and the emission lifetime, respectively. The Ar-saturated toluene solutions containing the porphyrins in square quartz cells ($l = 1.0$ cm) were bubbled with 0.25, 0.5, and 1% O$_2$ in Ar gas and the emission spectra of each samples were measured.

References

S1. Y. Kuramochi, Y. Kawakami, A. Satake, *Inorg. Chem.* 2017, **56**, 11008-11018.

S2. J. V. Caspar, T. D. Westmoreland, G. H. Allen, P. G. Bradley, T. J. Meyer, W. H. Woodruff, *J. Am. Chem. Soc.* 1984, **106**, 3492-3500.
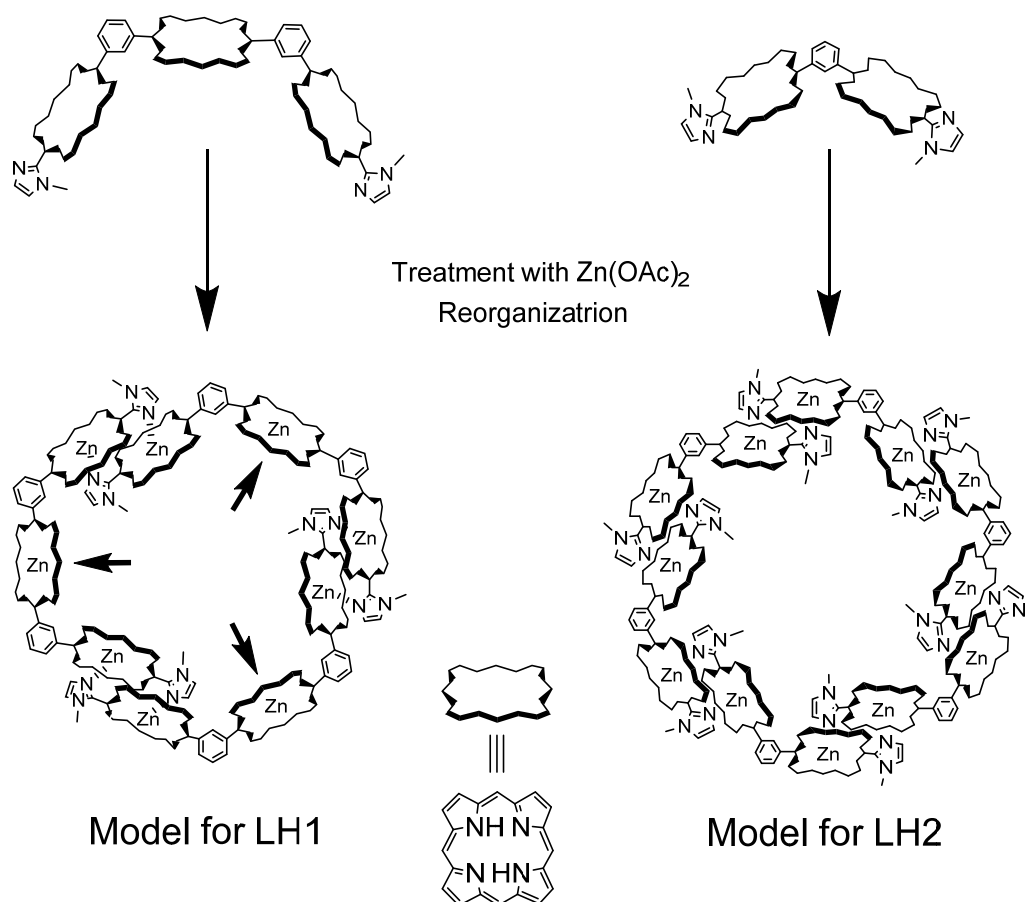
Treatment with Zn(OAc)$_2$
Reorganizatrion

Model for LH1

Model for LH2

Figure S1. Structures of the porphyrin macroring models for LH1 and LH2. Arrows indicate the uncoordinated Zn(II) porphyrins.
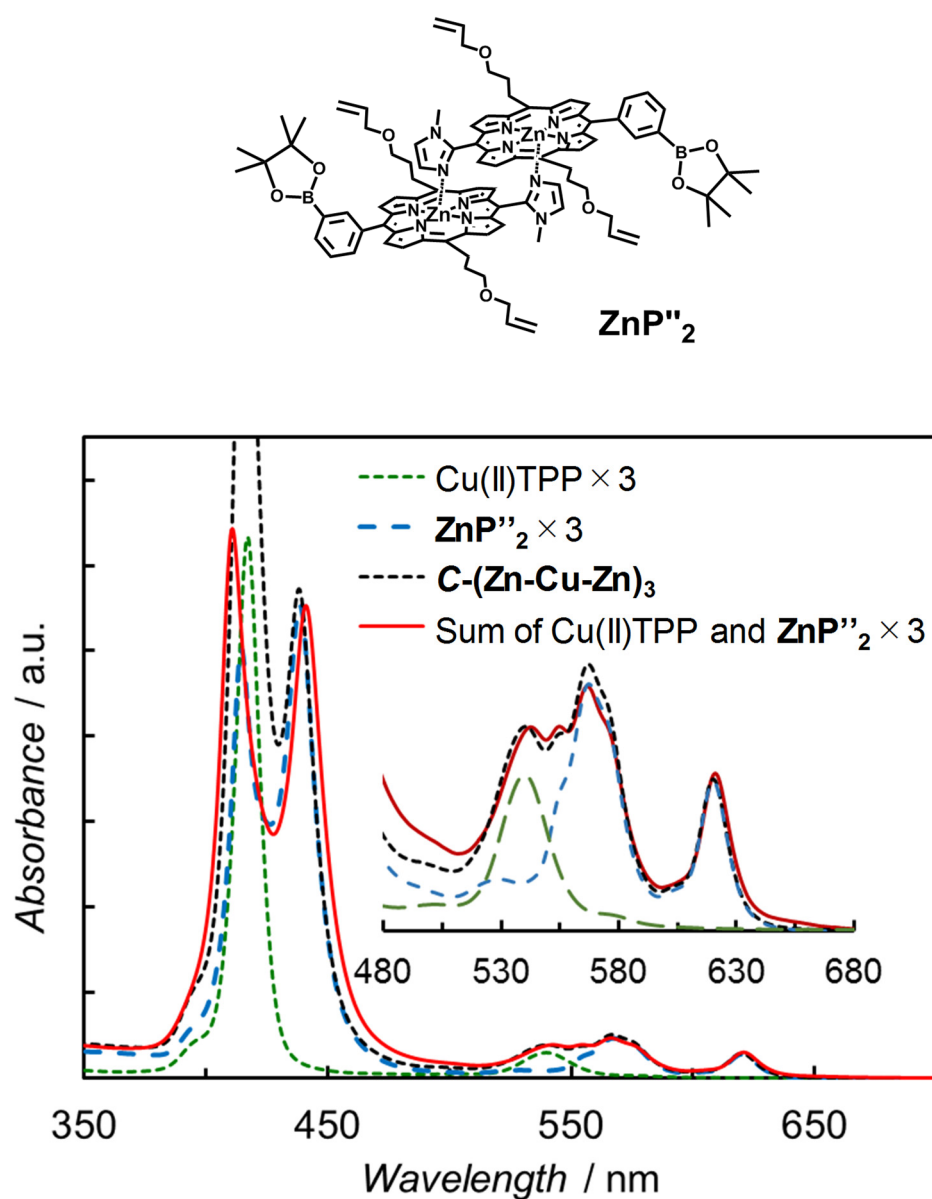
Figure S2. (top) Molecular structure of a porphyrin dimer, **ZnP″₂**. (bottom) UV-vis absorption spectra of **C-(Zn-Cu-Zn)₃** (red solid line), Cu(II)TPP (green broken line), **ZnP″₂** (blue broken line), and the sum of Cu(II)TPP and **ZnP″₂** as a 1:1 molar ratio (black dotted line) in air-saturated toluene at 298 K. In a previous report, the spectrum of Cu(II)TPP in CHCl₃ showed a peak at 620 nm (see: Y. Kuramochi, Y. Kawakami, A. Satake, *Inorg. Chem.* 2017, **56**, 11008). Further purification by preparative thin-layer chromatography of Cu(II)TPP eliminated the peak at 620 nm to show the spectrum as shown here, indicating that the peak at 620 nm corresponds to an impurity in Cu(II)TPP.
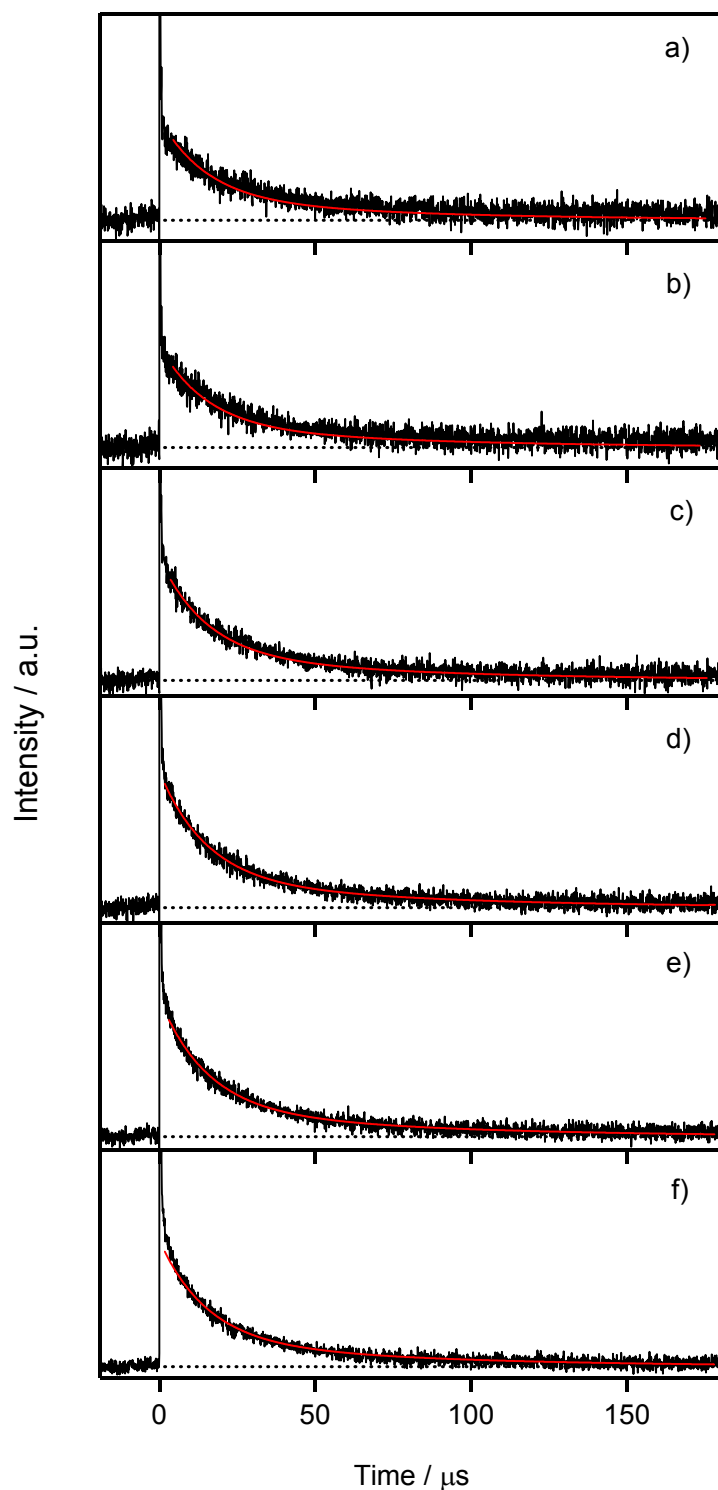
Figure S3. Laser power dependence of emission decay profiles of *C*-**(Zn-Cu-Zn)₃** monitored at 800 nm in toluene. Excitation power ratios for a):b):c):d):e):f) are roughly 0.5:1:2:3:5:10. Because the entrance slit of the monochrometer was adjusted to obtain appropriate signal intensities, vertical values are not relevant. In all parts of the figure, decay profiles were fitted with two components, 15 μs (78%) and 70 μs (22%).
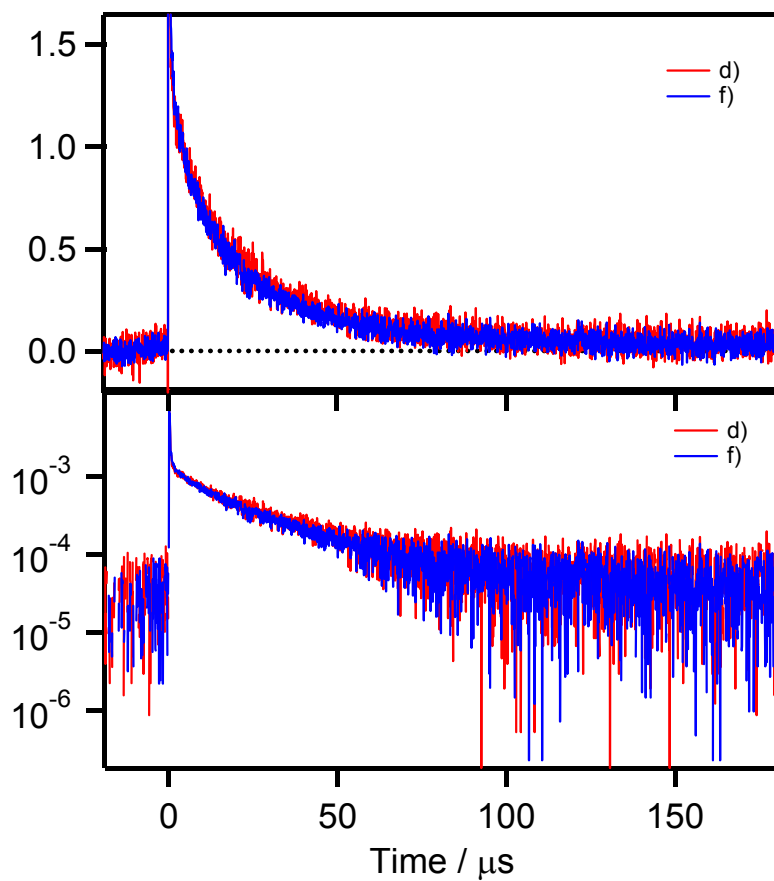
Figure S4. Comparison of emission decay profiles of *C*-(**Zn-Cu-Zn**)₃ monitored at 800 nm in toluene for different laser excitation powers, d) and f) in Figure S3.
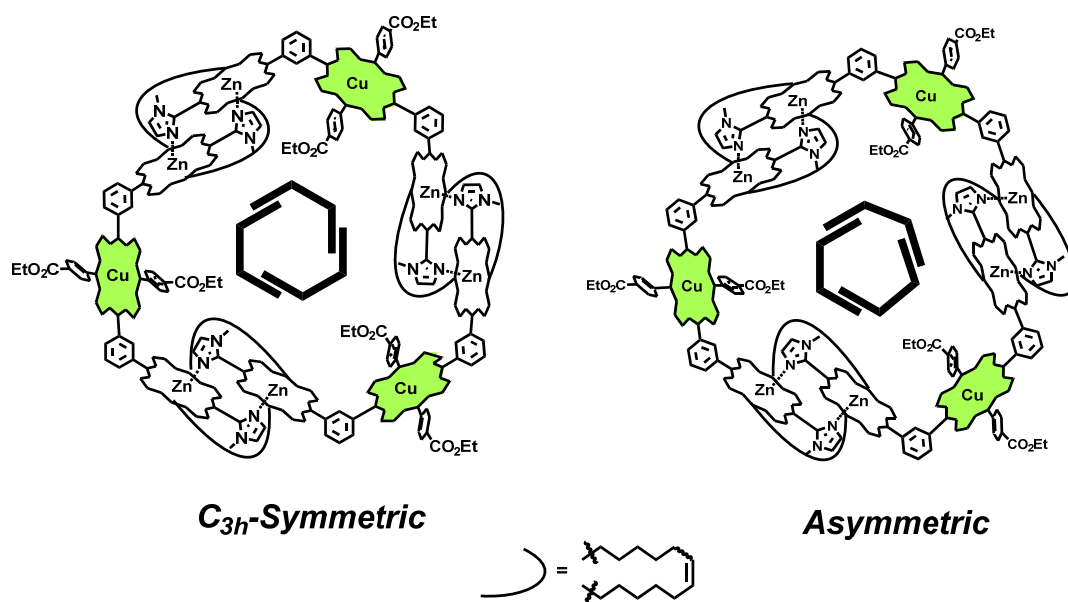
Figure S5. Topological isomers, C_{3h} symmetry and asymmetry, of **C-(Zn-Cu-Zn)₃**.
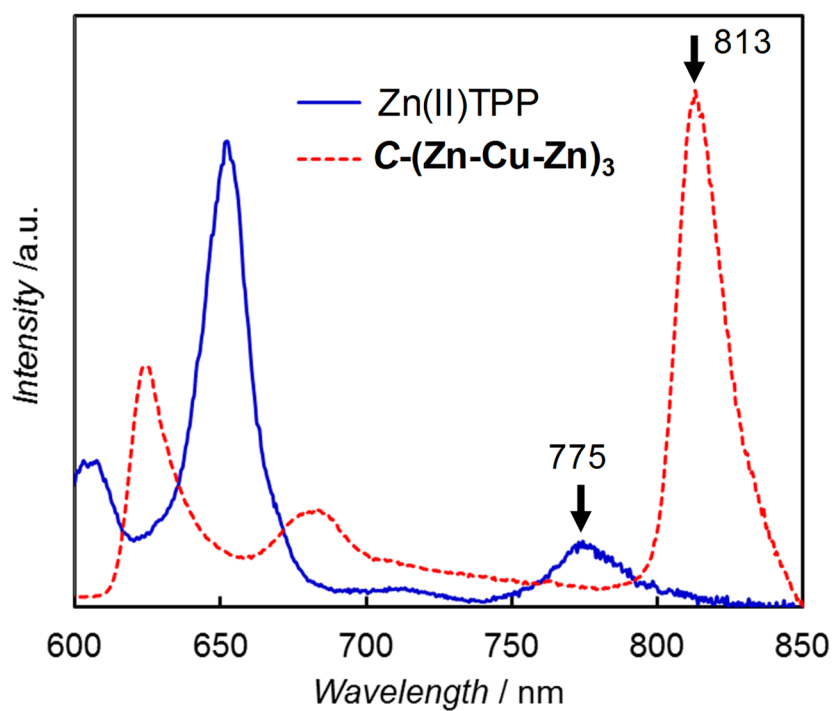
Figure S6. Emission spectra of Zn(II)TPP (blue solid line) and *C*-(**Zn-Cu-Zn**)₃ (red dotted line) at 77 K in degassed toluene. Excited at 540 nm. Arrows indicate the phosphorescence bands from the Zn(II) porphyrins. The phosphorescence band maximum for *C*-(**Zn-Cu-Zn**)₃, 813 nm, is close to that observed for the reference **ZnP′₂** (see Figure S7).
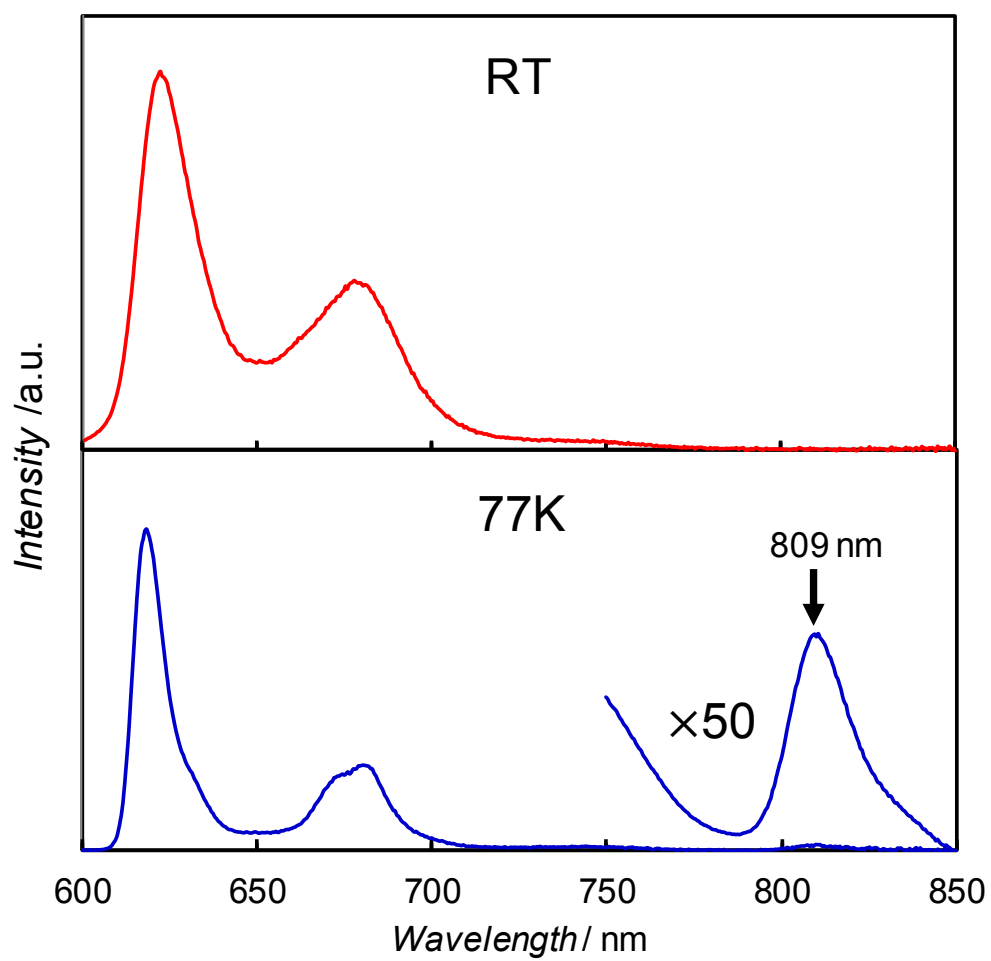
Figure S7. Emission spectra of **ZnP′$_2$** at rt (top) and 77 K (bottom) in toluene. Excited at 566 nm. The arrow indicates the phosphorescence band from the Zn(II) porphyrin.
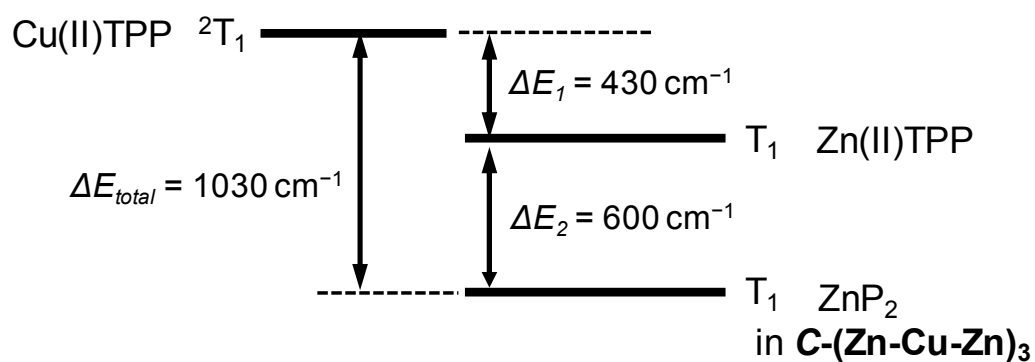
Cu(II)TPP $^2T_1$ ——————— - - - - - - - - - - -

$\Delta E_1 = 430\ \mathrm{cm}^{-1}$

T_1 Zn(II)TPP

$\Delta E_{total} = 1030\ \mathrm{cm}^{-1}$

$\Delta E_2 = 600\ \mathrm{cm}^{-1}$

- - - - - - - - - - ——————— T_1 ZnP_2
in **C-(Zn-Cu-Zn)$_3$**

Cu(II)TPP $^2S_0$ ———————————— S_0 ZnTPP, ZnP_2

Figure S8. Energy gap between the CuP and the ZnP$_2$ parts in **C-(Zn-Cu-Zn)$_3$**. $\Delta E_1 = 430\ \mathrm{cm}^{-1}$: M. S. Asano, M. Shibuki, T. Otsuka, *Chem. Lett.* 2016, **45**, 1114-1116. $\Delta E_2 = (1/775 - 1/813) \times 10^7 \approx 600\ \mathrm{cm}^{-1}$ (Figure S6).
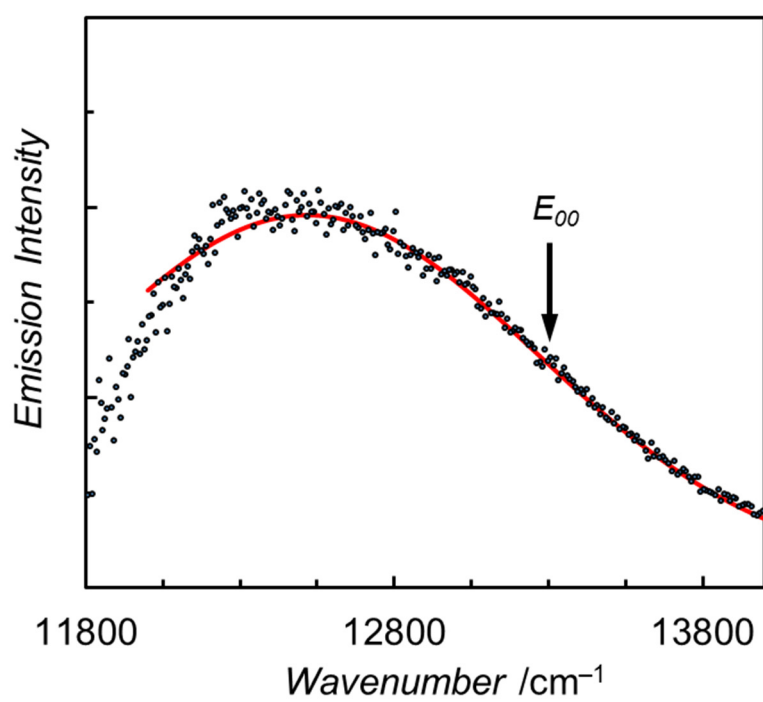
Figure S9. Emission spectra (black dots) of *C*-**(Zn-Cu-Zn)**$_3$ in degassed toluene at rt and simulation curve (red line) by means of double-mode Franck–Condon line-shape analysis: E_{00} = 13330 cm^{-1}, $\tilde{v}_1$ = 180 cm^{-1}, S_2 = 9.8, $\tilde{v}_1$ = 28 cm^{-1}, S_2 = 1.2, $\tilde{v}_{1/2}$ = 1720 cm^{-1}