Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

# Self-assembled luminescent Cu(I) tetranuclear metallacycles based on 3,3'-bipyridine ligand

Florent Moutier, Jana Schiller, Guillaume Calvez* and Christophe Lescop*

Univ Rennes, INSA Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France. E-mail: christophe.lescop@insa-rennes.

## Supporting Information

### Table of contents

## I. Experimental Section

For the syntheses reported, procedures were performed under air, in a simple flask. Commercially available solvents were used as received without further purification. Commercially available reagents $[Cu(CH_3CN)_4]PF_6$, dppm (dppm = 1,1'-bis(diphenylphosphino)methane) and CuBr were obtained from Sigma-Aldrich. 3,3'-bipyridine was obtained from TCI Chemicals. CuCl was obtained from Acros Organics. CuI was obtained from STREM Chemicals.

All solution NMR spectra were measured in $CD_2Cl_2$ on a Bruker 300 MHz AvI spectrometer using 5 mm standard NMR tubes. All $^{31}P$ and $^{1}H$ spectra were recorded with decoupling from either $^{31}P$ or $^{1}H$ during acquisition at a Larmor frequency of 300.13 MHz for $^{1}H$ and 121.50 MHz for $^{31}P$. Chemical shifts are reported relative to tetramethylsilane (TMS) for $^{1}H$ and 85 wt.% $H_3PO_4$ for $^{31}P$.

FT-IR measurements have been performed on a Perkin Elmer Frontier spectrometer using UATR (Universal Attenuated Total Reflectance) accessory. Spectra have been recorded between 650 $cm^{-1}$ and 4000 $cm^{-1}$, on pure samples.

UV-vis solid-state absorption measurements have been recorded on a Perkin-Elmer Lambda 650 spectrometer using a 60 mm integrating sphere. Spectra have been recorded between 800 nm and 200 nm, on pellets.

Steady-state emission spectra and luminescence quantum yield measurements were recorded on a *Horiba Jobin-Yvon* (*HJY*) Fluorolog-3 (FL3-2iHR550) fluorescence spectrofluorometer equipped with an IR R928P PMT / *HJY* FL-1073 detector and with an integrating sphere. Low temperature measurements were allowed by using an OptistatCF (*Oxford Inst.*) in the range of 77 K to 300 K. Excited-state lifetimes in the range of 80 K to 300 K were measured with a delta hub (TCSPC: Time-Correlated-Single-Photon-Counting) + delta diode system allowing to measure excited-state lifetimes between 500 ps et 10 μs and with a pulsed xenon source (FL-1035) allowing to measure excited-state lifetimes longer than 10 μs.

Solid sample was placed in a quartz sample holder inside the integrating sphere and the cryostat and maintained at the desired temperature until equilibrium was reached before recording the spectrum.

## General comments concerning characterizations of derivatives $\mathbf{C_{Cl}}$, $\mathbf{C_{Br}}$ and $\mathbf{C_{I}}$.

Derivatives $\mathbf{C_{Cl}}$, $\mathbf{C_{Br}}$ and $\mathbf{C_{I}}$, once isolated, revealed to be very low soluble in any solvents. Only $CD_2Cl_2$ solvent allowed to prepared solutions from which $^1$H NMR spectra and $^{31}P\{^1H\}$ NMR spectra could be recorded. Yet, it was not possible to obtain $^{13}C\{^1H\}$ NMR spectra for these compounds.

In addition, these compounds dissolved in $CH_2Cl_2$ have been investigated using mass spectrometry with positive electrospray. This measurement revealed in all case, the presence of $[Cu_2dppm_2X]^+$ fragments with m/z of 929.066, 973.016 and 1021.002 respectively. These fragments are in agreement with the identified molecular structures of $\mathbf{C_{Cl}}$, $\mathbf{C_{Br}}$ and $\mathbf{C_{I}}$. These results indicate that a dissociation of the metallacyclic structures of derivatives $\mathbf{C_{Cl}}$, $\mathbf{C_{Br}}$ and $\mathbf{C_{I}}$ occurs in the conditions applied for mass spectrometry with positive electrospray, precluding the observation of signals corresponding to the whole self-assembled tetrametallic fragments.

Standard solution 1D NMR ($^{31}P\{^1H\}$, and $^1$H NMR are reported in the ESI for the compounds described in this paper ($^{13}$C NMR spectra could not be measured due to a too low solubility of these compounds). These NMR patterns are typical of the solutions in which crystals of the derivatives $\mathbf{C_{Cl}}$, $\mathbf{C_{Br}}$ and $\mathbf{C_{I}}$ have been dissolved. **Yet, the general outcomes of such standard 1D NMR studies do not allow definitive conclusion about the precise architecture of such Cu(I)-based supramolecular assemblies in the solution and stand for a characterization of the NMR patterns of solutions in which crystals of have been dissolved**. Indeed, these Cu(I)-based derivatives are intrinsically highly fluxional, which hinders the observation of well-resolved NMR patterns that would be diagnostic of the very specific symmetry observed in the solid state structures. Such flexibility can be assigned to different rapid molecular re-organizations that can occur even at low temperature in solution. In addition, such patterns do not also allow indeed excluding that the assemblies self-dissociate in solution and re-organize along complex and multiple equilibria from which the tetranuclear metallacyclic species reported herein are always collected after crystallization experiments.

## Synthesis of derivative $\mathbf{C_{Cl}}$ :

To a dichloromethane solution (10 ml) of $[Cu(CH_3CN)_4]PF_6$ (0.040 g, 0.11 mmol) and CuCl (0.011 g, 0.11 mmol) was added a dichloromethane solution (5 ml) of dppm (0.085 g, 0.22 mmol). This solution was stirred for 1 hour. A dichloromethane solution (5 ml) of 3,3'bipyridine (0.017 g, 0.11 mmol) was added to the crude solution. The stirring was stopped and the solution was left undisturbed overnight at room temperature. The solution was filtered over cotton and was left upon n-pentane vapor diffusion to obtain the product $\mathbf{C_{Cl}}$ after crystallization.

The final product after filtration on paper filter was a pure colorless crystalline powder obtained with a yield of 66% (0.087 g, 0.035 mmol). This powder emits under UV-Vis excitation ($\lambda_{lamp}$ = 365nm) an eye-perceived light blue luminescence.

$^1$H NMR (300 MHz, $CD_2Cl_2$, ppm): δ 3.44 (broad s, 8H, $PCH_2P$), 6.97 (t, 4H, $^1J$(H-H) = 9 Hz, $H_{3,3'bipyridine}$), 7.02-7.42 (broad m, 80H, $H_{aromdppm}$), 7.59 (d, 4H, $^1J$(H-H) = 9 Hz, $H_{3,3'bipyridine}$), 8.40 (broad s, 4H, $H\alpha_{3,3'bipyridine}$), 8.48 (s, 2H, $H\alpha_{3,3'bipyridine}$).

$^{31}P\{^1H\}$ NMR (121 MHz, $CD_2Cl_2$, ppm): δ = -8.77 (s, $P_{dppm}$), -144.38 (sept, $^1J$(P-F) = 708 Hz, $PF_6^-$).

IR ($cm^{-1}$): 690 (vs), 737 (vs), 766 (s), 788 (s), 832 (vs), 931 (vw), 1002 (w), 1028 (w), 1096 (m), 1196 (w), 1245 (vw), 1280 (vw), 1308 (vw), 1351 (w), 1434 (s), 1484 (m), 1588 (w), 3057 (w)

Elemental analysis, calcd. (%) for $C_{122}H_{108}Cl_6Cu_4F_{12}N_4P_{10}$: C 55.61, H 4.13, N 2.13; found: C 55.37, H 4.47, N 2.35.

**Synthesis of derivative $C_{Br}$ :**

To a dichloromethane solution (10 ml) of $[Cu(CH_3CN)_4]PF_6$ (0.040 g, 0.11 mmol) and CuBr (0.016 g, 0.11 mmol) was added a dichloromethane solution (5 ml) of dppm (0.085 g, 0.22 mmol). This solution was stirred for 1 hour. A dichloromethane solution (5 ml) of 3,3'bipyridine (0.017 g, 0.11 mmol) was added to the crude solution. The stirring was stopped and the solution was left undisturbed overnight at room temperature. The solution was filtered over cotton and was left upon n-pentane vapor diffusion to obtain the product **$C_{Br}$** after crystallization.

The final product after filtration on paper filter was a pure colorless crystalline powder obtained with a yield of 84% (0.116 g, 0.05 mmol). This powder emits under UV-Vis excitation ($\lambda_{lamp}$ = 365nm) an eye-perceived light blue luminescence.

$^1$H NMR (300 MHz, $CD_2Cl_2$, ppm): δ = 3.28 (broad s, 4H, $PCH_2P$), 3.51 (broad s, 4H, $PCH_2P$), 6.95 (t, 4H, $^1J$(H-H) = 7 Hz, $H_{3,3'bipyridine}$), 7.07-7.48 (broad m, 80H, $H_{aromdppm}$), 7.67 (d, 4H, $^1J$(H-H) = 7 Hz, $H_{3,3'bipyridine}$), 8.43 (broad s, 4H, $H\alpha_{3,3'bipyridine}$), 8.54 (s, 4H, $H\alpha_{3,3'bipyridine}$).

$^{31}P\{^1H\}$ NMR (121 MHz, $CD_2Cl_2$, ppm): δ = -8.84 (s, $P_{dppm}$), -144.44 (sept, $^1J$(P-F) = 707 Hz, $PF_6^-$).

IR ($cm^{-1}$): 690 (vs), 737 (vs), 766 (s), 788 (s), 832 (vs), 931 (vw), 1002 (w), 1028 (w), 1096 (m), 1196 (w), 1245 (vw), 1280 (vw), 1308 (vw), 1351 (w), 1434 (s), 1484 (m), 1588 (w), 3057 (w)

Elemental analysis, calcd. (%) for $C_{123}H_{110}Br_2Cl_6Cu_4F_{12}N_4P_{10}$: C 52.60, H 3.95, N 1.99; found: C 52.38, H 3.43, N 2.23.

**Synthesis of derivative $C_I$ :**

To a dichloromethane solution (10 ml) of $[Cu(CH_3CN)_4]PF_6$ (0.04 g, 0.11 mmol) and CuI (0.021g, 0.11 mmol) was added a dichloromethane solution (5 ml) of dppm (0.085 g, 0.22 mmol). This solution was stirred for 1 hour. A dichloromethane solution (5 ml) of 3,3'bipyridine (0.017 g, 0.11 mmol) was added to the crude solution. The stirring was stopped and the solution was left undisturbed overnight at room temperature. The solution was filtered over cotton and was left upon n-pentane vapor diffusion to obtain the product $\mathbf{C_I}$ after crystallization.

The final product after filtration on paper filter was a pure colorless crystalline powder obtained with a yield of 60% (0.085 g, 0.03 mmol). This powder emits under UV-Vis excitation ($\lambda_{lamp}$ = 365nm) an eye-perceived light blue luminescence.

$^1$H NMR (300 MHz, $CD_2Cl_2$, ppm) : $\delta$ = 3.40 (broad s, 4H, $PCH_2P$), 3.62 (broad s, 4H, $PCH_2P$), 6.97 (t, 4H, $^1J$(H-H) = 6 Hz, $H_{3,3'bipyridine}$), 7.02-7.47 (broad m, 80H, $H_{aromdppm}$), 7.69 (d, 4H, $^1J$(H-H) = 6 Hz, $H_{3,3'bipyridine}$), 8.46 (broad s, 4H, $H\alpha_{3,3'bipyridine}$), 8.56 (s, 4H, $H\alpha_{3,3'bipyridine}$).

$^{31}P\{^1H\}$ NMR (121 MHz, $CD_2Cl_2$, ppm) : $\delta$ = -9.81 (s, $P_{dppm}$), -144.40 (sept, $^1J$(P-F) = 708 Hz, $PF_6^-$).

IR (cm$^{-1}$): 690 (vs), 737 (vs), 766 (s), 788 (s), 832 (vs), 931 (vw), 1002 (w), 1028 (w), 1096 (m), 1196 (w), 1245 (vw), 1280 (vw), 1308 (vw), 1351 (w), 1434 (s), 1484 (m), 1588 (w), 3057 (w)

Elemental analysis, calcd. (%) for $C_{123}H_{110}I_2Cl_6Cu_4F_{12}N_4P_{10}$: C 50.89, H 3.82, N 1.93; found: C 50.51, H 3.49, N 1.98.

## II. X-Ray Crystallographic study

Single crystal data collection for $\mathbf{C_{Cl}}$, $\mathbf{C_{Br}}$ and $\mathbf{C_I}$ were performed at 150 K with a D8 Venture Bruker AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo-*K*α radiation (λ = 0.71073 Å). Reflections were indexed, Lorentz-polarization corrected and integrated by the *DENZO* program of the KappaCCD software package. The data merging process was performed using the SCALEPACK program.[S1] Structure determinations were performed by direct methods with the solving program SIR97,[S2] that revealed all the non-hydrogen atoms. SHELXL program[S3] was used to refine the structures by full-matrix least-squares based on $F^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Single crystals of all these derivatives were always coated in paratone oil, mounted at low temperature on the diffractometer goniometer as quickly as possible in the case of these solvated crystals. X-ray data collections were performed at low temperature. In all cases, in the crystal lattices of the coordination complexes studied, dichloromethane solvent molecules were found in addition to the cationic coordination complexes and their counter-anions.

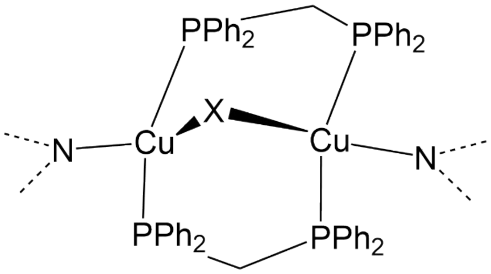
The included dichloromethane solvent molecules were found to be highly disordered and a correct modelling of the disorder of these solvent molecules was not always possible leading to rather high anisotropic displacement parameters for some of their atoms. We have therefore proceeded to a 'squeeze' treatment[S4] in order to remove the scattering contribution of these molecules which cannot be satisfactorily modelled (5 $CH_2Cl_2$ molecules per asymmetric unit for derivatives $\mathbf{C_{Cl}}$ and $\mathbf{C_{Br}}$ ; 6 $CH_2Cl_2$ molecules per asymmetric unit for derivatives $\mathbf{C_I}$**)**. In the case of the derivative $\mathbf{C_I}$ hexafluorophosphate counter-anions were also found very disordered and the 'squeeze' treatment[S4] also removed the scattering contribution of these molecules which cannot be satisfactorily modelled. As a result, since these disordered molecules occupy a significant volume of the unit cell, several ALERTs A appear in the checkcif reports since " VERY LARGE Solvent Accessible VOIDs" are present in the structure resolution.

Concerning the derivative $\mathbf{C_I}$, the aromatic carbon atoms of one dppm ligand (namely C(52) and C(53)) are found with high anisotropy parameters inducing thermal ellipsoids excessively extended, which results in ALERTs A appearing in the checkcif report. This is very likely the result of a statistic delocalisation of these atoms. Yet, a modelling of this delocalisation was not possible, leading to unstable refinement cycles.

Table S1 gives selected metric data for the derivatives $\mathbf{C_{Cl}}$, $\mathbf{C_{Br}}$ and $\mathbf{C_I}$.

Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.[S5] CCDC reference numbers 2074606, 2074608 and 2074607 contain the supplementary crystallographic data for the reference measurements of the X-ray crystal structures of the derivatives $\mathbf{C_{Cl}}$, $\mathbf{C_{Br}}$ and $\mathbf{C_I}$, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

**Table S1**. Selected intermetallic distances [Å] and angles [°] in the derivatives $\mathbf{C_X}$.



| | $\mathbf{C_{Cl}}$ | $\mathbf{C_{Br}}$ | $\mathbf{C_{I}}$ |
|---|---|---|---|
| **Cu-Cu** | 3.180(4) | 3.261(5) | 3.362(5) |
| **Cu - N** | 2.121 (3) and 2.121 (3) | 2.109(4) and 2.121(5) | 2.119(6) and 2.124(5) |
| **Cu - X** | 2.4034(12) and 2.4048 (11) | 2.5218(11) and 2.5211(10) | 2.6646(11) and 2.6636(12) |
| **Cu - P** | 2.2687(10),<br>2.2569(10),<br>2.2604(11) and<br>2.2527(11) | 2.2682(15),<br>2.2567(14),<br>2.2595(16) and<br>2.2546(16) | 2.2474(17),<br>2.2576(16),<br>2.2549(19) and<br>2.2539(19) |
| **Cu-Cu-N** | 150.25(3),<br>150.37(4) | 150.76(5),<br>150.27(6) | 151.51(5),<br>151.15(5) |
| **Cu(1)-X-Cu(2)** | 82.80(3) | 80.58(2) | 78.24(3) |

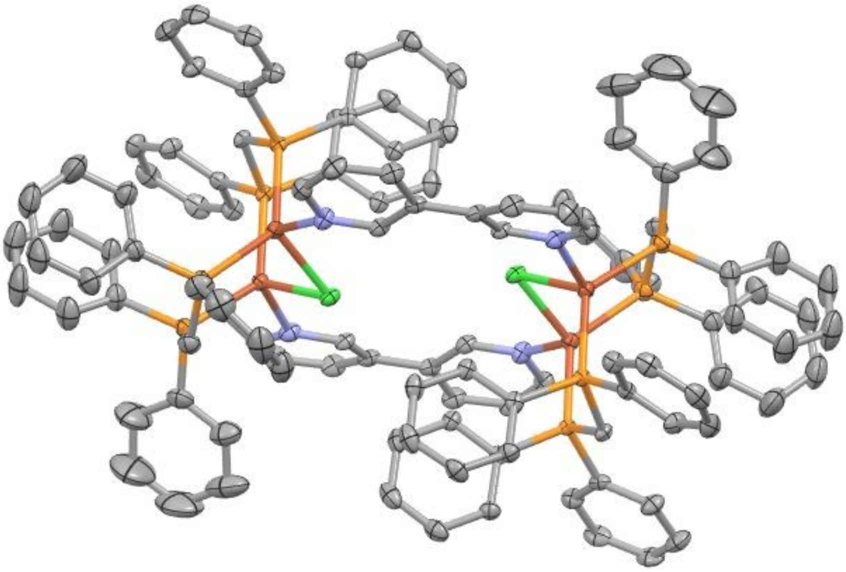


**Fig. S1.** ORTEP views of the molecular structure of the dicationic derivative $\mathbf{C_{Cl}}$. Hydrogen atoms, hexafluorophosphate counter-anions and included $CH_2Cl_2$ solvent molecules have been omitted for clarity. Atoms color codes: dark orange : copper, light orange : phosphorus, grey : carbon, blue : nitrogen, light green : chlorine

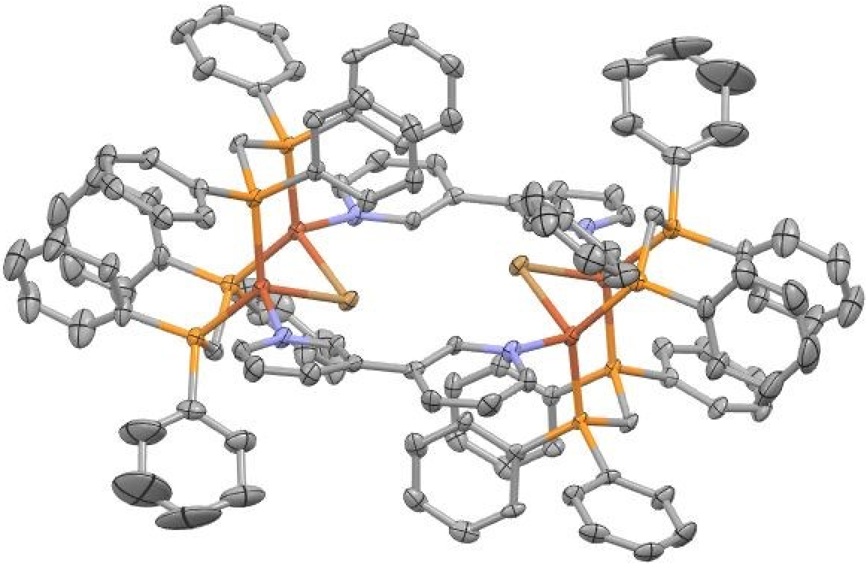


**Fig. S2.** ORTEP views of the molecular structure of the dicationic derivative $\mathbf{C_{Br}}$. Hydrogen atoms, hexafluorophosphate counter-anions and included $CH_2Cl_2$ solvent molecules have been omitted for clarity. Atoms color codes: dark orange : copper, light orange : phosphorus, grey : carbon, blue : nitrogen, brown : bromine.

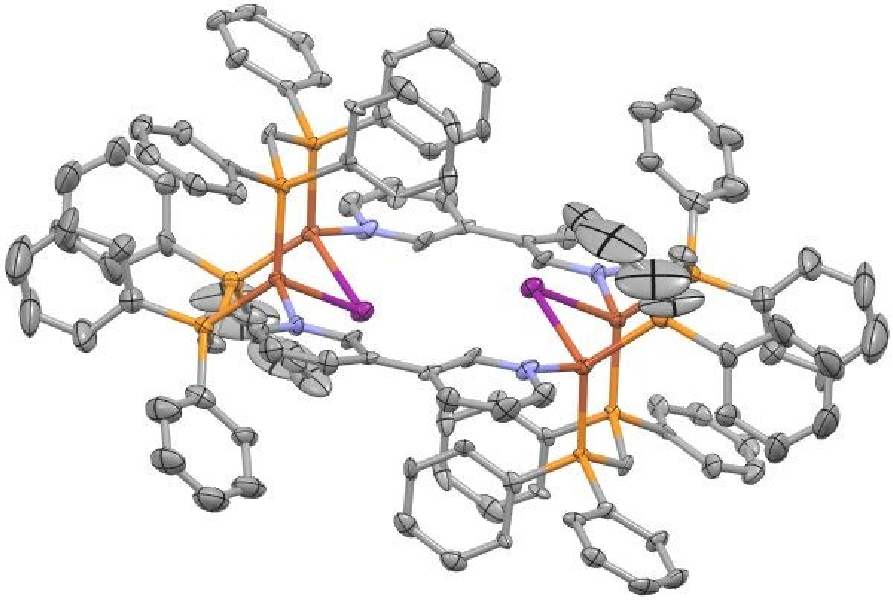


**Fig. S3.** ORTEP views of the molecular structure of the dicationic derivative $\mathbf{C_{I}}$. Hydrogen atoms, hexafluorophosphate counter-anions and included $CH_2Cl_2$ solvent molecules have been omitted for clarity. Atoms color codes: dark orange : copper, light orange : phosphorus, grey : carbon, blue : nitrogen, violet : iodine.

## III. Photophysical study

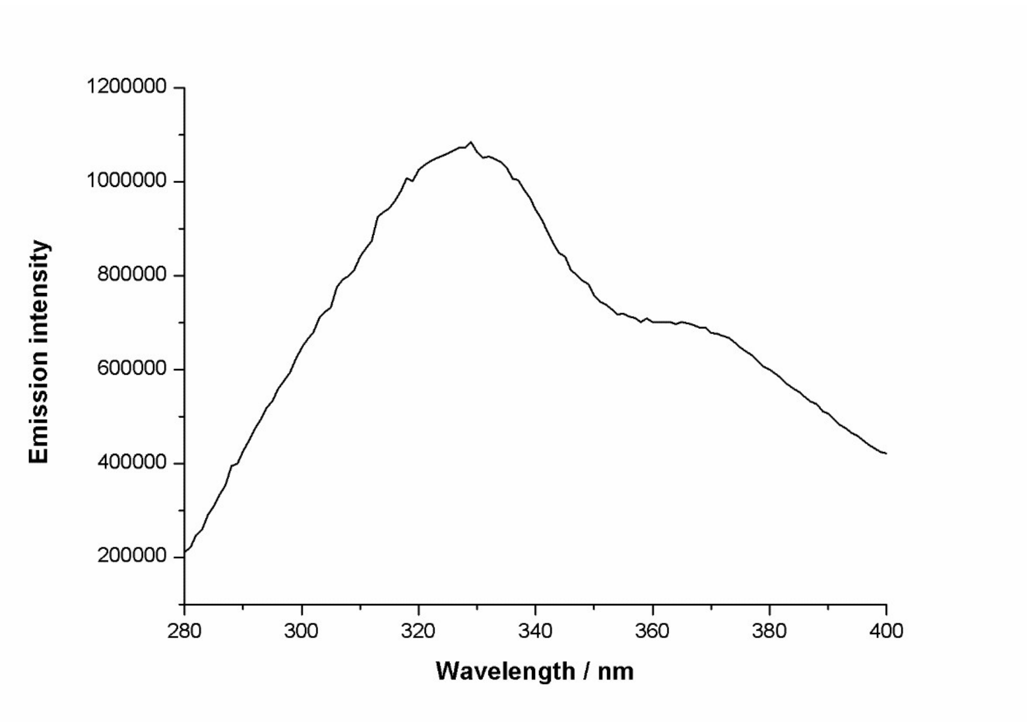


**Fig. S4.** Solid-state excitation spectrum of $\mathbf{C_{Cl}}$ at 300 K.

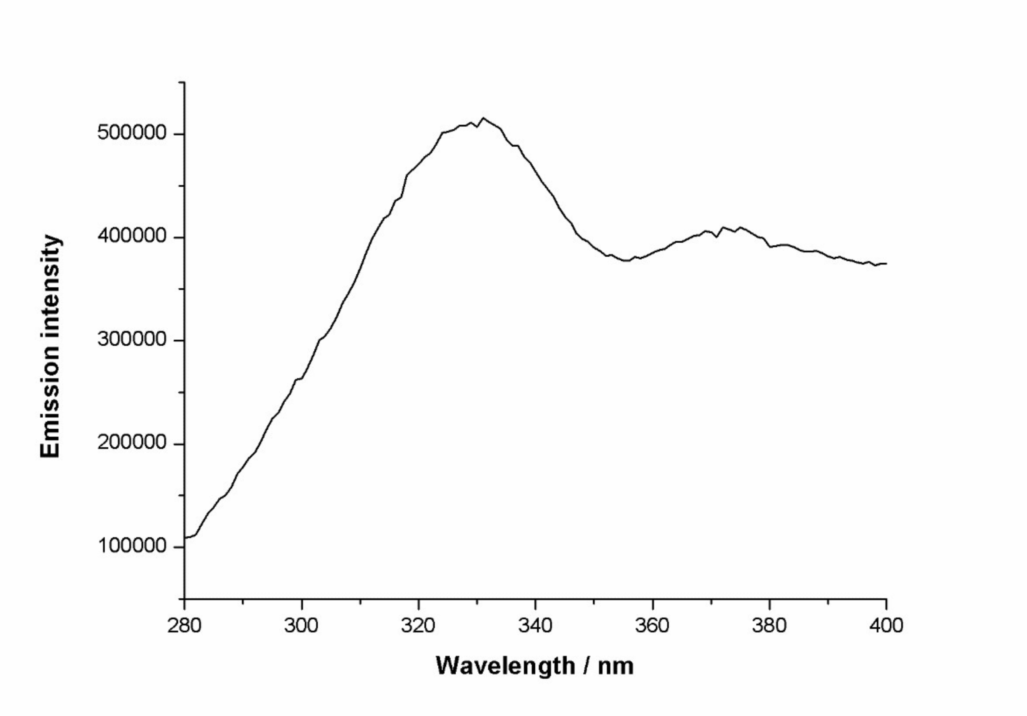


**Fig. S5.** Solid-state excitation spectrum of $\mathbf{C_{Br}}$ at 300 K.

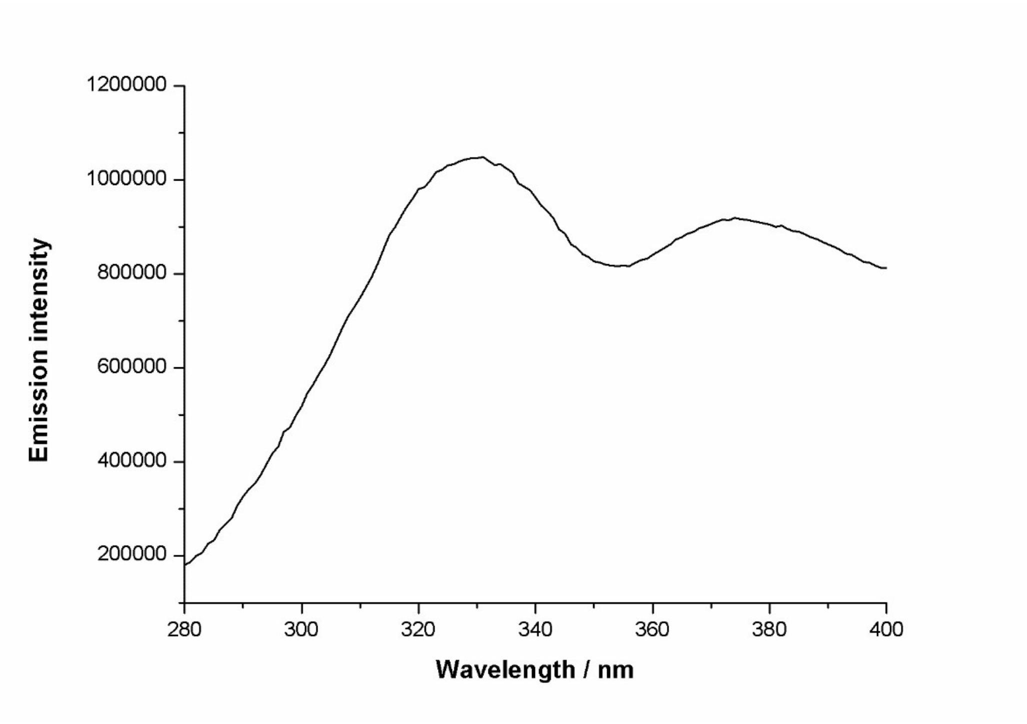


**Fig. S6.** Solid-state excitation spectrum of **$C_I$** at 300 K.

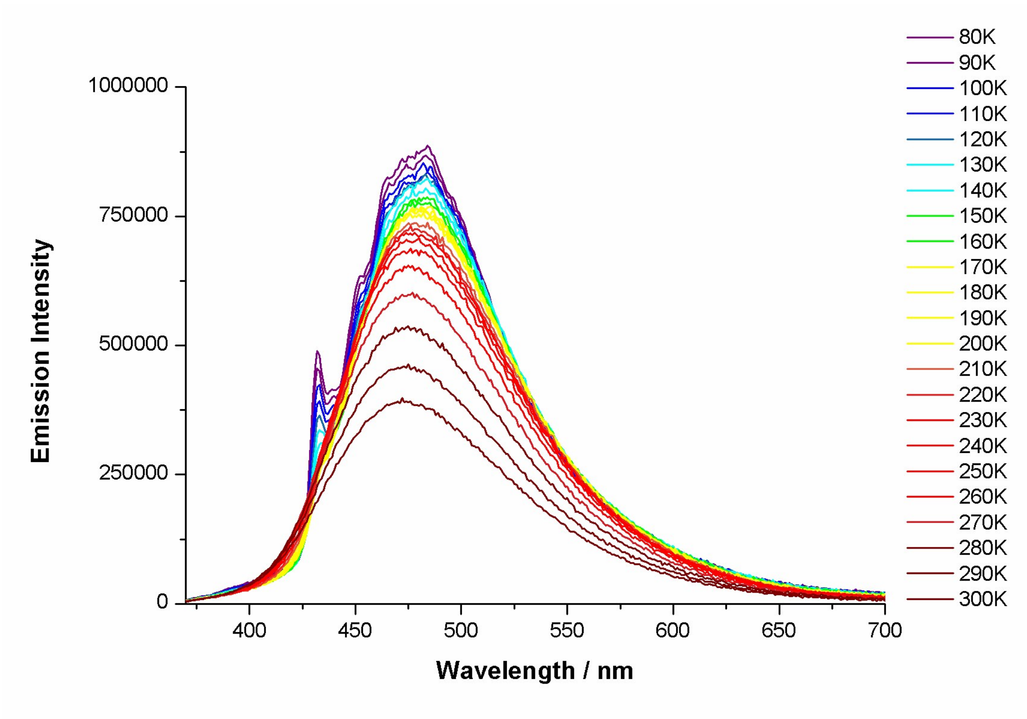


**Fig. S7.** Temperature dependent non-normalized solid-state emission spectra of **$C_{Cl}$** ($\lambda_{ex}$ = 325 nm), from 80 K to 300 K (measurements were performed every 10K).

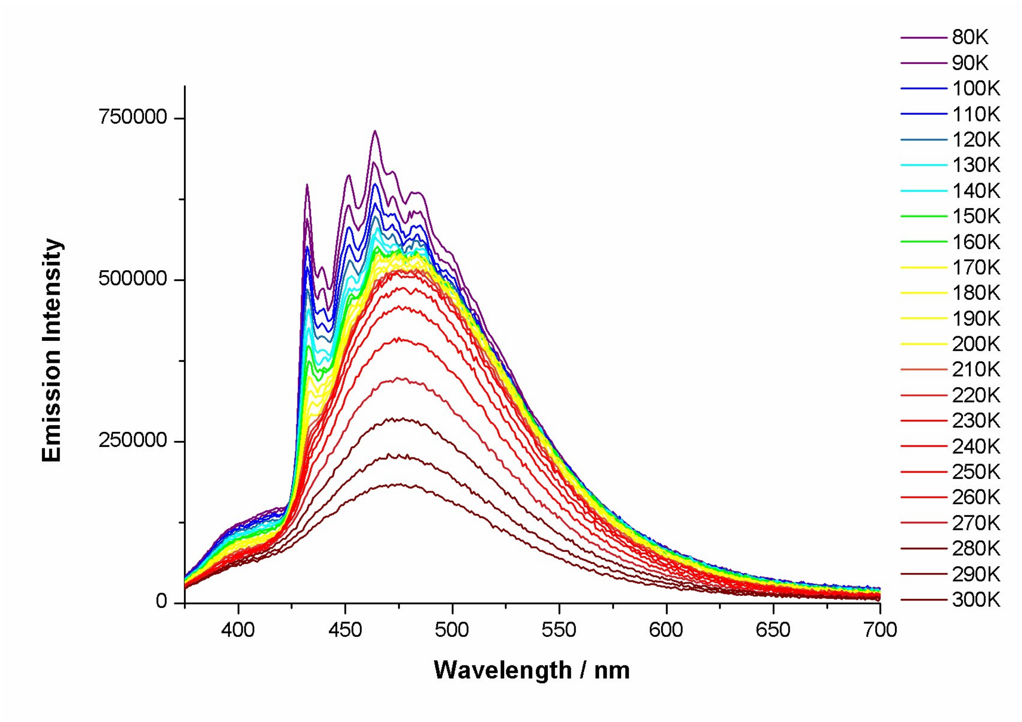


**Fig. S8.** Temperature dependent non-normalized solid-state emission spectra of $\mathbf{C_{Br}}$ ($\lambda_{ex}$ = 325 nm), from 80 K to 300 K (measurements were performed every 10K).

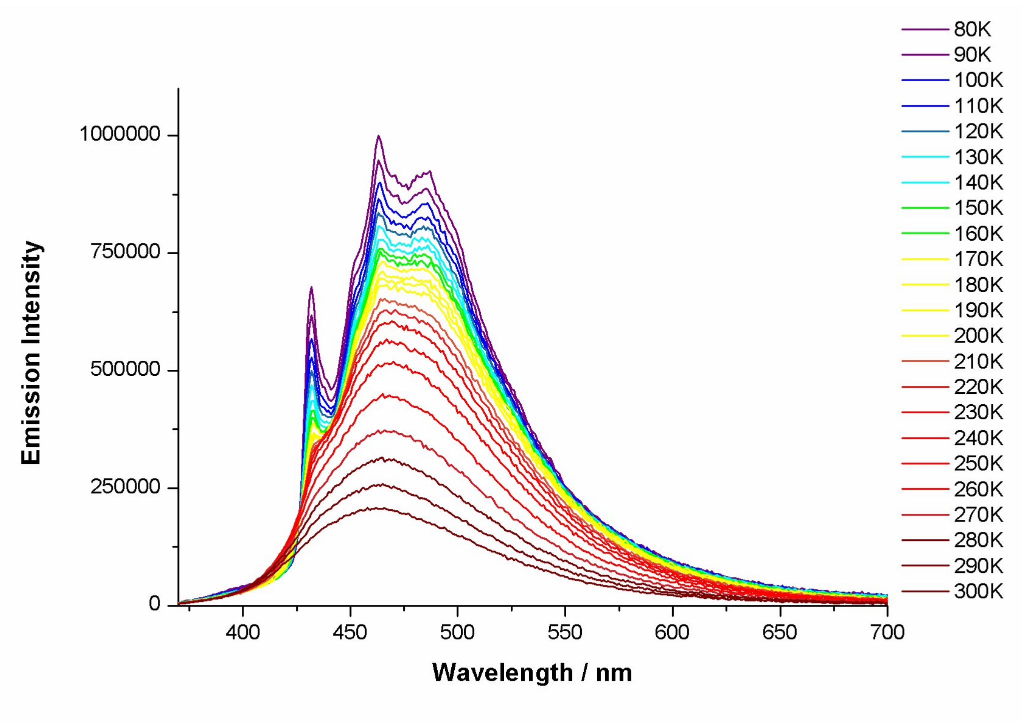


**Fig. S9.** Temperature dependent non-normalized solid-state emission spectra of $\mathbf{C_{I}}$ ($\lambda_{ex}$ = 325 nm), from 80 K to 300 K (measurements were performed every 10K).

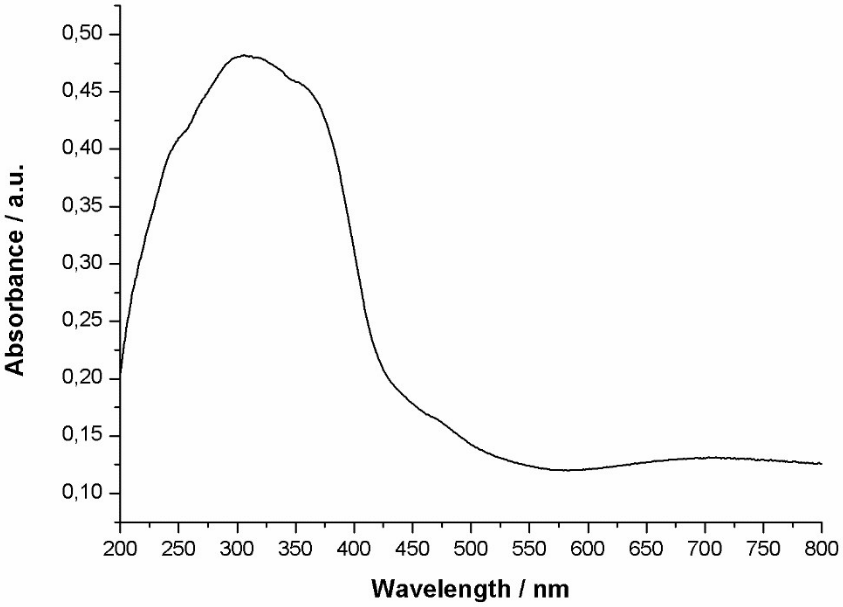


**Fig. S10.** Solid-state UV-Vis absorption spectrum of $\mathbf{C}_{\mathbf{Cl}}$.

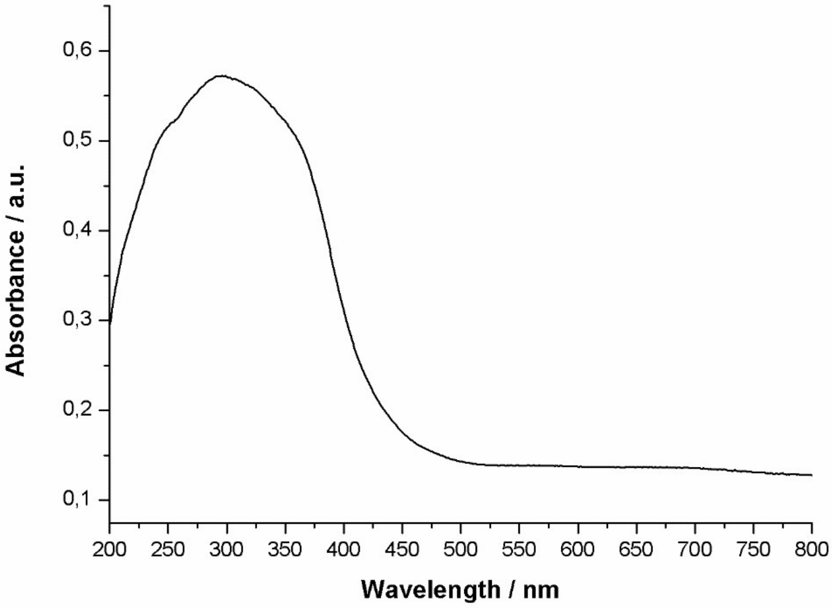


**Fig. S11.** Solid-state UV-Vis absorption spectrum of $\mathbf{C}_{\mathbf{Br}}$.

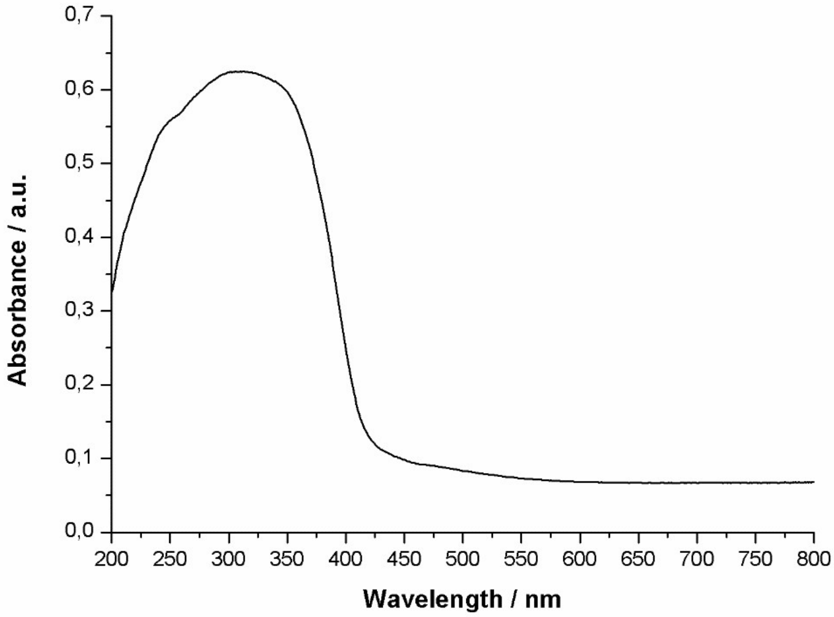


**Fig. S12.** Solid-state UV-Vis absorption spectrum of $\mathbf{C_I}$.

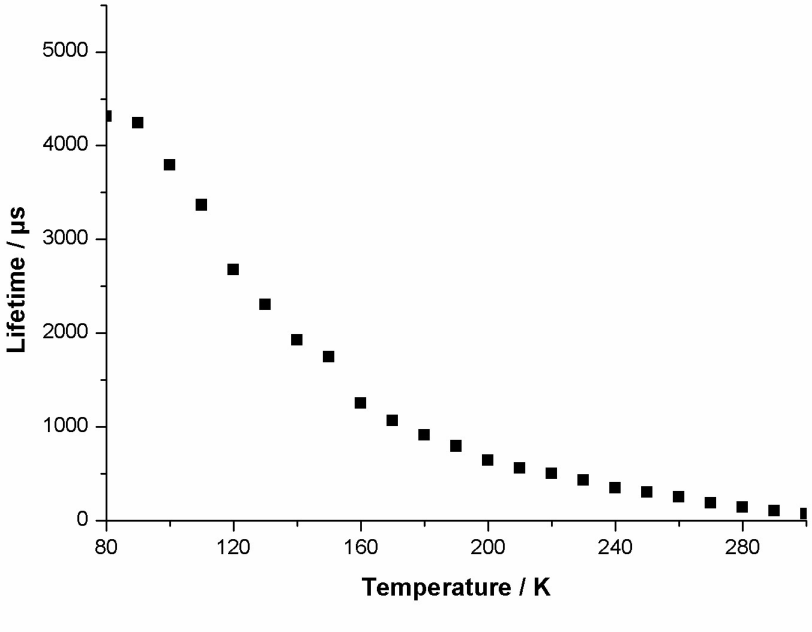


**Fig. S13.** Temperature dependent decay time of the excited state of $\mathbf{C_{Cl}}$, from 80 K to 300 K (measurements were performed every 10 K).

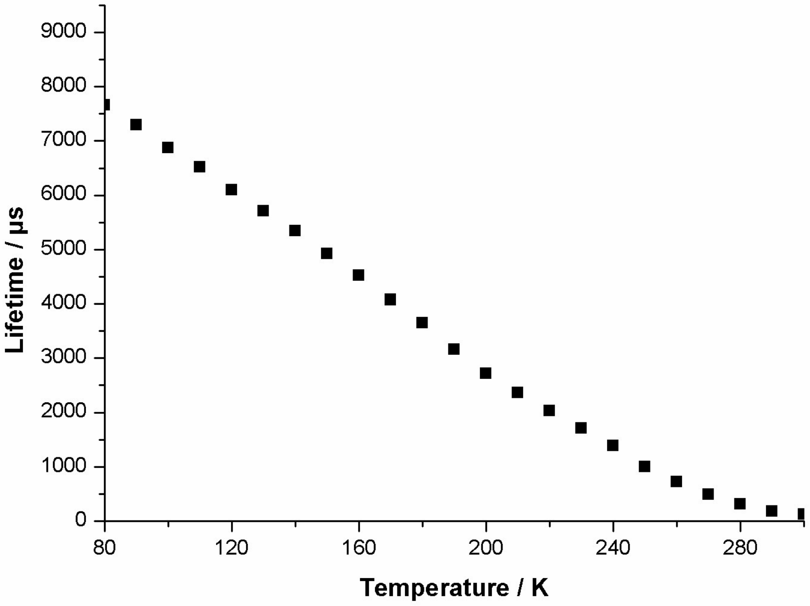


**Fig. S14.** Temperature dependent decay time of the excited state of **$C_{Br}$** ($\lambda_{ex}$ = 370 nm), from 80 K to 300 K (measurements were performed every 10 K).

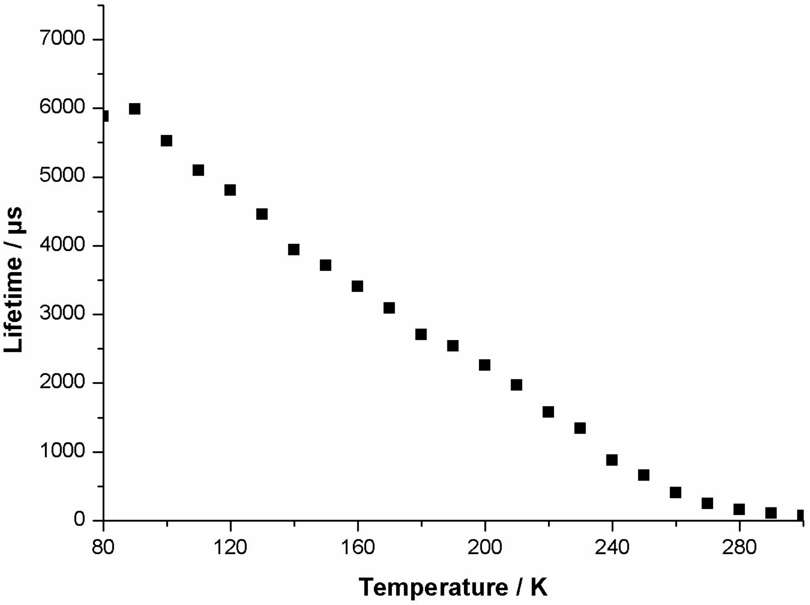


**Fig. S15.** Temperature dependent decay time of the excited state of **$C_I$** ($\lambda_{ex}$ = 370 nm), from 80 K to 300 K (measurements were performed every 10 K).

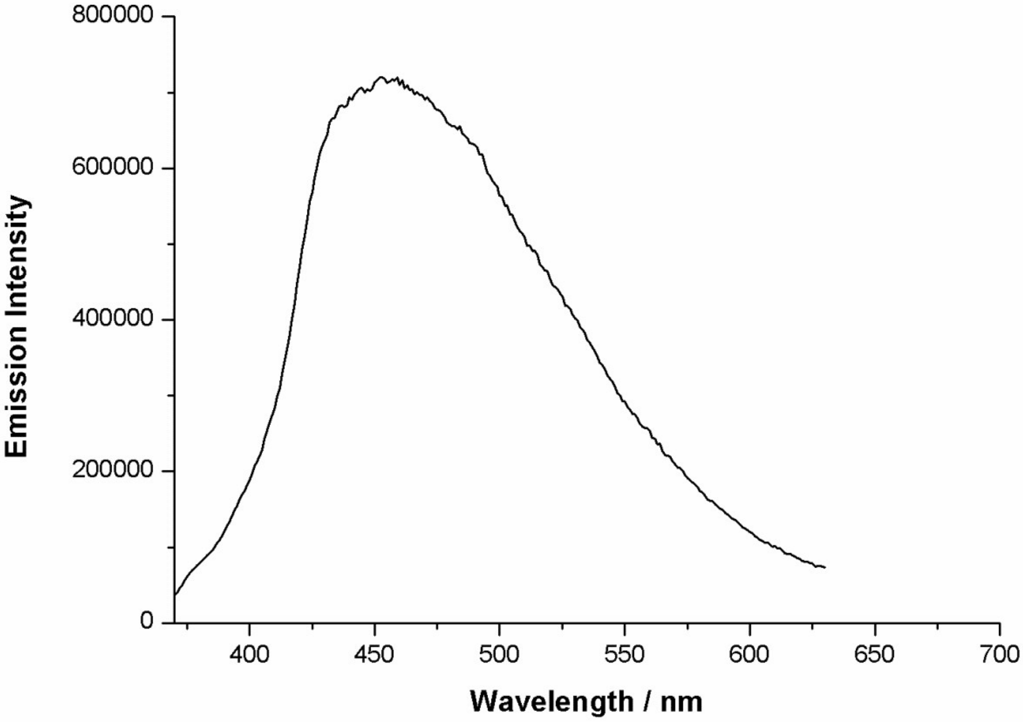


**Fig. S16.** Emission spectrum of the frozen phase of **B**, recorded at 80 K with $\lambda_{ex}$ = 320 nm.

## IV. TG-DTA Analysis

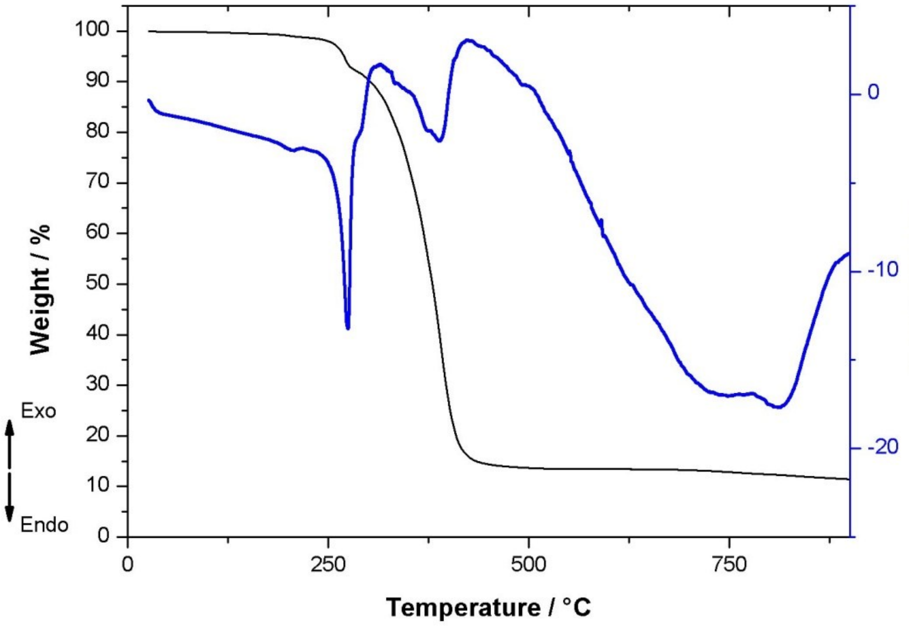


**Fig. S17.** TG-DTA measurement of $\mathbf{C_{Cl}}$ from RT to 900 °C with a heat ramp of 5 °C/minutes.

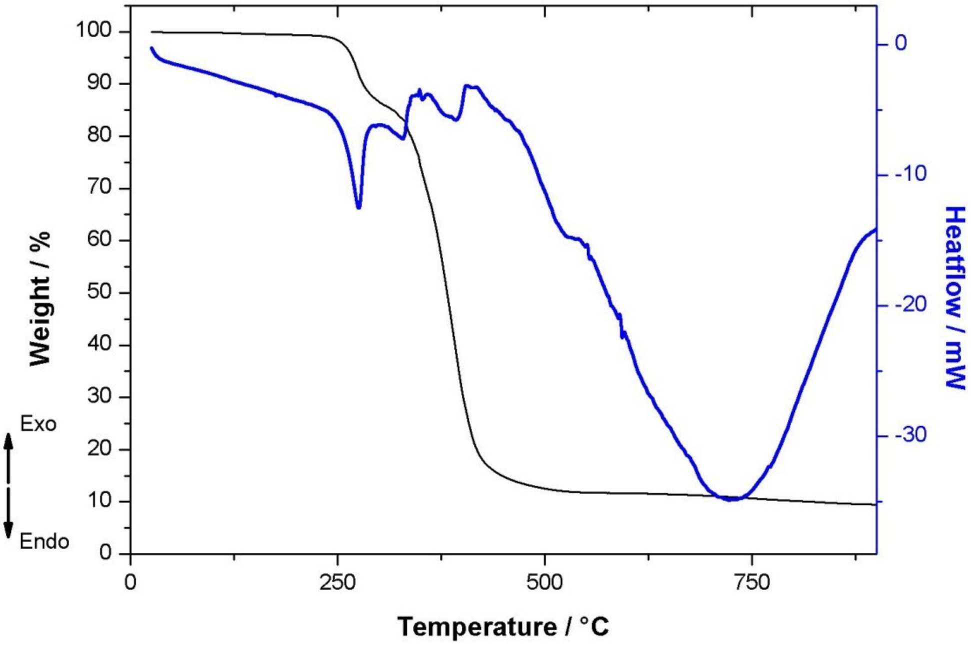


**Fig. S18.** TG-DTA measurement of $\mathbf{C_{Br}}$ from RT to 900 °C with a heat ramp of 5 °C/minutes.

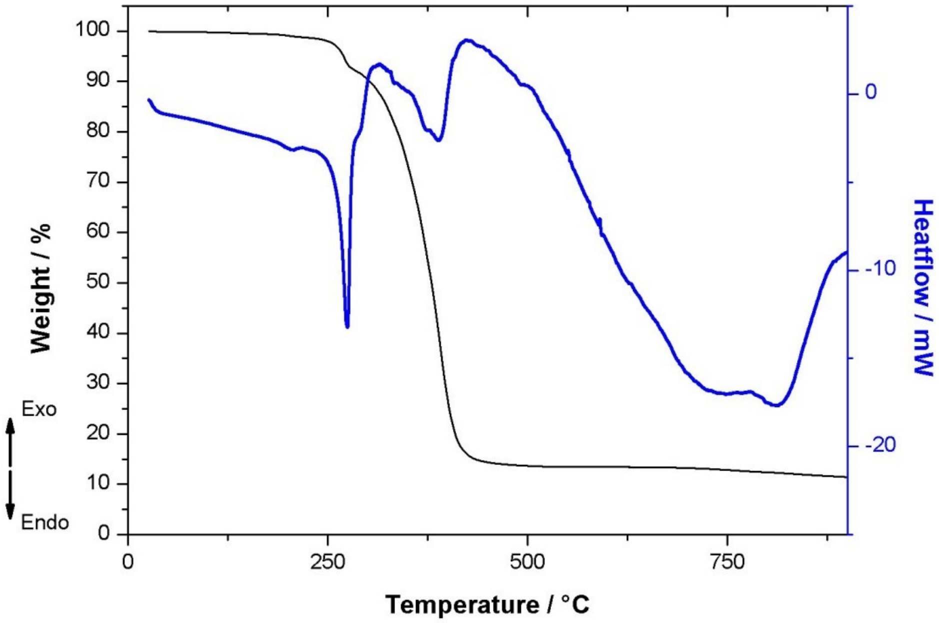


**Fig. S19.** TG-DTA measurement of $\mathbf{C}_{\mathrm{I}}$ from RT to 900 °C with a heat ramp of 5 °C/minutes.

## V. References

[S1] Z. Otwinowski, W. Minor, *In Methods in Enzymology*, (Ed.: C.W. Carter, Jr. & R.M. Sweet), New York: Academic Press, 1997, **276**, 307.

[S2] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. J. Spagna, *Applied Cryst.* 1999, **32**, 115.

[S3] G. M. Sheldrick, SHELX97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

[S4] (a) A. L. J. Spek, *Appl. Crystallogr.* 2003, **36**, 13. (b) P. van der Stuis, A. L. Spek, *Acta Crystallogr.* 1990, **46**, 194.

[S5] International Tables for X-ray Crystallography, Vol. C, Ed. Kluwer, Dordrech, 1992.