



Supplementary Materials for

High-performance light-emitting diodes based on carbene-metal-amides

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Materials and Methods

Synthesis of carbene metal amides

General Considerations. Unless stated otherwise all reactions were carried out in air. Solvents were distilled and dried as required. Sodium tert-butoxide, HNPh₂, carbazole and 3,6-di-tBucarbazole were purchased from Sigma-Aldrich and used as received. Complexes (CAAC)MCl (M = Cu and Au) were obtained as described (28). Spectra of ¹H, ¹³C{¹H} were recorded using a Bruker Avance DPX-300 MHz NMR spectrometer. ¹H NMR (300.13 MHz) and ¹³C{¹H} (75.47 MHz) were referenced to CD₂Cl₂ at δ 5.32 (¹³C, δ 53.84). All electrochemical experiments were performed using an Autolab PGSTAT 302N computer-controlled potentiostat. Cyclic voltammetry (Fig. S14) was performed using a three-electrode configuration consisting of either a glassy carbon macrodisk working electrode (GCE) (diameter of 3 mm; BASi, Indiana, USA) combined with a Pt wire counter electrode (99.99%; GoodFellow, Cambridge, UK) and an Ag wire pseudoreference electrode (99.99%; GoodFellow, Cambridge, UK). The GCE was polished between experiments using alumina slurry (0.3 μm), rinsed in distilled water and subjected to brief ultrasonication to remove any adhered alumina microparticles. The metal electrodes were then dried in an oven at 100 °C to remove any residual traces of water, the GCE was left to air dry and residual traces of water were removed under vacuum. The Ag wire pseudoreference electrodes were calibrated to the ferrocene/ferrocenium couple in MeCN at the end of each run to allow for any drift in potential, following IUPAC recommendations (29). All electrochemical measurements were performed at ambient temperatures under an inert Ar atmosphere in MeCN containing complex under study (1.4 mM) and supporting electrolyte [n-Bu₄N][PF₆] (0.13 M). Data were recorded with Autolab NOVA software (v. 1.11). Elemental analyses were performed by the London Metropolitan University.

Synthesis of (CAAC)AuCz (CMA1). A mixture of (CAAC)AuCl (0.2 g, 0.33 mmol), NaO^tBu (33 mg, 0.34 mmol) and carbazole (57 mg, 0.33 mmol) in dry THF (20 mL) under an argon atmosphere was stirred for 6 h. The mixture was centrifuged and solution of the product was decanted. All volatiles were evaporated in vacuum to give an off-white powder. Yield: 0.23 g (0.31 mmol, 94 %). Product usually contains THF as a solvate and therefor was kept under vacuum for 2 h at 80 °C to remove solvate molecules.

¹H NMR (300 MHz, CD₂Cl₂): δ 7.92 (d, *J* = 7.8 Hz, 2H, carbazole CH⁴), 7.69 (t, *J* = 7.8 Hz, 1H, aryl), 7.46 (d, *J* = 7.8 Hz, 2H, aryl), 7.08 (t, *J* = 7.8 Hz, 2H, carbazole CH²), 6.90 (t, *J* = 7.8 Hz, 2H, carbazole CH³), 6.65 (d, *J* = 7.8 Hz, 2H, carbazole CH¹), 4.34 (d, *J* = 13.5 Hz, 2H, CH₂), 2.92 (sept, *J* = 6.6 Hz, 2H, CHMe₂), 2.44–1.82 (m, 14H, adamantyl CH and CH₂), 1.44 (s, 6H, C(CH₃)), 1.34 (d, *J* = 6.6 Hz, 12H, CHMe₂). ¹³C NMR (75 MHz, CD₂Cl₂) δ 244.6 (C carbene), 150.0 (*ipso*-CN carbazole), 146.2 (*o*-C), 136.7 (*ipso*-C), 129.9 (*p*-CH), 125.7 (*m*-CH), 124.4 (*ipso*-C carbazole), 123.7 (carbazole CH²), 119.4 (carbazole CH⁴), 116.2 (carbazole CH³), 114.2 (carbazole CH¹), 77.4 (C_q), 64.5 (C_q), 49.2 (CH₂), 39.4 (CH₂), 37.7 (CH), 35.8 (CH₂), 34.8 (CH₂), 29.5, 28.6, 27.8, 26.5, 23.4 (CH₃). Anal. Calcd. for C₃₉H₄₇N₂Au (740.76): C, 63.23; H, 6.39; N, 3.78. Found: C, 63.34; H, 6.43; N, 3.71.

Synthesis of (CAAC)CuCz (CMA2). Following the procedure described for CMA1, the complex was made from (CAAC)CuCl (0.2 g, 0.42 mmol), NaO^tBu (44 mg, 0.42 mmol) and carbazole (70 mg, 0.42 mmol) as a yellow powder. Yield: 0.22 g (0.36 mmol, 86%).

¹H NMR (300 MHz, CD₂Cl₂): δ 7.90 (d, *J* = 7.4 Hz, 2H, carbazole CH⁴), 7.72 (t, *J* = 7.8 Hz, 1H, aromatic CH), 7.49 (d, *J* = 7.8 Hz, 2H, aryl), 7.04 (t, *J* = 7.4 Hz, 2H, carbazole CH²), 6.89 (t, *J* = 7.4 Hz, 2H, carbazole CH³), 6.33 (d, *J* = 7.4 Hz, 2H, carbazole CH¹), 3.89 (d, *J* = 12.3 Hz, 2H, CH₂), 2.97 (sept, *J* = 6.6 Hz, 2H, CHMe₂), 2.33–1.88 (m, 14H, adamantyl CH and CH₂), 1.42 (s, 6H, CMe₂), 1.35 (d, *J* = 6.6 Hz, 6H, CHMe₂), 1.18 (d, *J* = 6.6 Hz, 6H, CHMe₂). ¹³C NMR (75 MHz, CD₂Cl₂) δ 254.1 (C carbene), 150.3 (*ipso*-CN carbazole), 146.1 (*o*-C), 136.4 (*ipso*-C), 129.9 (*p*-CH), 125.6 (*m*-CH), 124.4 (*ipso*-C carbazole), 123.4 (carbazole CH²), 119.2 (carbazole CH⁴), 115.5 (carbazole CH³), 114.8 (carbazole CH¹), 79.1 (C_q), 65.4 (C_q), 48.4 (CH₂), 38.9 (CH₂), 37.7 (CH), 36.5 (CH₂), 34.5 (CH₂), 29.64, 29.62, 28.7, 27.5, 26.5, 22.7 (CH₃). Anal. Calcd. for C₃₉H₄₇N₂Cu (607.35): C, 77.13; H, 7.80; N, 4.61. Found: C, 77.07; H, 7.89; N, 4.70.

Synthesis of (CAAC)AuNPh₂ (CMA3). Following the procedure described for CMA1, the complex was made from (CAAC)AuCl (0.2 g, 0.33 mmol), NaOtBu (33 mg, 0.33 mmol) and diphenylamine (56 mg, 0.33 mmol) as a yellow powder. Yield: 0.24 g (0.32 mmol, 98%).

¹H NMR (300 MHz, CD₂Cl₂): δ 7.58 (t, *J* = 7.8 Hz, 1H, aryl), 7.34 (d, *J* = 7.8 Hz, 2H, aryl), 6.87 (t, *J* = 7.2 Hz, 4H, *m*-CH aniline), 6.60 (d, *J* = 7.2 Hz, 4H, *o*-CH aniline), 6.46 (t, *J* = 8.1 Hz, 2H, *p*-CH aniline), 4.05 (d, *J* = 13.8 Hz, 2H, CH₂), 2.81 (sept, *J* = 6.6 Hz, 2H, CHMe₂), 2.35–1.74 (m, 14H, adamantyl CH and CH₂), 1.36 (s, 6H CMe₂), 1.31 (d, *J* = 6.6 Hz, 6H, CHMe₂), 1.30 (d, *J* = 6.6 Hz, 6H, CHMe₂). ¹³C NMR (75 MHz, CD₂Cl₂) δ 242.6 (carbene C), 155.5 (*i*-C_{amide}), 145.7 (*o*-C), 136.5 (*i*-C), 129.7 (*p*-CH), 128.6 (*m*-C_{amide}), 125.5 (*m*-CH), 120.9 (*o*-C_{amide}), 116.9 (*p*-C_{amide}), 76.8 (C_q), 64.3 (C_q), 49.2 (CH₂), 39.4 (CH₂), 37.4 (CH), 35.2 (CH₂), 34.8 (CH₂), 29.4, 28.3, 27.7, 26.2, 23.4 (CH₃). Anal. Calcd. for C₃₉H₄₉N₂Au (742.78) C, 63.06; H, 6.65; N, 3.77. Found: C, 63.19; H, 6.71; N, 3.72.

Synthesis of (CAAC)AuDTBCz (CMA4). Following the procedure described for CMA1, the complex was made from (CAAC)AuCl (0.2 g, 0.33 mmol), NaOtBu (33 mg, 0.34 mmol) and 3,6-di-*t*Bucarbazole (92 mg, 0.33 mmol) as a yellow powder. Yield: 0.255 g (0.33 mmol, 91%).

¹H NMR (300 MHz, CD₂Cl₂): δ 7.93 (d, *J* = 2.1 Hz, 2H, carbazole CH⁴), 7.69 (t, *J* = 8.0 Hz, 1H, aromatic CH), 7.46 (d, *J* = 8.0 Hz, 2H, aryl), 7.15 (dd, *J* = 8.8 and 2.1 Hz, 2H, carbazole CH²), 6.58 (d, *J* = 8.8 Hz, 2H, carbazole CH¹), 4.34 (d, *J* = 11.8 Hz, 2H, CH₂), 2.90 (sept, *J* = 7.2 Hz, 2H, CHMe₂), 2.34–1.87 (m, 14H, adamantyl CH and CH₂), 1.42 (s, 6H, CMe₂), 1.39 (s, 18H, ^tBu), 1.35 (d, *J* = 7.2 Hz, 6H, CHMe₂) overlapping with 1.34 (d, *J* = 7.2 Hz, 6H, CHMe₂). ¹³C NMR (75 MHz, CD₂Cl₂) δ 244.6 (C carbene), 148.4 (*ipso*-CN carbazole), 146.1 (*o*-C), 146.0 (*ipso*-C), 138.7 (*ipso*-C³ carbazole ^tBu), 136.6 (*ipso*-C), 129.8 (*p*-CH), 125.5 (*m*-CH), 124.0 (*ipso*-C carbazole), 121.4 (carbazole CH²), 115.3 (carbazole CH⁴), 113.3 (carbazole CH¹), 77.2 (C_q), 64.4 (C_q), 49.1 (CH₂),

39.3 (CH₂), 37.5 (CH), 35.7 (CH₂), 34.7 (C, ^tBu), 34.6 (CH₂), 29.49, 28.5, 27.7, 26.4, 23.3 (CH₃). Anal. Calcd. for C₄₇H₆₃N₂Au (852.98): C, 66.18; H, 7.44; N, 3.28. Found: C, 66.27; H, 7.56; N, 3.22.

For crystallographic and electrochemical characterization of CMA compounds see Figs. S10 & S14, and Table S2.

X-Ray crystallography

The crystals suitable for X-ray study for CMA2 and CMA4 were obtained by layering CH₂Cl₂ solution with hexanes at -20 °C. Gold complexes (CMA1 and CMA3) were crystallized by slow evaporation of benzene solution. Crystals were mounted in oil on glass fibres and fixed in the cold nitrogen stream on a diffractometer. X-ray diffraction experiment was carried out with an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, using graphite monochromated Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 140 K. Data were processed using the CrystAlisPro-CCD and -RED software (30).

The principal crystallographic data **CMA1**: C₃₉H₄₇AuN₂, orthorhombic, space group $P2_12_12_1$, $a = 9.4256(1) \text{ \AA}$, $b = 15.6507(2) \text{ \AA}$, $c = 21.8140(2) \text{ \AA}$, $V = 3217.94(6) \text{ \AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.529 \text{ g cm}^{-3}$, $\mu = 4.601 \text{ mm}^{-1}$, yellow/prism, crystal size $0.45 \times 0.42 \times 0.31 \text{ mm}$, $F(000) = 1496$, $T_{\text{min}}/T_{\text{max}} = 0.3296/0.2313$, $R_1 = 0.0156$ (from 6203 unique reflections with $I > 2\sigma(I)$) and $wR_2 = 0.0379$ (from all 6307 unique reflections), $GOF = 1.046$, $\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}} = 0.706/-0.310$. **CMA2**: C₃₉H₄₇AuN₂·CH₂Cl₂, monoclinic, space group $P2_1/n$, $a = 10.8520(2) \text{ \AA}$, $b = 18.8311(3) \text{ \AA}$, $c = 18.3279(4) \text{ \AA}$, $\beta = 106.337(2)^\circ$, $V = 3594.17(12) \text{ \AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.279 \text{ g cm}^{-3}$, $\mu = 0.786 \text{ mm}^{-1}$, colourless/prism, crystal size $0.49 \times 0.41 \times 0.23 \text{ mm}$, $F(000) = 1464$, $T_{\text{min}}/T_{\text{max}} = 0.8398/0.6993$, $R_1 = 0.0361$ (from 7150 unique reflections with $I > 2\sigma(I)$) and $wR_2 = 0.0989$ (from all 8668 unique reflections), $GOF = 1.063$, $\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}} = 0.738/-0.697$. **CMA3**: C₃₉H₄₉AuN₂·C₆H₆, monoclinic, space group $P2_1/c$, $a = 12.3977(2) \text{ \AA}$, $b = 20.1046(3) \text{ \AA}$, $c = 15.7158(2) \text{ \AA}$, $\beta = 107.794(2)^\circ$, $V = 3729.78(9) \text{ \AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.462 \text{ g cm}^{-3}$, $\mu = 3.978 \text{ mm}^{-1}$, yellow/plate, crystal size $0.26 \times 0.23 \times 0.15 \text{ mm}$, $F(000) = 1672$, $T_{\text{min}}/T_{\text{max}} = 0.5868/0.4244$, $R_1 = 0.0226$ (from 7931 unique reflections with $I > 2\sigma(I)$) and $wR_2 = 0.0529$ (from all 9002 unique reflections), $GOF = 1.045$, $\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}} = 1.357/-0.998$. **CMA4**: C₄₇H₆₃AuN₂·2CH₂Cl₂, monoclinic, space group $P2_1/c$, $a = 12.7613(4) \text{ \AA}$, $b = 15.3884(3) \text{ \AA}$, $c = 24.1466(5) \text{ \AA}$, $\beta = 95.427(2)^\circ$, $V = 4720.6(2) \text{ \AA}^3$, $Z = 4$, $d_{\text{calc}} = 1.439 \text{ g cm}^{-3}$, $\mu = 3.377 \text{ mm}^{-1}$, colourless/plate, crystal size $0.26 \times 0.17 \times 0.09 \text{ mm}$, $F(000) = 2088$, $T_{\text{min}}/T_{\text{max}} = 0.7509/0.4738$, $R_1 = 0.0360$ (from 11579 unique reflections with $I > 2\sigma(I)$) and $wR_2 = 0.0798$ (from all 14388 unique reflections), $GOF = 1.077$, $\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}} = 1.836/-1.205$. Alert B is originated from the restriction of the resolution range of the data which was imposed by SHEL statement on the final refinement step. One of the ^tBu-groups was disordered into two positions with equal occupancies for CMA4. DFIX statement was used to adopt a tetrahedral geometry for the disordered groups of atoms. The structures were solved by direct methods and refined by the full-matrix least-squares against F^2 in an anisotropic (for non-hydrogen atoms) approximation. All hydrogen atom positions were refined in isotropic approximation in “riding” model with the $U_{\text{iso}}(\text{H})$ parameters equal to $1.2 U_{\text{eq}}(\text{C}_i)$, for methyl groups equal to $1.5 U_{\text{eq}}(\text{C}_{ii})$, where $U(\text{C}_i)$ and $U(\text{C}_{ii})$ are respectively the equivalent thermal parameters of the carbon atoms to which

the corresponding H atoms are bonded. All calculations were performed using the SHELXTL software (31).

DFT and time-dependent DFT computations

The ground states and excited states were optimized by the density functional theory (DFT) (32) and time-dependent density functional theory (TD-DFT) using the hybrid density functional PBE0 method (33, 34) in combination with def2-TZVP basis set of Ahlrichs and coworkers (35, 36). Relativistic effective core potential of 60 electrons was used to describe the core electrons of Au (37, 38), without consideration of spin-orbit coupling effects. The method was selected based on recommendations of its use for third-row transition metal complexes (39) and specifically for closely related Au-complexes (40) together with its demonstrated suitability for excited state calculations (41-44). The employed PBE0/def2-TZVP combination has been previously utilized with success in studies of luminescent Cu- and Au-complexes (28, 45, 46). The accuracy of the PBE0 method was further validated for CMA1 by comparison with the hybrid-meta exchange M06 functional accounting for noncovalent interactions (47). The two methods produced nearly identical excitation energies. The molecular structures of CMA compounds obtained with DFT and TD-DFT calculations are consistent with the X-ray crystal structures (Fig. S10), confirming the accuracy of the calculations.

Vertical transition energies were estimated by constraining the excited singlet to the ground state geometry (S_1^{P*}), while the S_1^P and T_1^R energies were estimated by fixing the dihedral angle and allowing the rest of the molecule to relax. For S_1^P , this simulates vibrational relaxation in a constrained geometry, as implicated in solid films. The relative state energies are presented in Table S4.

Vibrational frequencies were calculated for CMA1 to confirm the nature of the stationary points. S_0 , S_1^R , T_1^P and T_1^R states were confirmed as minima in the potential energy surface. S_1^P was confirmed as a transition state, the imaginary frequency corresponding to ligand rotation. Excited state vibrational frequency calculations were carried out by TURBOMOLE version 6.3 (48). All other calculations were carried out by Gaussian 09 (49). Cartesian coordinates for these geometries are given in Table S5.

Cryogenic ns- μ s time-resolved photoluminescence measurements

The solid-state samples for PL studies were spin-coated from anhydrous tetrahydrofuran solutions (10 mg/mL) onto pre-cleaned quartz substrates. The samples were placed under high vacuum for 15 min to remove the solvent. Time-resolved PL spectra were recorded using an electrically-gated intensified CCD (ICCD) camera (Andor iStar DH740 CCI-010) connected to a calibrated grating spectrometer (Andor SR303i). Photoexcitation was provided by femtosecond laser pulses which were created by second harmonic generation (SHG) in a BBO crystal from the fundamental output (pulse energy = 1.55 eV, pulse width = 80 fs) of a Ti:Sapphire laser system (Spectra Physics Solstice), at a repetition rate of 1 kHz. The photons from the laser pulses had a wavelength of 400 nm. A 420 nm long-pass filter was used to prevent scattered laser signal from entering the camera. Temporal evolution of the PL emission was obtained by stepping the ICCD gate delay with respect to the excitation pulse. The minimum gate width of the ICCD was

~2.5 ns. The cooling of the samples was provided by liquid helium, and the temperature of the samples was regulated using a temperature-controlled cryostat.

Ultrafast (fs-ps) transient grating photoluminescence measurements

A Ti:Sapphire amplifier system (Spectra-Physics Solstice) operating at 1 KHz generating 80-fs pulses was split into the pump and probe beam arms. The pump beam was generated by second harmonic generation (SHG) in a BBO crystal and focused onto the sample. The excitation density was $1 \times 10^{19} \text{ cm}^{-3}$ for thin films, excitation fluence was $300 \mu\text{J cm}^{-2}$ for solutions. Photoluminescence is collimated using a silver off-axis parabolic mirror and focused onto the gate medium. About $80 \mu\text{J/pulse}$ of the 800 nm laser output is used for the gate beams, which is first raised 25 mm above the plane of the PL to produce a boxcar geometry and split into a pair of gate beams using a 50/50 beam splitter. The gate beams are focused onto the gate medium (fused silica), crossing at an angle of $\sim 5^\circ$ and overlapping with the focused PL. The two gate beams interfere and create a transient grating in the gate medium due to a modulation of the refractive index via the optical Kerr effect. Temporal overlap between the two gate beams is achieved via a manual delay stage. The PL is then deflected on the transient grating causing a spatial separation of the gated signal from the PL background. Two lenses collimate and focus the gated signal onto the spectrometer entrance (Princeton Instruments SP 2150) after long- and short-pass filters remove scattered pump and gate light, respectively. Gated PL spectra are measured using an intensified CCD camera (Princeton Instruments, PIMAX4). The (~ 10 ns) electronic shutter of the intensified CCD camera was used to further suppress long-lived PL background. PL spectra at each gate time delay are acquired from ~ 10000 laser shots. The time delay between pump and gate beams is controlled via a motorized optical delay line on the excitation beam path and a LabVIEW data acquisition program.

Transient absorption (TA) spectroscopy

The output of a Ti:Sapphire amplifier system (Spectra-Physics Solstice) operating at 1 KHz and generating 90-fs pulses was split into the pump and probe beam paths. The visible and near-infrared broadband probe beams were generated in home-built noncollinear optical parametric amplifiers. The 400 nm narrowband (10 nm full-width at half-maximum) pump beam was provided by a TOPAS optical parametric amplifier (Light Conversion). The transmitted pulses were collected with an InGaAs dual-line array detector (Hamamatsu G11608-512) driven and read out by a custom-built board from Stresing Entwicklungsbüro. The excitation density for the visible measurements was $5 \times 10^{17} \text{ cm}^{-3}$. The excitation density for the near-infrared measurements was $1 \times 10^{19} \text{ cm}^{-3}$.

Raman Spectroscopy

Raman measurements were conducted by back-scattering (HORIBA T64000) a 532 nm (CW diode) line with a subtractive triple-stage. Spectra were collected between 18 and 1700 cm^{-1} where the CCD detector (HORIBA Synapse Open-Electrode) has a monotonically increasing quantum efficiency of between 0.43 and 0.50. Acquisitions employed a $100\times$ optical objective and used minimal laser intensity to avoid laser damage. Powder samples were measured in air at room-temperature.

Fabrication of solution-processed OLEDs

Indium tin oxide (ITO)-coated glass substrates were cleaned with acetone (10 min) and isopropanol (10 min) in an ultrasonic bath. The substrates were blown dry using an N₂ flow gun, followed by O₂ plasma etching for 10 min. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS, Clevis P VP AI 4083) was filtered and spin-coated onto the substrates in air to form a ~30 nm layer, and was annealed at 200 °C for 15-30 min under nitrogen atmosphere. TFB (Cambridge Display Technology) was spin-coated from anhydrous toluene (Sigma-Aldrich) solution onto the PEDOT:PSS to form a layer of ~180 nm, followed by annealing at 200 °C for 20 min. The emissive layer was spin-coated from anhydrous dimethylformamide (Sigma-Aldrich) solution onto the TFB surface to achieve a ~20 nm layer. The weight concentration of CMA emitters in PVK (Sigma-Aldrich) was ~20%. This was followed by annealing at 90 °C for 10 min. ~70 nm thick BPhen (97%, Sigma-Aldrich) was then spin-coated from anhydrous methanol (Sigma-Aldrich) onto the emissive layer, followed by annealing at 60 °C for 10 min. From thickness profilometry, we found that sequential deposition of these solution-processed layers did not cause measurable thickness reduction of any of the underlying layers, suggesting minimum intermixing of the multilayer interfaces. Lithium fluoride (99.99%, Sigma-Aldrich) (0.6 nm) and aluminium (100 nm) were successively evaporated onto the samples through a shadow mask in a thermal evaporator under high vacuum ($< 3 \times 10^{-6}$ mbar), resulting in a device area of about 5.25 mm². After the assembly of electrical contacts, the devices were encapsulated under glass and stored in N₂ for 12-48 h before testing.

OLED performance characterization

The EL spectra of the devices were recorded using the calibrated ICCD-spectrometer set-up used in the PL measurements. The accuracy of the spectral data was cross-checked against a Labsphere CDS-610 spectrometer, as well as a Minolta CS-1000 luminance meter. Current density-voltage-luminance (J-V-L) characteristics were measured using a Minolta CS-200 luminance meter and a Keithley 2400 source-meter. The EQE of the devices were calculated based on the Lambertian emission profile measured. In addition, the accuracy of the EQE measurements for a subset of devices was checked using a calibrated silicon photodiode with known spectral response function, a Minolta CS-1000 luminance meter, as well as an integrating sphere. The histogram represents many batches of samples based on CMA4, with controlled layer thicknesses varied within $\pm 20\%$ of those specified above in order to empirically identify the optimum device structure.

Transient-electroluminescence measurements

The devices were electrically excited by a function generator using 1 kHz square voltage (current) pulses with a pulse width of 0.5 ms for the on-cycles (forward bias). The off-cycles of the device operation were provided by a reverse bias of -4 V to reduce charge accumulation effects. The instrument response time of the function generator was ~10 ns. The transient-EL of the samples was recorded by the same ICCD spectrometer used in the PL measurements.

Supplementary Text

Rate equations for the calculation of activation energy

We consider the excited state kinetics for a general organic emitter with intersystem crossing between singlet and triplet states. In this analysis, we focus on the delayed emission, for which the initial excited state population (after prompt emission and ISC) primarily comprises triplets in the T_1 state. This is consistent with reversible quenching of the delayed photoluminescence by exposure to oxygen. The kinetics of the delayed PL is therefore primarily governed by the temporal evolution of the triplet population.

The singlet decay processes are characterised by k_r^S (radiative decay of singlets) and k_{nr}^S (non-radiative decay of singlets). Similarly, in this model, k_r^T (radiative decay of triplets) and k_{nr}^T (non-radiative decay of triplets) are assumed to be possible in the triplet decay channels.

Conversion from singlets to triplets is characterised by the intersystem crossing (ISC) rate k_{ISC} , while the reverse process (RISC) is given by k_{RISC} . The kinetics of the singlet and triplet populations can be described by the following equations:

$$\frac{d[S]}{dt} = (-k_r^S - k_{nr}^S - k_{ISC})[S] + k_{RISC}[T] \quad (S1)$$

$$\frac{d[T]}{dt} = (-k_r^T - k_{nr}^T - k_{RISC})[T] + k_{ISC}[S] \quad (S2)$$

where $[S]$ and $[T]$ are singlet and triplet populations, respectively. During the delayed PL process ($t \gg 1$ ns), the singlet population is small and varies much more slowly than $(k_r^S + k_{nr}^S + k_{ISC})$. Therefore, the relation $\frac{d[S]}{dt} \approx 0$ can be assumed. Setting Eqn. S1 to zero, yields:

$$(-k_r^S - k_{nr}^S - k_{ISC})[S] + k_{RISC}[T] = 0 \quad (S3)$$

which can be rearranged to:

$$[S] = \frac{k_{RISC}}{k_r^S + k_{nr}^S + k_{ISC}}[T] \quad (S4)$$

Substitute Eqn. S4 into Eqn. S2, we obtain:

$$\frac{d[T]}{dt} = (-k_r^T - k_{nr}^T - k_{RISC})[T] + \frac{k_{ISC}k_{RISC}}{k_r^S + k_{nr}^S + k_{ISC}}[T] \quad (S5)$$

Therefore, under these assumptions the decay rate constant of the delayed emission $k_{delayed}$, is given by

$$k_{delayed} = k_r^T + k_{nr}^T + k_{RISC} \left(1 - \frac{k_{ISC}}{k_r^S + k_{nr}^S + k_{ISC}}\right) \quad (S6)$$

In principle, both k_{ISC} and k_{RISC} may be thermally accelerated, e.g. through the promotion of molecular rotation. We examine below which is dominant. For simplicity, we assume the rates of the other decay processes remain constant.

Eqn. S6 can be re-written as:

$$k_{delayed} = k_r^T + k_{nr}^T + k_{RISC} - \frac{k_{RISC}}{\frac{k_r^S + k_{nr}^S}{k_{ISC}} + 1} \quad (S7)$$

According to Eqn. S7, if k_{ISC} is the dominant temperature-dependent process, increasing temperature will result in a lower $k_{delayed}$, which corresponds to longer lifetime of the delayed PL. By contrast, if k_{RISC} is the dominant temperature-dependent process, Eqn. S6 predicts a higher $k_{delayed}$ as the temperature increases. The latter agrees with experiment (Fig. 2A) so we conclude k_{RISC} is the dominant temperature-dependent process. In contrast to mechanistically similar process TADF, the thermal energy discussed here is that required to overcome the rotational barrier between the planar triplet and lower-lying rotated states.

We define a temperature-independent triplet decay rate constant

$$k_0 = k_r^T + k_{nr}^T \quad (S8)$$

and a temperature-independent coefficient

$$\alpha = 1 - \frac{k_{ISC}}{k_r^S + k_{nr}^S + k_{ISC}} \quad (S9)$$

By inspecting Eqn. S9, it is clear that α is a constant between 0 and 1.

The temperature-dependent part of Eqn. S6 can then be written as

$$k_T = \alpha k_{RISC} \quad (S10)$$

which corresponds to the temperature-dependent emission rate described in the main text.

Then Eqn. S6 can be simplified to

$$k_{delayed} = k_0 + k_T \quad (S11)$$

Therefore, the function to describe the delayed PL process can be written as

$$PL_{delayed} = PL_{delayed0} e^{-(k_0+k_T)t} \quad (S12)$$

where $PL_{delayed}$ and $PL_{delayed0}$ are the intensity and the initial ($t = 0$) intensity of the delayed PL component respectively.

Assume the temperature-dependent rate constant has the form

$$k_T = \beta e^{-\frac{E_A}{k_B T}} \quad (S13)$$

where E_A is the thermal activation energy, k_B is Boltzmann constant, T is the temperature in Kelvin and β is a constant.

Therefore, we have:

$$\ln(k_T) = -\left(\frac{E_A}{k_B}\right)\left(\frac{1}{T}\right) + C \quad (S14)$$

Supplementary Figures

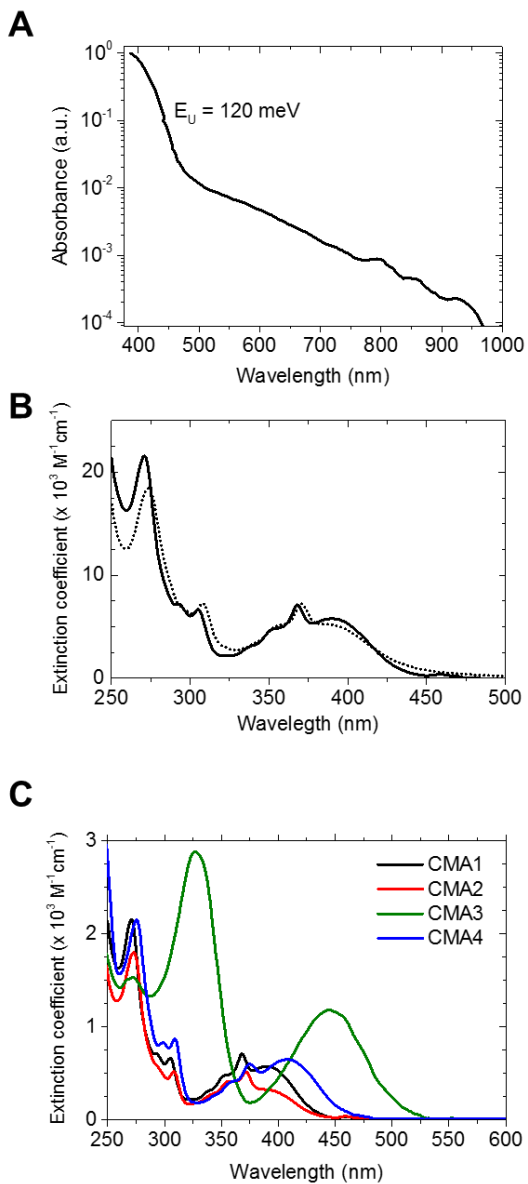


Fig. S1 Additional absorption data. **A)** Photothermal deflection spectrum of CMA1 spin-cast film indicating the Urbach tail with characteristic energy E_U (120 meV) and a slowly varying background absorption extending to the near-IR. **(B)** Molar extinction of CMA1 in THF solution (solid) and absorption in neat solid film (dot) including UV region. To convert from molar extinction ($\text{M}^{-1} \text{ cm}^{-1}$) to film absorption (cm^{-1}), multiply by 2. **(C)** Molar extinction coefficient of CMA1-4 in THF solution.

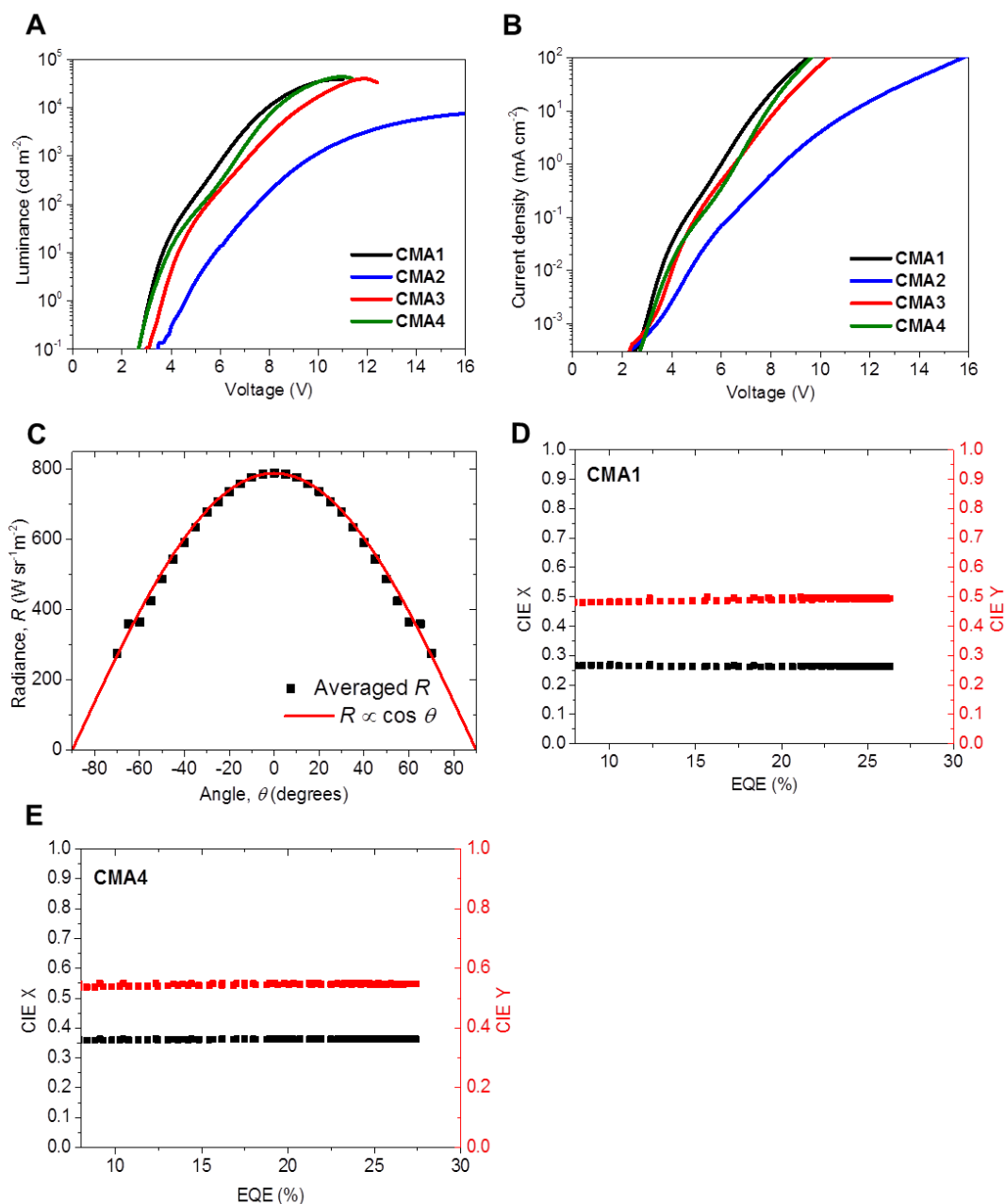


Fig. S2 Additional device performance data. (A) Luminance versus voltage. **(B)** Current density versus voltage. **(C)** Angular emission profile of a representative device, consistent with Lambertian emission characteristics as fitted by the red line. **(D), (E)** CIE coordinates as a function of EQE for OLEDs fabricated from CMA1 and CMA4. All devices utilize 20 wt% CMA in PVK host, device area 5.25 mm^2 .

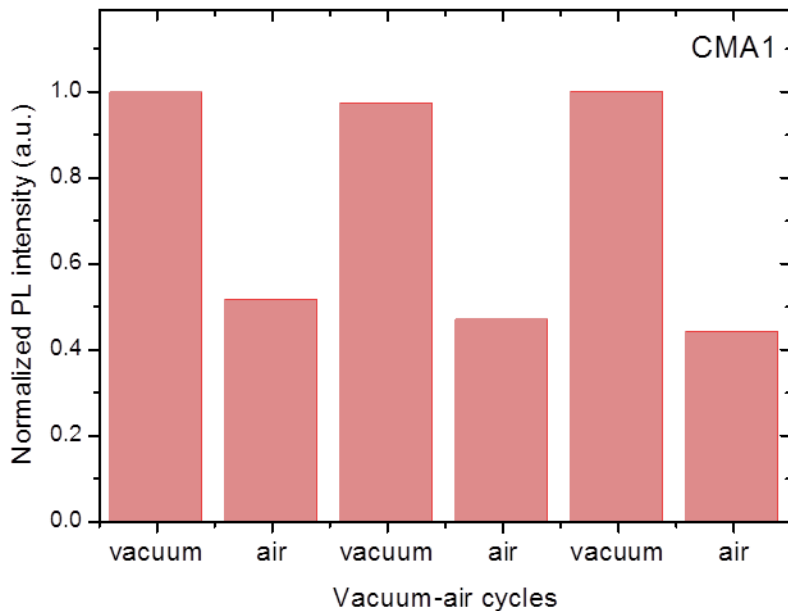


Fig. S3 Reversible PL quenching by exposure to oxygen for CMA1. Change in PL intensity of a thin film of CMA1 under sequential (left to right) vacuum-air cycles, normalized to the intensity of the first measurement. Vacuum of $< 10^{-5}$ mBar, achieved using a turbomolecular pump. Samples stabilized for 10 minutes under vacuum or in air prior to each measurement. The reversibility implicates triplets in the luminescence pathway, since these can quench by transfer to the triplet ground state of molecular oxygen.

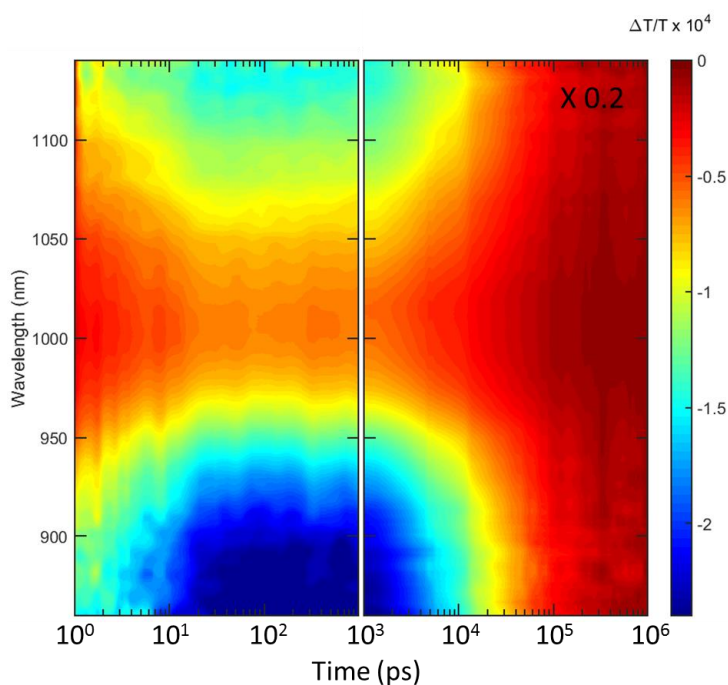


Fig. S4 Near-Infrared transient absorption data for CMA1. TA of neat CMA1 film on ps- μ s timescales, 400nm pump, excitation density $1 \times 10^{19} \text{ cm}^{-3}$. There are no NIR features associated with the singlet, but two PIA features at $\sim 860 \text{ nm}$ and $> 1050 \text{ nm}$ have identical growth and decay kinetics to the 645 nm triplet PIA seen in Fig. 2D at the same excitation density.

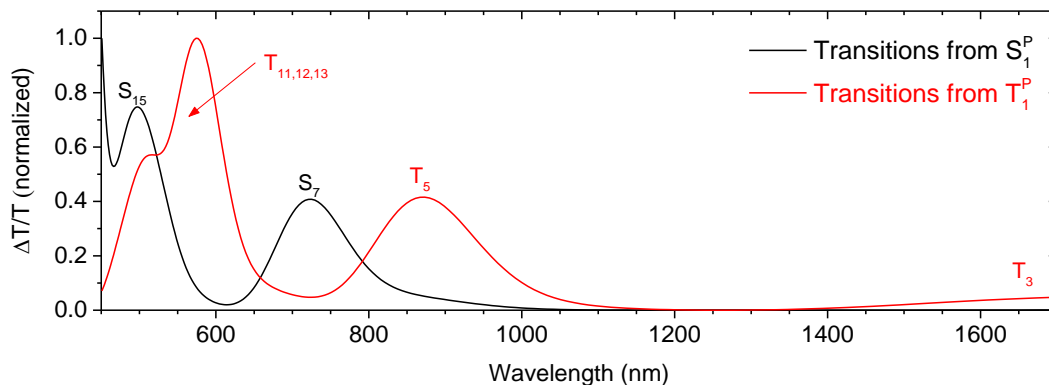


Fig. S5 Calculated PIA spectra for CMA1 in co-planar geometry. Excited state transitions from S_1/T_1 to S_N/T_N for CMA1 considering the first 20 singlet and triplet excited states in the co-planar geometry, from TD-DFT calculations. Each transition is weighted by its calculated oscillator strength and a Gaussian broadening of 150 meV is assumed. Within the available measurement range, 2-3 triplet PIA features are expected and 1-2 singlet PIA features, with the $S_1 \rightarrow S_7$ transition bracketed by two of the triplet PIAs. Tabulated data are presented in Table S6.

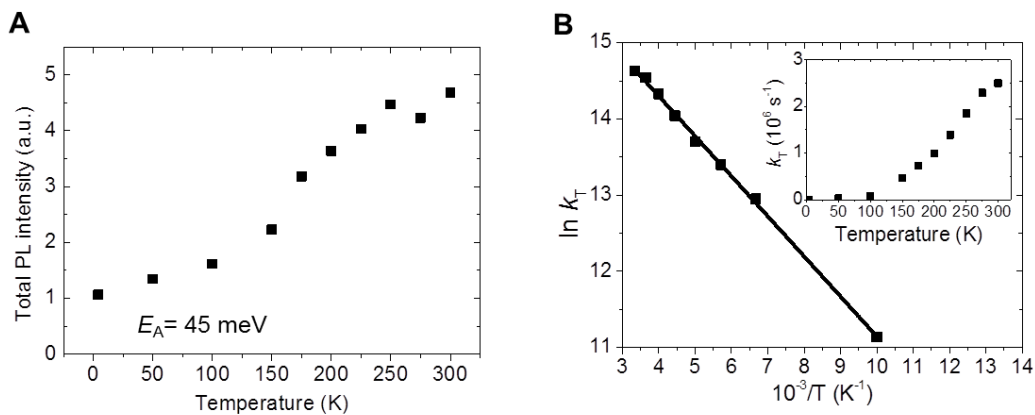


Fig. S6 Additional temperature-dependent PL of CMA1 neat film. (A) Temperature-dependent total PL intensities calculated by integrating the time-dependent decays over the complete measurement window. (B) Temperature-dependent decay rate k_T , showing an activation energy of 45 meV above 100K.

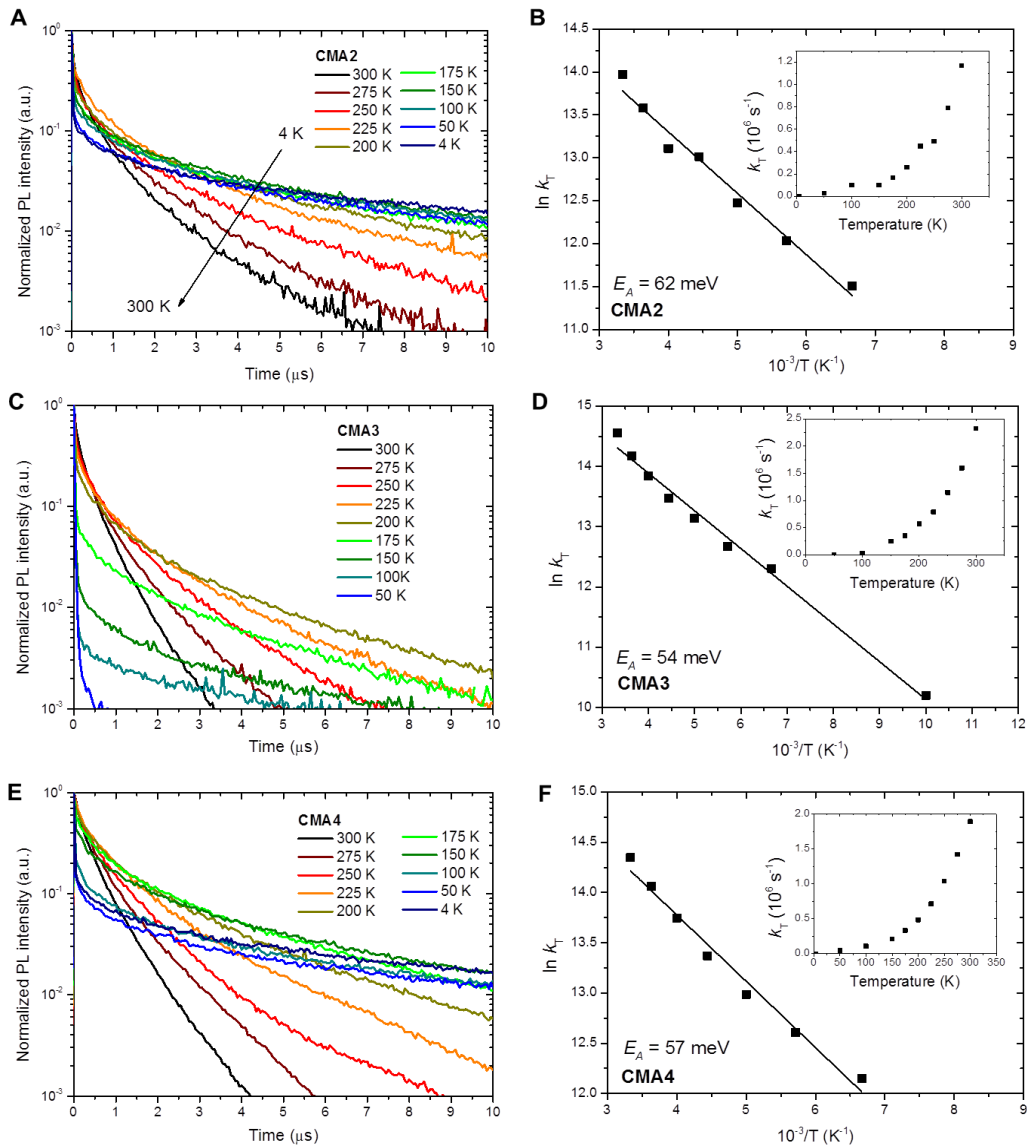


Fig. S7 Transient photoluminescence characterization of CMA2-4. (A, C, E) Temperature-dependent ns- μs PL kinetics measured using an electrically gated ICCD for neat films of CMA2-4. **(B, D, F)** Activation energies for the rate of delayed emission from CMA2-4.

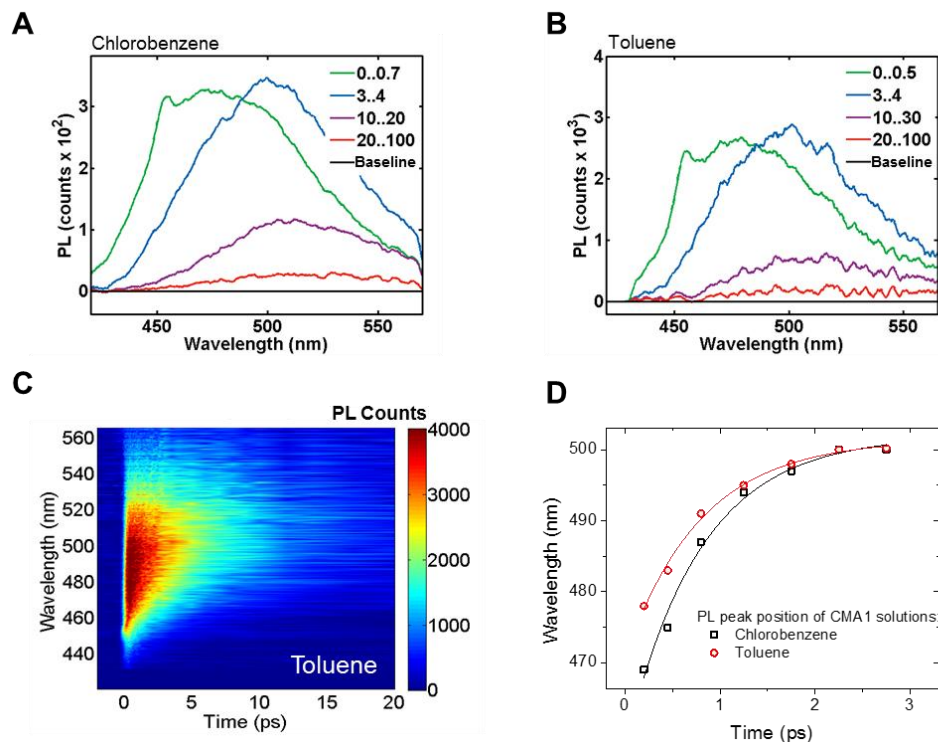


Fig. S8 Transient PL measurements of CMA1 in solutions. (A) Kerr-gated PL spectra of CMA1 dissolved in chlorobenzene. (B) Kerr-gated PL spectra of CMA1 dissolved in toluene. (C) Ultrafast PL map of CMA1 in toluene. (D) Peak position shift over time for CMA1 in chlorobenzene (black squares) and toluene (red circles) with exponential fits as guides to the eye. The initial shift is slightly faster in toluene, but the final emission and decay rate are nearly identical for both solvents.

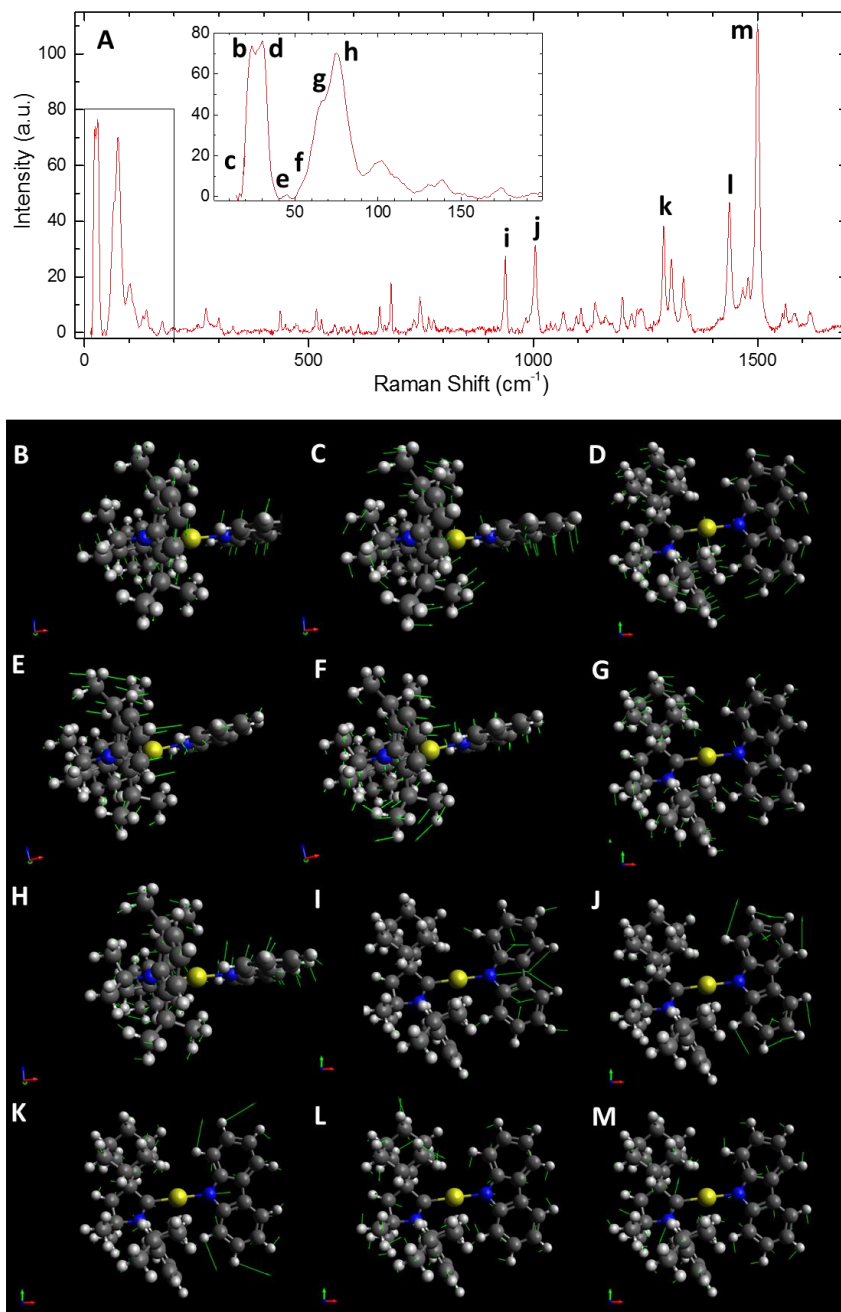


Fig. S9 Experimental Raman spectrum and primary Raman-active normal modes of CMA1 from DFT calculations. Relative atomic motion indicated by green arrows. (A) Measured Raman spectrum, inset highlights the cluster of low-frequency modes with high Raman activity. b-m correspond to peaks assigned to modes B-M. (B) relative rotation of carbene and amide about the axis of the C-M-A linkage, calculated frequency 21.41 cm^{-1} . (C, D, G, H) relative rotation of carbene and amide about other axes, calculated frequencies 20.80 cm^{-1} , 27.46 cm^{-1} , 69.86 cm^{-1} , 82.68 cm^{-1} . (E, F) relative rotation of substituted phenyl group on amide moiety, calculated frequencies 48.19 cm^{-1} , 54.11 cm^{-1} . (I, J, K, L, M) vibrational and “ring stretch” modes, calculated frequencies 956.69 cm^{-1} , 1045.93 cm^{-1} , 1328.29 cm^{-1} , 1483.38 cm^{-1} , 1542.32 cm^{-1} .

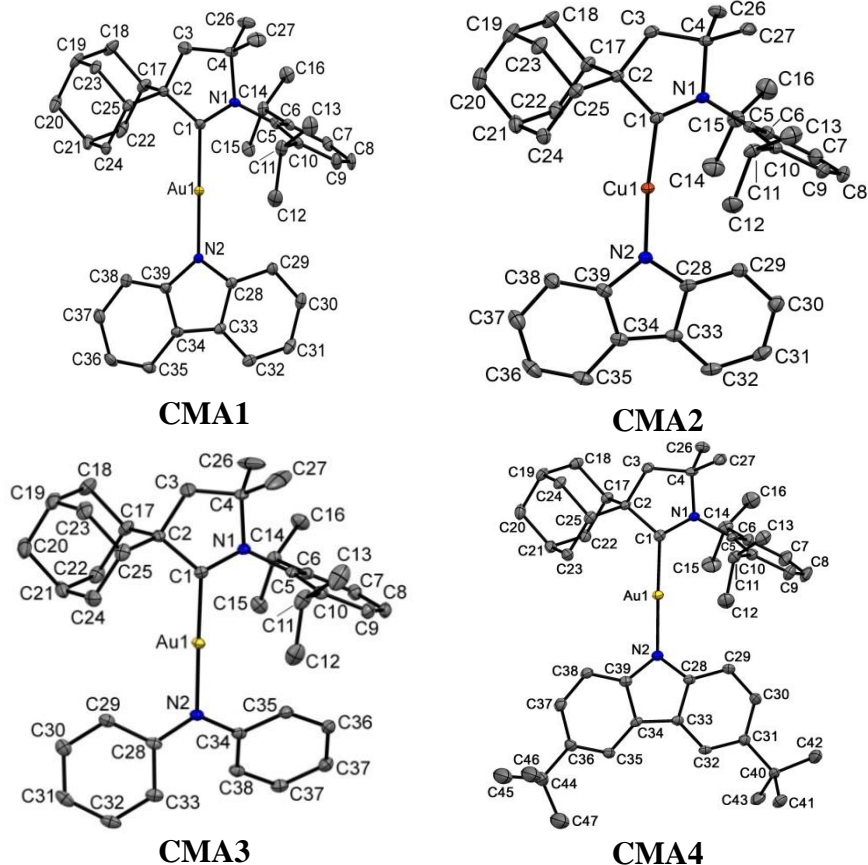


Fig. S10 Crystal structures of (CAAC)AuCz (CMA1), (CAAC)CuCz (CMA2), (CAAC)AuNPh₂ (CMA3) and (CAAC)AuDTBCz (CMA4). Ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): CMA1: Au1–C1 1.991(3), Au1–N2 2.026(2), C1–C2 1.528(4), C1–N1 1.299(4), N2–C28 1.379(4), N2–C39 1.381(4), C1–Au1–N2 178.78(11); dihedral angle between best planes C1–C2–C3–C4–N1 (CAAC) and C28–N2–C39–C33–C34 (carbazole) = 16.5°. CMA2: Cu–C1 1.8846(15), Cu–N2 1.8626(14), C1–C2 1.527(2), C1–N1 1.305(2), C1–Cu–N2 174.34(6); dihedral angle between best planes C1–C2–C3–C4–N1 and C28–N2–C39–C33–C34 = 2.8°. CMA3: Au1–C1 1.985(2), Au1–N2 2.040(2), C1–C2 1.532(3), C1–N1 1.304(3), N2–C28 1.393(3), N2–C34 1.401(3), C1–Au1–N2 177.27(9); dihedral angle between best plane C1–C2–C3–C4–N1 (CAAC) and C28–N2–C34 = 14.9°. CMA4: Au1–C1 1.997(3), Au1–N2 2.020(2), C1–C2 1.536(4), C1–N1 1.307(4), N2–C28 1.395(4), N2–C39 1.384(4), C1–Au1–N2 178.25(11); dihedral angle between best planes C1–C2–C3–C4–N1 (CAAC) and C28–N2–C39–C33–C34 (carbazole) = 14.7°.

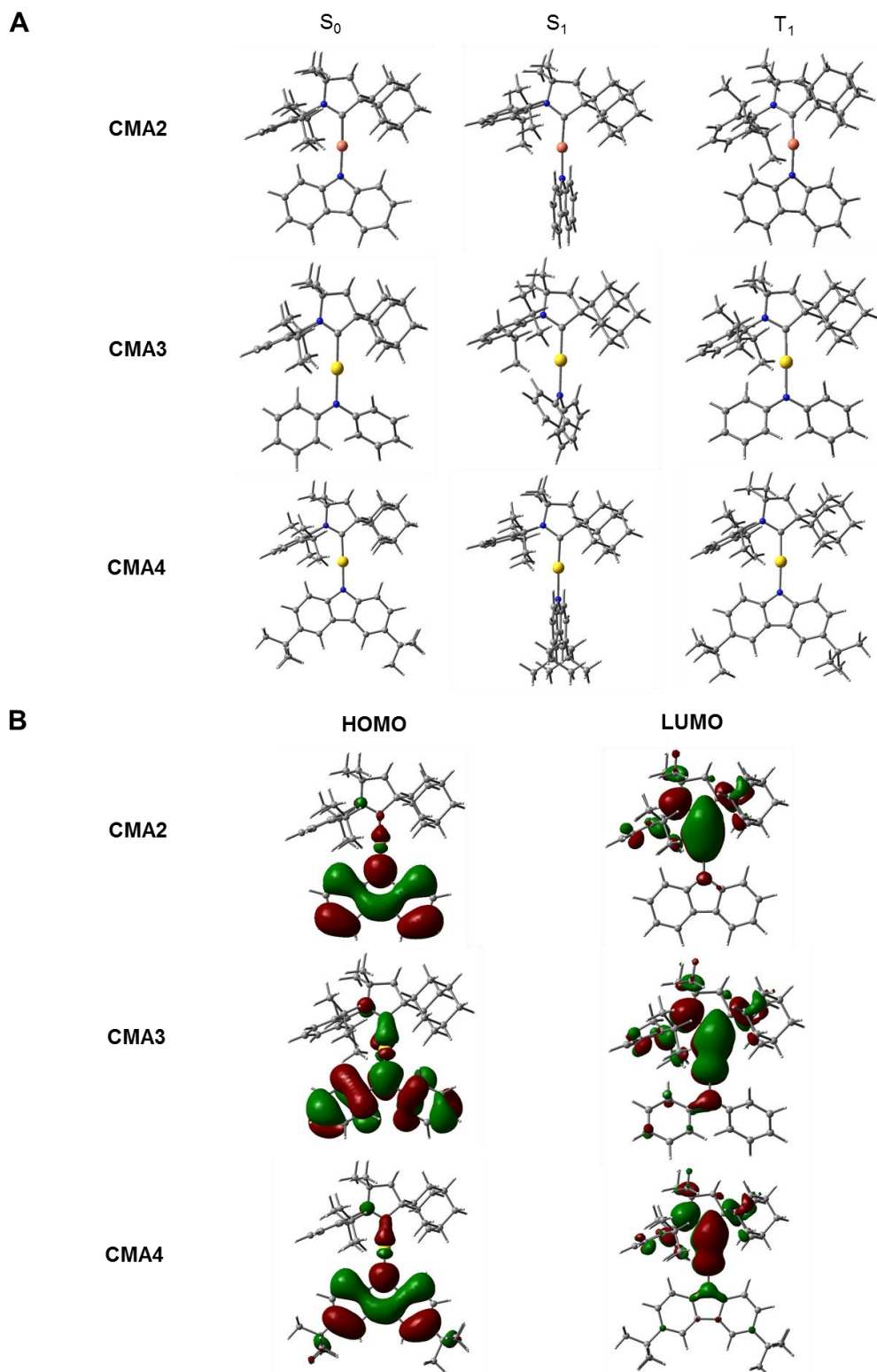


Fig. S11 DFT and TD-DFT calculations for CMA2-4. (A) Optimized molecular geometries for S_0 , S_1 , and T_1 . **(B)** HOMO and LUMO wave functions, isovalue = 0.02 (electrons/bohr³)^{1/2}.

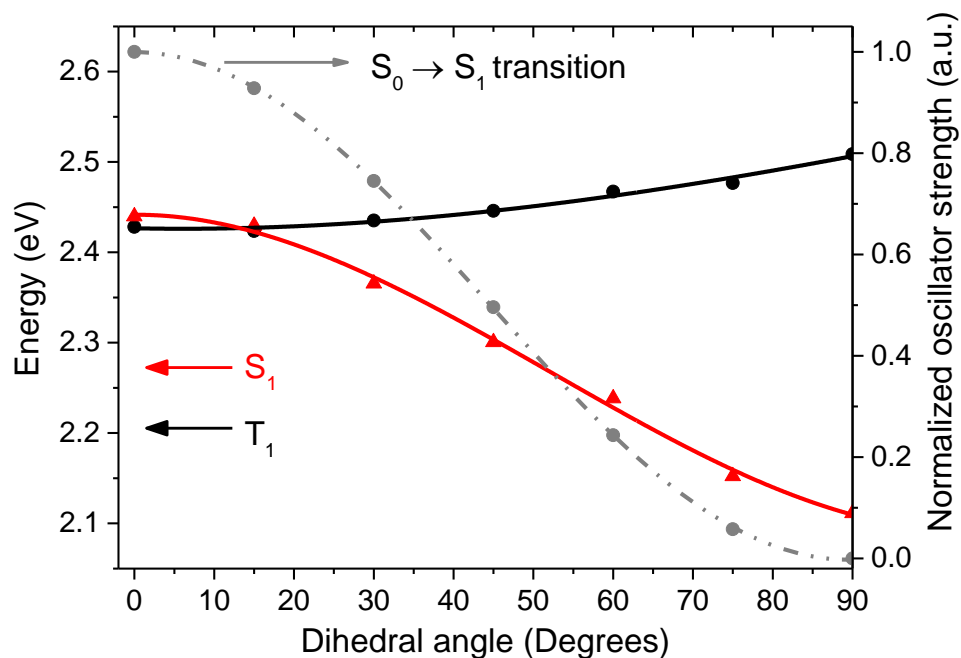


Fig. S12 Variation of energy and oscillator strength with dihedral angle for CMA1. Variation of S_1 and T_1 energies and normalized oscillator strength of the $S_0 \rightarrow S_1$ transition obtained from TD-DFT calculations for CMA1, after geometric relaxation with the carbene-amide dihedral angle fixed. By comparison with spectroscopy, the calculated singlet energies are underestimated by 5-10%, whereas the lowest triplet energy accurately predicts the phosphorescence. Accounting for this discrepancy increases the dihedral angle at which singlet and triplet are degenerate, from approximately 15° to approximately 45° . Solid lines are polynomial (energy) and sinusoidal (oscillator strength) fits as guides to the eye.

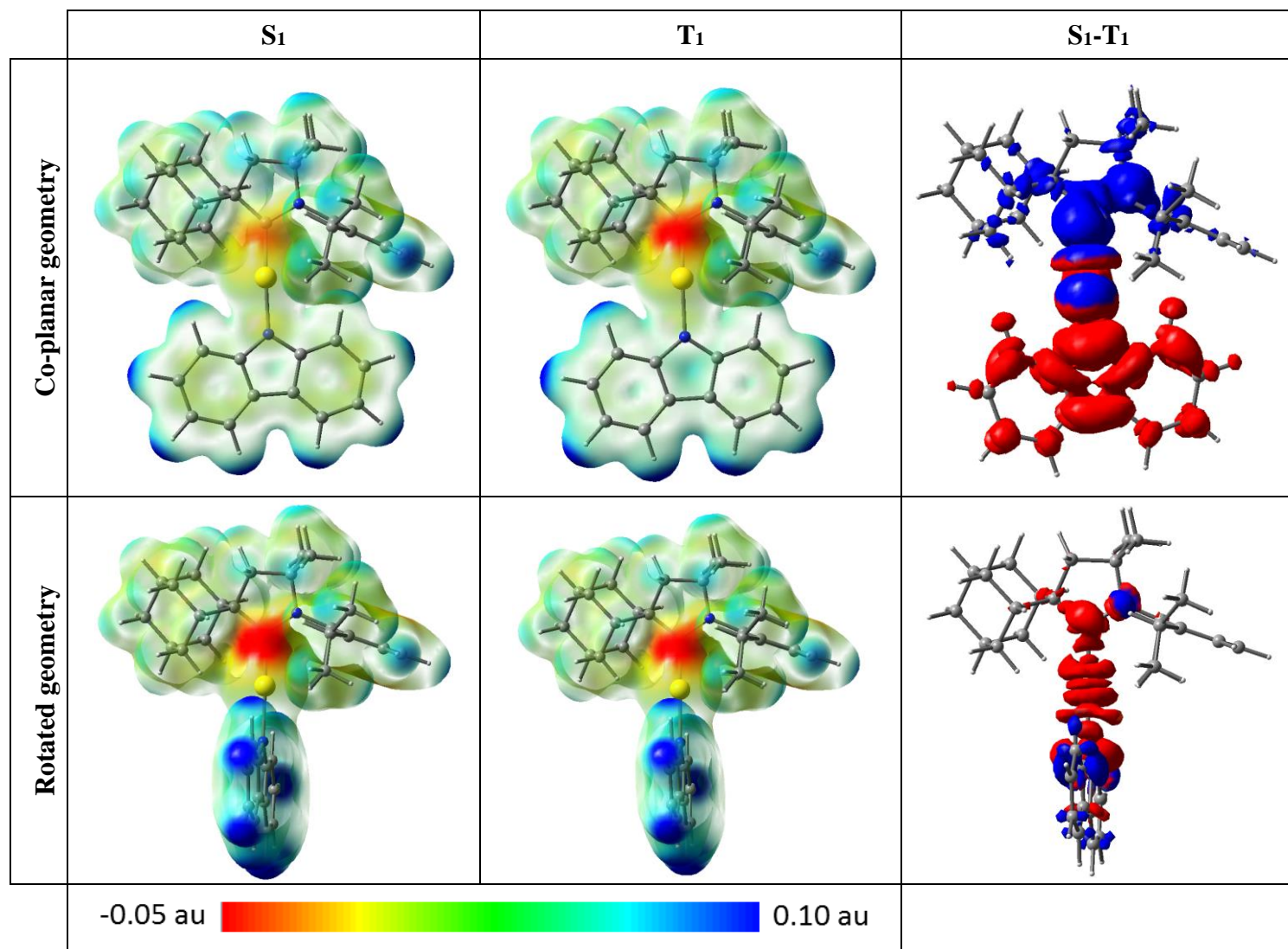


Fig S13 Electrostatic potential energy maps for the excited S_1 and T_1 states from TD-DFT calculations. Isodensity = $0.01 e/\text{au}^3$. The right column presents a subtraction to illustrate areas which are relatively more electron rich for S_1 (red) and T_1 (blue). For comparison in the co-planar geometry, the relaxed T_1 geometry is used (using the S_1^P geometry yields very similar maps). For the rotated geometry, the relaxed S_1 geometry is used.

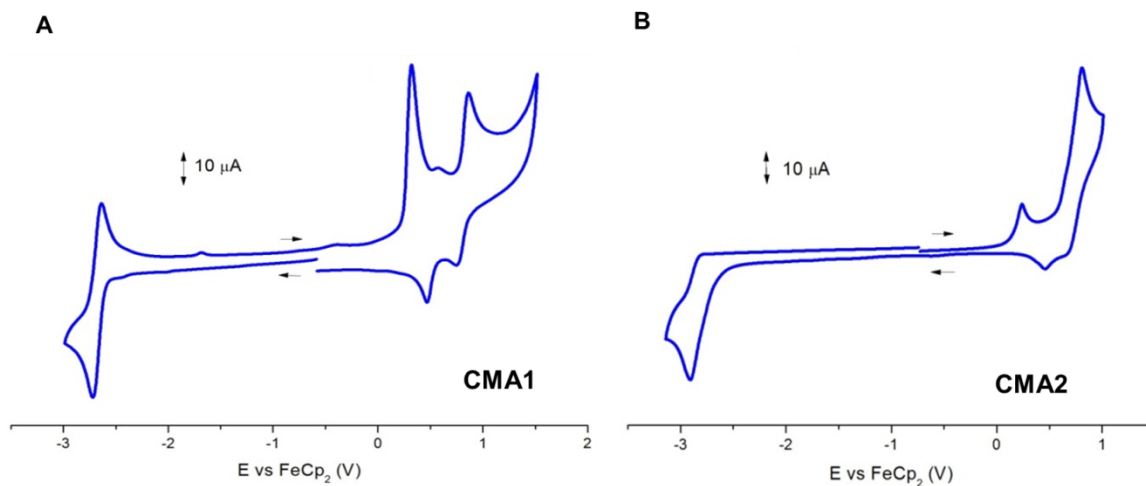


Fig. S14 Cyclic voltammogram. (A) CMA1. (B) CMA2. Data was recorded using a glassy carbon electrode in MeCN solution with [n-Bu₄N]PF₆ as supporting electrolyte with a scan rate of 0.1 V s⁻¹.

Table S1 Decomposition temperatures for CMA1-4 by thermal gravimetric analysis (TGA).

Compound	T_d (°C)
CMA1	334
CMA2	303
CMA3	271
CMA4	336

Table S2 Formal electrode potentials for CMA1-4. Formal electrode potentials ($E_{1/2}$ for irreversible and quasi-reversible processes (*) vs. FcCp_2), onset potentials (E vs. FcCp_2), E_{HOMO}/E_{LUMO} (eV) and band gap values (E_g , eV) for the redox changes exhibited by the complexes under study in MeCN solution (1.4 mM), supporting electrolyte $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ (0.13 mol dm^{-3}), measured at 0.1 V s^{-1} . $E_{HOMO} = -(E_{\text{onset ox Fc/Fc}^+} + 5.39) \text{ eV}$, based on first oxidation potential, and $E_{LUMO} = -(E_{\text{onset red Fc/Fc}^+} + 5.39) \text{ eV}$, based on first reduction potential. Cyclic voltammetry of CMA1 and CMA2 are shown in Fig. S14.

Compound	Reduction (V)		E_{LUMO} (eV)	Oxidation (V)			E_{HOMO} (eV)	E_g (eV)
	$E_{M(I)/M(0)}$	$E_{\text{onset red}}$		$E_{1\text{st}}$	$E_{\text{onset ox}}$	$E_{2\text{nd}}$		
CMA1	-2.68*	-2.60	-2.79	+0.26	+0.22	+0.77	-5.61	2.82
CMA2	-2.84*	-2.73	-2.66	+0.12	+0.07	+0.71	-5.46	2.80
CMA3	-2.78*	-2.69	-2.70	-0.13	-0.17	+0.49	-5.22	2.52
CMA4	-2.86*	-2.78	-2.61	+0.13	+0.08	+0.65	-5.47	2.86

Table S3 Comparison of molecular structural features obtained experimentally by X-ray crystallography and by DFT calculation for CMA1.

	Experimental (X-ray crystallography)	DFT Calculation
Au-C	1.994 Å	1.991 Å
Au-N	2.027 Å	2.015 Å
C-Au-N	178.7°	178.0°

Table S4 TD-DFT calculation of excited state energies for CMA1-4. S_1^R and T_1^P are fully relaxed states. S_1^P and T_1^R are calculated by allowing geometric relaxation while keeping the carbene-amide dihedral angle fixed at 0° and 90°, respectively. S_1^{P*} and T_1^{P*} are constrained to the ground state geometry.

Compound	S_1^R (eV)	T_1^P (eV)	$S_1^R - T_1^P$ (eV)	S_1^{P*} (eV)	T_1^{P*} (eV)	S_1^P (eV)	T_1^R (eV)
CMA1	2.11	2.43	-0.32	2.63	2.69	2.44	2.51
CMA2	2.05	2.39	-0.34	2.49	2.67	2.21	2.40
CMA3	1.81	2.05	-0.24	2.47	2.34	2.12	2.13
CMA4	1.99	2.29	-0.30	2.53	2.57	2.35	2.35

Table S5 Coordinates and stability characterization of CMA1 geometries from TD-DFT calculations.

S₀	S₁^P	S₁^R	T₁^P	T₁^R
Minimum	Transition state	Minimum	Minimum	Minimum
0 imaginary frequencies	1 imaginary frequency = carbazole rotation (i8.24cm ⁻¹)	0 imaginary frequencies	0 imaginary frequencies	0 imaginary frequencies
Cartesian coordinates: Au 0.469 0.346 -0.082 N 2.471 0.569 -0.042 C 4.580 1.486 0.003 C -0.782 -2.829 1.325 N -1.999 -1.151 -0.012 C -2.477 2.108 -1.329 H -2.353 1.567 -2.274 C -1.451 3.809 0.195 H -0.581 4.453 0.355 C -3.498 -1.242 -0.003 C -0.078 -4.029 1.359 H 0.245 -4.423 2.315 C -2.763 1.885 1.137 H -2.835 1.193 1.983 C 3.635 4.090 0.018 H 3.281 5.116 0.025 C -1.501 0.058 -0.102 C 3.392 -0.454 -0.034 C -1.290 3.046 -1.118 H -1.242 3.748 -1.958 H -0.350 2.487 -1.123 C 0.370 -1.573 3.153 H 0.872 -0.936 2.422 H 1.039 -2.404 3.387 H 0.222 -0.993 4.068 C -0.810 -2.984 -1.123 C 0.243 -4.712 0.202 H 0.792 -5.645 0.255 C -1.556 2.807 1.344 H -1.682 3.338 2.294 H -0.632 2.227 1.424 C -2.719 4.658 0.130 H -2.842 5.229 1.057 H -2.645 5.383 -0.687 C 3.187 1.745 -0.018 C -1.182 -2.341 0.070 C -2.639 1.069 -0.189 C 0.267 -1.915 -3.108 H 0.739 -1.162 -2.474 H 0.091 -1.475 -4.092 H 0.975 -2.739 -3.228 C 5.798 -0.817 0.004 H 6.813 -0.433 0.024 C 3.167 -1.830 -0.047 H 2.157 -2.227 -0.065 C -3.748 2.965 -1.390 H -3.663 3.664 -2.229 H -4.633 2.351 -1.588 C -0.975 -2.081 2.629 H -1.596 -1.206 2.433 C -1.049 -2.409 -2.505 H -1.703 -1.540 -2.409 C 4.714 0.056 -0.007 C 2.716 3.057 -0.009 H 1.651 3.262 -0.021 C -3.855 0.162 -0.471 H -4.776 0.503 -0.004 H -4.031 0.142 -1.551	Cartesian coordinates: Au 0.499 0.318 0.095 N 2.637 0.485 0.188 C 4.752 1.366 -0.002 C -0.857 -2.908 1.283 N -2.063 -1.118 0.106 C -2.421 2.115 -1.441 H -2.302 1.501 -2.341 C -1.354 3.888 -0.035 H -0.466 4.519 0.087 C -3.540 -1.100 0.179 C -0.172 -4.119 1.226 H 0.163 -4.582 2.148 C -2.739 2.081 1.021 H -2.839 1.461 1.916 C 3.844 3.953 0.478 H 3.515 4.969 0.658 C -1.494 0.113 -0.129 C 3.489 -0.529 -0.098 C -1.201 3.021 -1.283 H -1.104 3.655 -2.172 H -0.291 2.417 -1.219 C 0.310 -1.817 3.214 H 0.814 -1.115 2.545 H 0.970 -2.675 3.370 H 0.167 -1.324 4.180 C -0.981 -2.917 -1.156 C 0.101 -4.734 0.019 H 0.627 -5.682 -0.005 C -1.512 2.981 1.184 H -1.628 3.586 2.091 H -0.616 2.366 1.318 C -2.591 4.772 -0.182 H -2.705 5.415 0.698 H -2.484 5.430 -1.052 C 3.371 1.627 0.226 C -1.300 -2.323 0.083 C -2.594 1.155 -0.232 C -0.057 -1.752 -3.170 H 0.450 -1.023 -2.535 H -0.310 -1.265 -4.116 H 0.642 -2.565 -3.388 C 5.846 -0.955 -0.482 H 6.876 -0.628 -0.570 C 3.176 -1.885 -0.255 H 2.152 -2.226 -0.166 C -3.660 3.008 -1.586 H -3.546 3.641 -2.474 H -4.559 2.406 -1.746 C -1.037 -2.251 2.635 H -1.627 -1.348 2.485 C -1.319 -2.280 -2.489 H -1.959 -1.418 -2.292 C 4.832 -0.063 -0.217 C 2.913 2.927 0.461 H 1.857 3.113 0.615 C -3.831 0.257 -0.457 H -4.762 0.675 -0.076 H -3.959 0.117 -1.536	Cartesian coordinates: Au 0.581 0.222 -0.110 N 2.676 0.278 0.015 C 4.893 0.242 -0.613 C -1.551 -2.544 1.579 N -2.159 -0.958 -0.197 C -1.902 2.442 -1.524 H -1.665 1.921 -2.459 C -0.989 3.945 0.255 H -0.095 4.471 0.609 C -3.593 -0.780 -0.491 C -1.120 -3.816 1.943 H -1.077 -4.079 2.995 C -2.672 2.170 0.818 H -2.978 1.464 1.596 C 4.253 0.007 -3.308 H 4.031 -0.081 -4.364 C -1.406 0.213 -0.277 C 3.442 0.403 1.139 C -0.676 3.220 -1.051 H -0.387 3.944 -1.823 H 0.174 2.543 -0.915 C -0.563 -1.156 3.397 H 0.158 -0.772 2.673 H -0.115 -2.012 3.909 H -0.759 -0.379 4.142 C -1.168 -3.132 -0.755 C -0.739 -4.746 0.995 H -0.416 -5.736 1.298 C -1.426 2.917 1.298 H -1.646 3.417 2.249 H -0.616 2.204 1.484 C -2.115 4.949 0.014 H -2.343 5.494 0.937 H -1.803 5.691 -0.731 C 3.539 0.191 -1.040 C -1.622 -2.211 0.211 C -2.363 1.377 -0.495 C 0.437 -2.719 -2.622 H 0.974 -2.011 -1.990 H 0.536 -2.401 -3.664 H 0.920 -3.696 -2.524 C 5.763 0.493 1.832 H 6.825 0.477 1.617 C 3.002 0.546 2.455 H 1.944 0.570 2.677 C -3.028 3.457 -1.767 H -2.707 4.172 -2.534 H -3.923 2.964 -2.157 C -1.854 -1.551 2.682 H -2.246 -0.650 2.213 C -1.037 -2.787 -2.224 H -1.454 -1.789 -2.366 C 4.828 0.382 0.829 C 3.215 0.078 -2.393 H 2.178 0.051 -2.703 C -3.600 0.641 -1.050 H -4.549 1.132 -0.840 H -3.497 0.589 -2.139	Cartesian coordinates: Au 0.494 0.416 -0.169 N 2.536 0.675 -0.028 C 4.650 1.582 -0.011 C -0.826 -2.775 1.264 N -1.929 -1.241 -0.310 C -2.486 2.268 -1.151 H -2.183 1.937 -2.151 C -1.822 3.676 0.811 H -1.039 4.323 1.223 C -3.380 -1.362 -0.543 C -0.057 -3.916 1.473 H 0.124 -4.252 2.488 C -3.084 1.534 1.142 H -3.211 0.684 1.818 C 3.721 4.097 -0.744 H 3.383 5.086 -1.029 C -1.470 0.075 -0.215 C 3.422 -0.316 0.315 C -1.423 3.209 -0.587 H -1.311 4.072 -1.256 H -0.457 2.695 -0.553 C -0.131 -1.382 3.227 H 0.431 -0.707 2.577 H 0.552 -2.149 3.602 H -0.491 -0.806 4.084 C -0.473 -3.034 -1.138 C 0.479 -4.628 0.415 H 1.060 -5.526 0.597 C -1.998 2.451 1.709 H -2.281 2.766 2.720 H -1.055 1.904 1.791 C -3.136 4.449 0.724 H -3.432 4.809 1.716 H -3.012 5.332 0.085 C 3.270 1.818 -0.224 C -1.083 -2.357 -0.060 C -2.670 1.006 -0.269 C 0.840 -2.056 -3.033 H 1.219 -1.261 -2.388 H 0.778 -1.664 -4.053 H 1.566 -2.874 -3.033 C 5.788 -0.671 0.663 H 6.813 -0.321 0.692 C 3.127 -1.646 0.601 H 2.104 -2.006 0.573 C -3.803 3.049 -1.236 H -3.669 3.909 -1.903 H -4.595 2.435 -1.674 C -1.308 -2.007 2.478 H -1.930 -1.188 2.117 C -0.535 -2.533 -2.567 H -1.196 -1.666 -2.578 C 4.751 0.174 0.344 C 2.795 3.074 -0.591 H 1.735 3.234 -0.751 C -3.735 0.083 -0.898 H -4.759 0.311 -0.602 H -3.682 0.200 -1.985	Cartesian coordinates: Au -0.580 -0.256 -0.143 N -2.640 -0.331 -0.010 C -4.779 -0.500 0.831 C 1.480 2.488 1.679 N 2.124 1.013 -0.182 C 1.949 -2.356 -1.607 H 1.691 -1.816 -2.525 C 1.090 -3.929 0.139 H 0.212 -4.486 0.486 C 3.561 0.883 -0.490 C 1.021 3.728 2.110 H 0.972 3.934 3.174 C 2.733 -2.129 0.735 H 3.030 -1.437 1.529 C -3.872 -0.989 3.410 H -3.542 -1.184 4.424 C 1.405 -0.179 -0.287 C -3.526 -0.162 -1.049 C 0.748 -3.179 -1.145 H 0.472 -3.890 -1.934 H -0.120 -2.529 -0.986 C 0.522 0.997 3.431 H -0.206 0.648 2.696 H 0.071 1.819 3.996 H 0.732 0.182 4.130 C 1.081 3.190 -0.620 C 0.621 4.700 1.212 H 0.277 5.666 1.567 C 1.511 -2.919 1.206 H 1.753 -3.439 2.141 H 0.686 -2.232 1.420 C 2.238 -4.898 -0.137 H 2.488 -5.461 0.770 H 1.937 -5.629 -0.898 C -3.394 -0.545 1.122 C 1.560 2.230 0.294 C 2.393 -1.310 -0.553 C -0.536 2.843 -2.487 H -1.059 2.106 -1.875 H -0.644 2.561 -3.539 H -1.029 3.809 -2.348 C -5.902 -0.106 -1.493 H -6.936 -0.165 -1.173 C -3.221 0.052 -2.389 H -2.187 0.103 -2.709 C 3.098 -3.336 -1.887 H 2.788 -4.037 -2.671 H 3.978 -2.810 -2.269 C 1.803 1.445 2.728 H 2.204 0.573 2.211 C 0.942 2.915 -2.103 H 1.374 1.930 -2.294 C -4.866 -0.247 -0.599 C 2.931 -0.793 2.410 H -1.867 -0.832 2.609 C 3.602 -0.519 -1.094 H 4.566 -0.991 -0.909 H 3.487 -0.436 -2.180

C 5.487 2.542 0.030	C 5.660 2.401 0.019	C 5.911 0.168 -1.533	C 5.555 2.607 -0.166	C -5.701 -0.693 1.834
H 6.555 2.349 0.045	H 6.717 2.225 -0.150	H 6.951 0.203 -1.228	H 6.617 2.450 -0.011	H -6.766 -0.662 1.635
C -1.661 -2.924 3.702	C -1.765 -3.153 3.630	C -2.875 -2.065 3.694	C -2.130 -2.869 3.434	C 2.823 1.920 3.759
H -2.610 -3.343 3.364	H -2.709 -3.529 3.232	H -3.809 -2.366 3.219	H -2.967 -3.357 2.934	H 3.751 2.256 3.294
H -1.856 -2.316 4.589	H -1.978 -2.607 4.553	H -3.103 -1.287 4.427	H -2.531 -2.254 4.245	H 3.066 1.108 4.451
H -1.027 -3.757 4.016	H -1.156 -4.020 3.898	H -2.490 -2.927 4.245	H -1.517 -3.649 3.892	H 2.432 2.748 4.355
C 4.260 -2.677 -0.034	C 4.212 -2.761 -0.528	C 3.957 0.659 3.453	C 4.186 -2.486 0.921	C -4.277 0.190 -3.279
H 4.099 -3.750 -0.043	H 3.998 -3.815 -0.657	H 3.641 0.769 4.483	H 3.988 -3.526 1.147	H -4.072 0.359 -4.329
C -0.103 -4.178 -1.024	C -0.290 -4.124 -1.159	C -0.747 -4.392 -0.340	C 0.285 -4.173 -0.875	C 0.635 4.418 -0.139
H 0.198 -4.688 -1.932	H -0.052 -4.596 -2.106	H -0.409 -5.109 -1.081	H 0.741 -4.707 -1.701	H 0.278 5.164 -0.842
C 5.012 3.840 0.036	C 5.196 3.699 0.262	C 5.580 0.048 -2.889	C 5.077 3.869 -0.534	C -5.234 -0.937 3.130
H 5.707 4.672 0.057	H 5.902 4.521 0.277	H 6.373 -0.011 -3.624	H 5.779 4.686 -0.660	H -5.948 -1.091 3.931
C -1.717 -3.404 -3.453	C -2.059 -3.231 -3.428	C -1.769 -3.769 -3.137	C -1.071 -3.582 -3.540	C 1.647 3.949 -2.978
H -2.637 -3.820 -3.038	H -2.941 -3.672 -2.958	H -2.823 -3.868 -2.876	H -2.043 -3.971 -3.234	H 2.704 4.051 -2.726
H -1.051 -4.240 -3.683	H -1.417 -4.053 -3.755	H -1.320 -4.765 -3.088	H -0.385 -4.430 -3.624	H 1.186 4.935 -2.875
H -1.959 -2.916 -4.400	H -2.381 -2.697 -4.325	H -1.707 -3.437 -4.177	H -1.176 -3.151 -4.539	H 1.575 3.666 -4.032
C -4.016 2.765 1.088	C -3.964 2.995 0.891	C -3.782 3.203 0.600	C -4.390 2.333 1.081	C 3.868 -3.126 0.479
H -4.931 2.170 1.019	H -4.893 2.420 0.841	H -4.726 2.726 0.323	H -5.226 1.711 0.747	H 4.796 -2.618 0.204
H -4.086 3.321 2.029	H -4.038 3.618 1.790	H -3.972 3.731 1.543	H -4.648 2.677 2.090	H 4.081 -3.673 1.405
C -4.023 -1.544 1.396	C -4.058 -1.168 1.618	C -4.483 -0.917 0.747	C -4.142 -1.860 0.688	C 4.453 1.008 0.748
H -3.684 -2.521 1.741	H -3.850 -2.140 2.065	H -4.412 -1.925 1.162	H -3.816 -2.867 0.958	H 4.352 2.000 1.193
H -5.114 -1.566 1.362	H -5.142 -1.027 1.619	H -5.526 -0.750 0.466	H -5.210 -1.909 0.461	H 5.500 0.881 0.458
H -3.724 -0.791 2.126	H -3.617 -0.395 2.248	H -4.228 -0.201 1.527	H -4.012 -1.210 1.552	H 4.222 0.262 1.507
C -3.922 3.742 -0.084	C -3.824 3.884 -0.344	C -3.356 4.204 -0.473	C -4.219 3.536 0.154	C 3.455 -4.110 -0.616
H -4.839 4.339 -0.135	H -4.718 4.509 -0.450	H -4.168 4.917 -0.656	H -5.165 4.084 0.082	H 4.282 -4.797 -0.825
C 5.568 -2.180 -0.009	C 5.526 -2.310 -0.639	C 5.315 0.630 3.151	C 5.492 -2.009 0.952	C -5.595 0.116 -2.840
H 6.403 -2.871 0.000	H 6.317 -3.020 -0.850	H 6.040 0.718 3.951	H 6.299 -2.687 1.206	H -6.401 0.231 -3.556
C -4.019 -2.311 -0.948	C -4.185 -2.238 -0.599	C -4.118 -1.771 -1.525	C -3.727 -2.306 -1.689	C 4.051 1.918 -1.496
H -3.720 -2.125 -1.978	H -3.924 -2.203 -1.655	H -3.579 -1.690 -2.468	H -3.272 -1.988 -2.627	H 3.504 1.854 -2.437
H -5.111 -2.303 -0.910	H -5.272 -2.156 -0.518	H -5.172 -1.562 -1.723	H -4.811 -2.321 -1.831	H 5.109 1.744 -1.710
H -3.682 -3.308 -0.656	H -3.894 -3.212 -0.200	H -4.046 -2.799 -1.163	H -3.408 -3.327 -1.469	H 3.955 2.932 -1.100

Table S6 Energies for the first 20 excited states for CMA1 in the S₁^P and T₁^P geometries from TD-DFT calculations. *E* is state energy. Calculated oscillator strengths (osc) are for vertical excitations from the S₁^P / T₁^P to the S_n / T_n wave functions in the appropriate geometry, normalized to the strength of the S₀ → S₁ vertical transition in the coplanar geometry. PIA indicates the expected position of the associated photoinduced absorption.

State	S ₁ ^P geometry				T ₁ ^P geometry			
	<i>E</i> (S _n) (eV)	ΔE (S _n -S ₁) (eV)	PIA (nm)	osc/S ₁ ^P	<i>E</i> (T _n) (eV)	ΔE (T _n -T ₁) (eV)	PIA (nm)	osc/S ₁ ^P
S ₁ /T ₁	2.44				2.43			
S ₂ /T ₂	3.05	0.61	2032	0.001	3.06	0.63	1968	0.012
S ₃ /T ₃	3.83	1.39	892	0.003	3.13	0.7	1771	0.034
S ₄ /T ₄	3.87	1.43	867	0.022	3.62	1.19	1042	0.009
S ₅ /T ₅	3.98	1.54	805	0.005	3.85	1.42	873	0.313
S ₆ /T ₆	4.07	1.63	760	0.018	3.91	1.48	837	0.023
S ₇ /T ₇	4.16	1.72	720	0.263	4.02	1.59	779	0.004
S ₈ /T ₈	4.55	2.11	587	0.001	4.17	1.74	712	0.015
S ₉ /T ₉	4.61	2.17	571	0.018	4.24	1.81	685	0.007
S ₁₀ /T ₁₀	4.69	2.25	551	0	4.33	1.9	652	0.047
S ₁₁ /T ₁₁	4.79	2.35	527	0.156	4.54	2.11	587	0.194
S ₁₂ /T ₁₂	4.82	2.38	521	0.05	4.58	2.15	576	0.228
S ₁₃ /T ₁₃	4.89	2.45	506	0.026	4.6	2.17	571	0.379
S ₁₄ /T ₁₄	4.92	2.48	500	0.006	4.78	2.35	527	0.002
S ₁₅ /T ₁₅	4.94	2.5	496	0.294	4.83	2.4	516	0.212
S ₁₆ /T ₁₆	5.05	2.61	475	0.166	4.87	2.44	508	0.145
S ₁₇ /T ₁₇	5.11	2.67	464	0.012	4.9	2.47	502	0.014
S ₁₈ /T ₁₈	5.34	2.9	427	0.408	4.96	2.53	490	0.05
S ₁₉ /T ₁₉	5.37	2.93	423	0.982	5.03	2.6	476	0.117
S ₂₀ /T ₂₀	5.4	2.96	419	1.418	5.08	2.65	467	0.011

Author Contributions

D.D. and L.Y. developed and characterized the OLED devices. A.S.R. set up the collaboration and performed the molecular design, synthesis, X-ray crystallography and electrochemistry. D.D., L.Y. and S.J. carried out the cryogenic ns- μ s transient and steady-state photoluminescence studies. D.D. and L.Y. performed the transient electroluminescence experiments. J.M.R. carried out the ultrafast photoluminescence studies. J.P.H.R. performed the transient absorption measurements. T.H.T. performed the Raman measurements. M.A.J. performed the photothermal deflection measurements. M.B. conceived the initial concept of the emission mechanism. M.L. carried out the quantum chemical calculations. D.C., M.B. and D.D. planned the project and designed the experiments. D.D., D.C., M.B., L.Y. and R.H.F. co-wrote the manuscript.