Significant Differences Between Solid State and Solution Photochemistry and Photophysics of Mesogenic Organometallic Gold Complexes

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1. Experimental Section

Instruments.

The ^1H (300 MHz) and ^{13}C (76 MHz) NMR spectra were recorded on a Bruker Avance 300 Ultrashield NMR spectrometer. The chemical shifts are given in ppm relative to the residual peaks of CDCl_3 . The IR spectra were recorded at 4 cm^{-1} on an ABB Bomem, MB series FTIR spectrometer equipped with an ATR module from Specac from 600 to 4000 cm^{-1} . The FT-Raman spectra were recorded from 0 to 4000 cm^{-1} , at 5 cm^{-1} resolution using a Bruker RFS 100/S spectrometer with the 1064 nm excitation and a light power equal to 250 mW equipped with a photomultiplier Ge-diode, cooled at liquid nitrogen temperature (77 K). The peak centred between 83 and 85 cm^{-1} is considered as residual artefact from the instrument and should not be considered. The elemental analyses were performed by the analytical service of the University of Lorraine in Nancy, France. The solid-state UV-visible spectra were recorded on a Varian Cary 300 Bio UV-Vis spectrophotometer at 298 K using raised-angle transmittance apparatus and a homemade 77 K sample-holder. Samples were dispersed between two quartz plates. Solid-state emission, excitation, emission lifetimes and CIE 1931 charts (chromaticity coordinates) were acquired on a phosphorimeter FLS980 from Edinburgh Instruments equipped with single monochromators. Samples were introduced in a capillary or dispersed between two quartz plates and spectra obtained were corrected for instrument response. The emission lifetime measurements were performed using a “flash” pulsed lamp. Lifetimes values were obtained using a time correlated single photon counting (TCSPC) system and data were treated from both deconvolution of multi-exponential analysis and exponential series methods. Solid state emission quantum yields were recorded using a Quanta- ϕ F-3029 integration sphere from Horiba plugged into a Horiba Fluorolog III (the power at the sample is 0.53 W/cm^2 at the sample ($\lambda_{\text{exc}} = 300\text{ nm}$)). The thermal analysis (TGA) traces were measured on a Perkin Elmer TGA 7 apparatus between 25 and $950\text{ }^\circ\text{C}$ at a scanning rate of $10^\circ\text{C.min}^{-1}$ under argon atmosphere. The differential scanning calorimetry (DSC) plots were measured on a DSC Q200 instrument equipped with a cooling system RCS 90 both from TA Instruments at a scanning rate of $10^\circ\text{C.min}^{-1}$. The samples for powder X-ray diffraction measurements were mixed with a small amount of paratone oil, cut to approximately $0.3 \times 0.3 \times 0.3\text{ mm}^3$, and placed on a sample holder mounted at 173.2 K on a Bruker APEX DUO X-ray diffractometer. Six correlated runs per sample with Phi Scan of 360 degrees and exposure times of

270 s were collected with the Cu micro-focus anode (1.54184 Å) and the CCD APEX II detector at a 150 mm distance. These runs, from -12 to $-72^\circ 2\theta$ and 6 to 36° , were then treated and integrated with the XRW2 Eval Bruker software to produce WAXD diffraction patterns from 2.5 to $82^\circ 2\theta$. The patterns were treated with Diffrac.Eva version 2.0 from Bruker.

Optical microscope.

The optical monitoring of the solid-to-solid phase transitions were performed using an Olympus BX51-P polarizing microscope using a 360° rotary polarizing filter. Images were recorded using a Diagnostic Instruments, inc. 14.2 Color Mosaic CCD camera fitted on the extension tube. The temperature control was performed by a Instec HCS402 temperature-controlled stage.

Transmission electron microscopy.

Transmission electron microscopy (TEM) images were taken using a Hitachi H-7500, the NP diameters were measured at a 80000x zoom. Carbon film grids from Electron Microscopy Sciences were used for all measurements. Particle dispersity was determined using the software *imageJ*. The photo- and thermally generated nanoparticles were removed from the substrate using dichloromethane and EtOH. Dichloromethane was evaporated under reduced pressure to afford a nanoparticle dispersion in EtOH. The same procedure was used to obtain suspension of thermally generated NPs. Each suspension was deposited on a 200-mesh carbon film grid using a micropipette set for 20 μ l. Each sample was analysed for NP size and size dispersity.

Photolysis apparatus.

Photochemical decomposition of the complexes was tested using a 405 nm LED fitted with an N-BK7 homogenizer with a calculated power output of 1300 mW and surface power density of 14.5 Wm^{-2} . The compounds were drop casted onto microscope slides and placed in front of the light source for 3 hours. The distance was set to allow most of the sample to be illuminated while staying within 1 cm of the homogenizer.

For the fs-TAS measurements of the photogenerated gold nanoparticles (Au NPs), the Au NPs were photogenerated *in situ* using solutions containing the gold complexes in CH_2Cl_2 . The excitation was carried out using the THG of the fundamental output of a Soltice (Spectra Physics)

Ti-sapphire laser ($\lambda_{\text{exc}} = 266 \text{ nm}$, rep. rate = 500 Hz; and spot size $\approx 300 \mu\text{m}$). The irradiation proceeded for 1 hour (300nJ/pulse at 500Hz) and the fs-TAS signal was monitored until it did not change anymore. This was ensured by continuously measuring the transient signal at a fixed pump-probe delay (5ps) with respect to the exposure time.

Near-Infrared Singlet Oxygen steady state detection and lifetime measurement

Photosensitized singlet oxygen emission spectra ($^1\Delta_g \rightarrow ^3\Sigma_g$; $\lambda_{\text{emi}} = 1275 \text{ nm}$) of the gold complexes in solution were recorded on a QM-400 spectrofluorometer by PTI equipped with a Ushio 75 W Xenon Short Arc Lamp and a NIR PMT R5509-43 (300 to 1400 nm) from Hamamatsu cooled with liquid nitrogen. Dichloromethane solutions were prepared with a concentration adjusted to match 1.0 in absorbance for the 300 nm absorption band, placed in sealed quartz cells and purged with oxygen gas for 10 minutes. Diffuse light, scattering and harmonic phenomena were filtered off in the 1225-1325 nm window with a 1200 nm longpass filter from ThorLabs placed before the emission monochromator. The radiative emission decay monitored at 1275 nm using dichloromethane and chloroform as the solvents were obtained with a similar set up but a Hamamatsu 15 W Xenon Flash Lamp was used as an excitation source. The results were fitted with Origin software with a one-phase exponential decay function with time constant parameter model ($I(\lambda, t) = I_0 + A \exp\{-t/\tau\}$).

Ultrafast transient absorption spectroscopy (fs-TAS).

The fs transient spectra were acquired on a homemade system using a Soltice (Spectra Physics) Ti-sapphire laser. Excitation was carried out using the THG of the fundamental output of the laser ($\lambda_{\text{exc}} = 266 \text{ nm}$, rep. rate = 500 Hz; and spot size $\approx 300 \mu\text{m}$). The white light continuum (probe) is generated inside a CaF₂ window and a custom-made dual CCD camera of 64×1024 pixels sensitive between 200 and 1100 nm (S7030, Spectronic Devices) is used for signal and reference detection. The delay line permitted us to probe up to 8 ns with an accuracy of $\sim 4 \text{ fs}$. The results were obtained by global analysis using the open source software Glotaran (<http://glotaran.org>) permitting extraction of a sum of independent exponentials ($I(\lambda, t) = C_1(\lambda) \times e^{-\frac{t_1}{\tau}} + C_2(\lambda) \times e^{-\frac{t_2}{\tau}} + \dots$). that fits the whole 3D transient map.

Density functional theory computations.

All density functional theory (DFT) calculations were performed with Gaussian 16¹ at the Université de Sherbrooke with the Mammouth supercomputer supported by Calcul Quebec. The DFT ground state calculations were carried out using the wb97xd/gen functional. A 6-31g(d, p) basis set was used for C, H, N and O atoms,²⁻⁷ while a LANL2DZ basis set was used for the Au atom.⁸ Starting structures were constructed on GaussView 5.0 then geometry optimization was performed without any solvent field. The structure was then re-optimized in a dichloromethane solvent field. TDDFT computations were performed on both the optimized singlet and triplet state structures using a dichloromethane solvent field. The MO representations use red and blue color as positive isosurface and negative isosurface, respectively, and a contour value of 0.03.

Structure resolution from powder X-ray diffraction patterns.

PXRD data were converted into *.raw format and imported into BIOVIA Material Studio 17.⁹ Patterns were processed via the Reflex module and the diffraction peaks were identified with a low amplitude cut-off of 2% and a smoothing of maxima of $0.08^{\circ}2\theta$. The diffractions peaks were indexed with the DICVOL90 algorithm.^{10,11} Solution were analyzed and unit cells were generated for each. Pre-drawn structures of complexes were randomly placed inside the unit cell, the crystal structure was then rebuilt with the crystal system obtained from DICVOL90 and each available space group was tried. The structures were optimised via the Forcite module with a fine Quality (all other parameters were kept to default). Finally, the resulting structure was refined with the Reflex Powder Refinement, with Pawley refinement type and fine convergence quality (all other parameters were kept to default). The results were compared and stacked to the experimental data.

Materials.

The chemicals used in this investigation were acquired from Sigma-Aldrich, Anachemia and Alfa Aesar and were used as received without further purification. Palladium catalysts were prepared according to a previously published method.¹² Solvents used for the photophysical measurements and for reactions involving metals were distilled shortly prior to usage and kept under inert atmosphere.

Synthesis.

Synthesis of **dimethylsulfidechlorogold(I)**: HAuCl_4 (0.15 mmol) was solubilized in a minimal amount of degassed EtOH. The solution was further degassed with argon and the vessel was sealed.

Dimethyl sulfide (DSM) (0.31 mmol) was slowly injected into the flask, a white precipitated formed and the yellow solution turned colorless, the mixture was stirred for an additional 5 minutes. The solid was isolated by filtration and washed with a small amount of cold EtOH. The solid was then quickly transferred into a flask and kept under argon atmosphere. The product was used as is.

Synthesis of **4-alkoxyiodobenzene**: Iodophenol (33.3 mmol), halogenoalkane (30.3 mmol), potassium carbonate (33.3 mmol) and 2-butanone were added to a round bottom flask and the mixture was refluxed overnight. Upon completion, the solid was filtered off and the filtrate was evaporated under vacuum. The resulting oily substance was solubilized in diethyl ether and was washed twice with 50 ml of NaOH 5% solution and once with a 50 ml of a saturated NaHCO₃ solution. The organic layer was dried over magnesium sulfate and the solvent was evaporated under vacuum. The crude product was further purified by column chromatography, using hexanes as the eluent, to afford the desired product. **4-hexyloxyiodobenzene**: transparent liquid, yield = 87%. ¹H NMR (300 MHz, CDCl₃) δ 7.68 – 7.40 (m, 2H), 6.87 – 6.57 (m, 2H), 3.93 (t, J = 6.6 Hz, 2H), 1.95 – 1.68 (m, 2H), 1.46 (ddd, J = 15.7, 11.7, 7.7 Hz, 2H), 1.40 – 1.29 (m, 4H), 0.95 (t, J = 6.7 Hz, 3H). **4-nonyloxyiodobenzene**: transparent liquid, yield = 49%. ¹H NMR (300 MHz, CDCl₃) δ 7.56 (d, J = 9.0 Hz, 2H), 6.69 (d, J = 8.9 Hz, 2H), 3.93 (t, J = 6.6 Hz, 2H), 1.86 – 1.72 (m, 2H), 1.45 (dd, J = 14.6, 6.6 Hz, 2H), 1.30 (s, 10H), 0.91 (t, J = 6.7 Hz, 3H). **4-dodecyloxyiodobenzene**: white solid. yield = 78%. ¹H NMR (300 MHz, CDCl₃) δ 7.57 (d, J = 9.0 Hz, 2H), 6.70 (d, J = 9.0 Hz, 2H), 3.93 (t, J = 6.6 Hz, 2H), 1.98 – 1.68 (m, 3H), 1.46 (q, J = 6.6 Hz, 2H), 1.31 (s, 24H), 0.93 (t, J = 6.7 Hz, 9H). **4-pentadecyloxyiodobenzene**: white solid. Yield = 7469%. ¹H NMR (300 MHz, CDCl₃) δ 7.56 (d, J = 8.9 Hz, 2H), 6.69 (d, J = 8.9 Hz, 2H), 3.93 (t, J = 6.6 Hz, 2H), 1.86 – 1.68 (m, 3H), 1.52 – 1.40 (m, 2H), 1.28 (s, 22H), 0.91 (t, J = 6.7 Hz, 3H).

Synthesis of **((4-(alkoxy)phenyl)ethynyl)trimethylsilane**: 1-Alkoxy-4-iodobenzene (10 mmol), CuI (0.1 mmol) and Pd(PPh₃)₂Cl₂ (0.2 mmol) were added to torch dried 100 ml 2-neck flask. The system was purged with argon and 40 ml of freshly distilled diethylamine was added. The mixture was brought to reflux for 5 minutes and trimethylsilylacetylene (15 mmol) was injected into the flask, the solution went from yellow to transparent and a black deposit formed. Once the reaction was completed (monitored by TLC) the solvent was removed under reduced pressure. The crude product was solubilized in 50 ml of DCM and washed twice with 30 ml of HCl 0.5N and once with 30 ml of brine. The organic phase was dried using MgSO₄. The resulting solid was purified by

chromatography column using hexanes as an eluent and progressively switching to DCM. ((**4-(methoxy)phenyl**)ethynyl)trimethylsilane: Yield = 92%. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 0.26 (s, 9H). ((**4-(hexyloxy)phenyl**)ethynyl)trimethylsilane: Yield = 68%. ^1H NMR (300 MHz, CDCl₃) δ 7.43 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 1.93 – 1.69 (m, 2H), 1.56 – 1.43 (m, 2H), 1.42 – 1.30 (m, 4H), 0.95 (t, J = 6.7 Hz, 3H), 0.28 (s, 9H). ((**4-(nonyloxy)phenyl**)ethynyl)trimethylsilane: Yield = 37%. ^1H NMR (300 MHz, CDCl₃) δ 7.45 – 7.38 (m, 2H), 6.87 – 6.79 (m, 2H), 3.96 (t, J = 6.6 Hz, 2H), 1.78 (d, J = 8.0 Hz, 2H), 1.57 – 1.24 (m, 12H), 0.92 (t, J = 6.7 Hz, 3H), 0.27 (s, 9H). ((**4-(dodecyloxy)phenyl**)ethynyl)trimethylsilane: Yield = 31%. ^1H NMR (300 MHz, CDCl₃) δ 7.42 (d, J = 8.9 Hz, 2H), 6.83 (d, J = 8.9 Hz, 2H), 3.96 (t, J = 6.6 Hz, 2H), 1.79 (dd, J = 14.5, 6.7 Hz, 3H), 1.48 (s, 2H), 1.32 (s, 22H), 0.94 (t, J = 6.7 Hz, 8H), 0.29 (s, 9H). ((**4-(pentadecyloxy)phenyl**)ethynyl)trimethylsilane: Yield = 55%. ^1H NMR (300 MHz, CDCl₃) δ 7.41 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 3.96 (t, J = 6.6 Hz, 2H), 1.78 (dd, J = 14.6, 6.7 Hz, 2H), 1.46 (s, 3H), 1.31 (d, J = 12.8 Hz, 27H), 1.00 (d, J = 6.6 Hz, 1H), 0.91 (t, J = 6.6 Hz, 6H), 0.27 (s, 9H).

Synthesis of **1-(alkoxy)-4-ethynylbenzene**: The desired amount of ((4-(alkoxy)phenyl)ethynyl)trimethylsilane was solubilised in THFTHD and a large excess of TBAF 1M in THF was slowly added and the solution was stirred for 5 minutes. The reaction was monitored by TLC. The solvent was removed under reduced pressure and the product was purified by column chromatography using hexanes and progressively switching to DCM. The resulting product was used without further characterization. **1-(methoxy)-4-ethynylbenzene**: Yield = 54%. ^1H NMR (300 MHz, Chloroform-*d*) δ 7.44 (d, J = 7.7 Hz, 2H), 6.85 (d, J = 7.7 Hz, 2H), 3.81 (s, 3H), 3.00 (s, 1H). **1-(hexyloxy)-4-ethynylbenzene**: Yield = 21%. ^1H NMR (300 MHz, CDCl₃) δ 7.45 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 3.98 (s, 2H), 3.01 (s, 1H), 1.81 (d, J = 7.5 Hz, 3H), 1.70 – 1.46 (m, 4H), 1.33 (s, 17H), 1.13 (ddd, J = 16.7, 12.8, 6.2 Hz, 1H), 0.94 (s, 15H). **1-(nonyloxy)-4-ethynylbenzene**: Yield = 79%. ^1H NMR (300 MHz, CDCl₃) δ 7.45 (d, J = 8.9 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H), 3.97 (t, J = 6.6 Hz, 2H), 3.02 (s, 1H), 1.80 (dd, J = 14.7, 6.6 Hz, 2H), 1.53 – 1.42 (m, 2H), 1.31 (d, J = 4.2 Hz, 14H), 1.01 (d, J = 6.6 Hz, 1H), 0.93 (t, J = 6.8 Hz, 7H). **1-(dodecyloxy)-4-ethynylbenzene**: Yield = 31%. ^1H NMR (300 MHz, CDCl₃) δ 7.45 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H), 3.97 (t, J = 6.6 Hz, 2H), 3.02 (s, 1H), 1.88 – 1.69 (m, 2H), 1.55 – 1.41 (m, 3H), 1.31 (s, 18H), 0.93 (t, J = 6.7 Hz, 4H). **1-(pentadecyloxy)-4-ethynylbenzene**: Yield

= 89%. ^1H NMR (300 MHz, CDCl_3) δ 7.44 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 3.97 (t, J = 6.6 Hz, 2H), 3.01 (s, 1H), 1.96 – 1.70 (m, 2H), 1.53 – 1.41 (m, 3H), 1.28 (s, 26H), 1.16 – 0.97 (m, 1H), 0.90 (dd, J = 7.2, 6.2 Hz, 6H).

Synthesis of N-(4-(alkoxy)phenyl)acetamide: 4-Acetamidophenol (33.3 mmol), halogenoalkane (30.3 mmol) and potassium carbonate (33.3 mmol) were added to a round bottom flask and 2-butanone (100 ml) was added and the mixture was refluxed overnight. Upon completion the solid was filtered off and the filtrate was evaporated under vacuum. The resulting oily substance was solubilized in diethyl ether and was washed twice with 50 ml of NaOH 5% solution and once with a 50 ml of a saturated NaHCO_3 solution. The organic layer was dried over magnesium sulfate and the solvent was evaporated under vacuum. The crude product was further purified by column chromatography, using hexanes $\rightarrow$ DCM as the eluent, to afford the desired product. **N-(4-(nonyloxy)phenyl)acetamide:** white solid, 57% yield ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, J = 8.9 Hz, 2H), 7.03 (s, 1H), 6.87 (d, J = 9.0 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 2.18 (s, 3H), 1.83 – 1.70 (m, 2H), 1.47 (d, J = 7.2 Hz, 1H), 1.32 (d, J = 12.4 Hz, 12H), 1.00 – 0.81 (m, 2H). **N-(4-(pentadecyloxy)phenyl)acetamide:** white solid, 74% yield ^1H NMR (400 MHz, Chloroform- d) δ 7.39 (d, J = 9.0 Hz, 2H), 7.08 (s, 1H), 6.87 (d, J = 9.0 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 2.18 (s, 3H), 1.78 (dd, J = 8.2, 6.5 Hz, 2H), 1.46 (t, J = 7.7 Hz, 2H), 1.28 (s, 22H), 0.95 – 0.84 (m, 3H).

Synthesis of 4-(alkoxy)benzenaminium hydrogen sulfate: 4-(alkoxy)phenylacetamide (15 mmol) was suspended in H_2SO_4 40% and the solution was refluxed until it forms an homogenous solution. The solution is then slowly cooled to room temperature, as it cools a precipitate forms. The solid was isolated by filtration and then recrystallized in ethanol 70% to afford a long fibrous pink solid. The products were used without further purification or analysis. **4-(nonyloxy)benzenaminium hydrogen sulfate:** 71% yield. **4-(pentadecyloxy)benzenaminium hydrogen sulfate:** 92% yield.

Synthesis of 4-(alkoxy)aniline: 4-(alkoxy)phenylammonium hydrogen sulfate (12 mmol) was transferred to a flask with DCM, benzyltriethylammonium chloride and NaOH 1M. The mixture was stirred at room temperature until solid had completely solubilized. The organic phase was then separated and evaporated under reduced pressure to afford 4-(alkoxy)aniline. **4-(nonyloxy)aniline:** 99% yield, ^1H NMR (400 MHz, Chloroform- d) δ 6.98 – 6.89 (m, 2H), 6.86 – 6.79 (m, 2H), 3.99 – 3.85 (m, 2H), 1.77 (dd, J = 8.3, 6.6 Hz, 2H), 1.46 (t, J = 7.7 Hz, 1H), 1.38 – 1.23 (m, 13H), 1.13 – 0.74 (m, 2H). **4-(pentadecyloxy)aniline:** 99% yield, ^1H NMR (300 MHz, Chloroform- d) δ 7.02 (d,

$J = 8.8$ Hz, 1H), 6.92 – 6.63 (m, 1H), 4.02 – 3.74 (m, 2H), 1.77 (s, 4H), 1.28 (s, 28H), 1.00 – 0.66 (m, 3H).

Synthesis of **N-(4-(alkoxy)phenyl)formamide**: 4-(alkoxy)aniline (9.7 mmol) was solubilized in toluene and formic acid 70% (9.7 mmol) was added. The mixture was refluxed and monitored by TLC. Upon completion the solvent was evaporated, and the crude product was recrystallized from chloroform and hexanes. **N-(4-(nonyloxy)phenyl)formamide**: 90% yield, ^1H NMR (300 MHz, Chloroform-*d*) δ 8.51 (d, $J = 11.6$ Hz, 0.5H), 8.36 (d, $J = 1.8$ Hz, 0.5H), 7.45 (d, $J = 9.0$ Hz, 1H), 7.03 (d, $J = 8.8$ Hz, 1H), 6.90 (dd, $J = 8.8, 6.1$ Hz, 2H), 3.96 (td, $J = 6.5, 1.1$ Hz, 2H), 1.79 (dd, $J = 10.0, 4.6$ Hz, 2H), 1.47 (s, 2H), 1.30 (s, 8H), 0.96 – 0.68 (m, 3H). **N-(4-(pentadecyloxy)phenyl)formamide**: 99% yield, ^1H NMR (300 MHz, Chloroform-*d*) δ 8.51 (d, $J = 11.6$ Hz, 1H), 8.36 (d, $J = 1.8$ Hz, 1H), 7.45 (d, $J = 8.9$ Hz, 1H), 7.03 (d, $J = 8.9$ Hz, 1H), 6.90 (dd, $J = 8.8, 6.0$ Hz, 2H), 3.96 (t, $J = 6.5$ Hz, 2H), 1.93 – 1.65 (m, 2H), 1.46 (s, 3H), 1.28 (s, 22H), 1.10 – 0.61 (m, 3H).

Synthesis of **1-(alkoxy)-4-isonitrilebenzene**: Under an argon atmosphere, 4-(alkoxy)formanilide (7.5 mmol) was solubilized in DCM and triethylamine (52.3 mmol). The flask was transferred to an ice bath for 10 minutes, to allow the solution to reach 0°C. A solution of triphosgene (2eq) in DCM was added dropwise through a septum using a syringe, the flask needs to be attached to a gas manifold in order to avoid pressure build up. The solution was stirred for 30 minutes to assure completion, the solution turned to a bright yellow cloudy mixture as the triphosgene was added. DCM was added and the mixture was then washed twice with water. The organic layer was dried over sodium sulfate and the solvent was evaporated under reduced pressure. The dark yellow crude product was then purified by column chromatography using silica gel that was treated with triethylamine in order to minimize product decomposition. Hexanes was used as the eluent to afford the desired product. The 4-(alkoxy)phenylisonitrille was stored at -20°C under argon. **1-(nonyloxy)-4-isonitrilebenzene**: 44% yield, ^1H NMR (300 MHz, Chloroform-*d*) δ 7.32 (d, $J = 8.9$ Hz, 2H), 6.87 (d, $J = 8.9$ Hz, 2H), 3.97 (t, $J = 6.5$ Hz, 2H), 2.14 – 1.69 (m, 2H), 1.49 – 1.19 (m, 12H), 1.05 – 0.58 (m, 3H). **1-(pentadecyloxy)-4-isonitrilebenzene**: 51% yield, ^1H NMR (300 MHz, Chloroform-*d*) δ 7.32 (d, $J = 8.9$ Hz, 2H), 6.87 (d, $J = 8.9$ Hz, 2H), 3.97 (t, $J = 6.5$ Hz, 2H), 2.03 – 1.67 (m, 2H), 1.47 (s, 2H), 1.28 (s, 22H), 1.01 – 0.74 (m, 3H).

Synthesis of **1-(alkoxy)-4-ethynylbenzenechlorogold(I)**: A degassed solution of 1-(alkoxy)-4-ethynylbenzene (0.15 mmol) in DCM was added to the flask containing AuCl(DMS) (0.15 mmol) and 22.3 mg of triethylamine was slowly added. The reaction was stirred under argon at room temperature for 45 minutes. The resulting yellow solid was isolated by filtration and washed with cold acetone. The clean product was dried under vacuum and was used without further purification.

Synthesis of **1-(alkoxy)-4-ethynylbenzene-1'-(alkoxy)-4'-isonitrilebenzenegold(I)**: Toluene (10 ml) was added to AuCl(ethynyl) (0.15 mmol) and 1-(alkoxy)-4-isonitrilebenzene (0.15 mmol). The mixture was kept under argon and stirred for 10 min, the solvent was then evaporated under reduced pressure. The resulting solid was purified by column chromatography, using hexanes and gradually changing the eluent for CH₂Cl₂, to remove most impurities and then using methanol saturated hexanes to isolate the product. **C₁N₉**: 60% yield, ¹H NMR (300 MHz, Chloroform-d) δ 7.44 (t, J = 9.2 Hz, 4H), 6.97 – 6.89 (m, 2H), 6.85 – 6.74 (m, 2H), 3.99 (t, J = 6.5 Hz, 2H), 3.80 (s, 3H), 1.79 (dt, J = 8.0, 6.5 Hz, 2H), 1.45 (q, J = 6.9 Hz, 2H), 1.40 – 1.22 (m, 11H), 0.94 – 0.85 (m, 3H). **C₆N₁₅**: 48% yield, ¹H NMR (300 MHz, Chloroform-d) δ 7.44 (t, J = 9.3 Hz, 4H), 7.02 – 6.91 (m, 2H), 6.80 (d, J = 8.8 Hz, 2H), 3.98 (dt, J = 18.8, 6.6 Hz, 4H), 1.81 (d, J = 7.1 Hz, 2H), 1.28 (s, 18H), 0.90 (t, J = 6.6 Hz, 7H). **C₉N₁₅**: 23% yield. **C₁₂N₁₅**: 27% yield, ¹H NMR (300 MHz, Chloroform-d) δ 7.45 (t, J = 9.1 Hz, 4H), 6.96 (d, J = 9.0 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 3.98 (dt, J = 18.8, 6.5 Hz, 4H), 1.80 (dt, J = 13.1, 6.7 Hz, 4H), 1.44 (t, J = 7.3 Hz, 2H), 1.28 (s, 27H), 0.90 (t, J = 6.6 Hz, 5H). **C₁₅N₉**: 24% yield, ¹H NMR (400 MHz, Chloroform-d) δ 7.45 (dd, J = 12.3, 8.9 Hz, 4H), 6.96 (d, J = 9.1 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 1.80 (dt, J = 17.3, 7.6 Hz, 4H), 1.54 – 1.41 (m, 5H), 1.30 (d, J = 13.5 Hz, 35H), 0.94 – 0.86 (m, 7H).

2. ^1H NMR

Figure S1 : ^1H NMR spectrum of **N-(4-(nonyloxy)phenyl)acetamide** in CDCl_3 .

Figure S2 : ^1H NMR spectrum of **4-(nonyloxy)aniline** in CDCl_3 .

Figure S3 : ¹H NMR spectrum of N-(4-(nonyloxy)phenyl)formamide in CDCl₃.

Figure S4 : ^1H NMR spectrum of **1-(nonyloxy)-4-isonitrilebenzene** in CDCl₃.

Figure S5: ¹H NMR spectrum of N-(4-(pentadecyloxy)phenyl)acetamide in CDCl₃.

Figure S6: ^1H NMR spectrum of **4-(pentadecyloxy)aniline** in CDCl_3 .

Figure S7: ^1H NMR spectrum of N-(4-(pentadecyloxy)phenyl)formamide in CDCl_3 .

Figure S8: ¹H NMR spectrum of **1-(pentadecyloxy)-4-isonitrilebenzene** in CDCl₃.

Figure S10: ^{13}C NMR spectrum of C_1N_9 in CDCl_3 .

Figure S12: ^{13}C NMR spectrum of C_6N_{15} in CDCl_3 .

Figure S13: ^1H NMR spectrum of C_9N_{15} in CDCl_3 .

Figure S14: ^{13}C NMR spectrum of C_9N_{15} in $CDCl_3$.

Figure S15 : 1H NMR spectrum of $C_{12}N_{15}$ in CDCl₃.

Figure S16: ^{13}C NMR spectrum of $C_{12}N_{15}$ in $CDCl_3$.

Figure S17 : ^1H NMR spectrum of C_{15}N_9 in CDCl_3 .

Figure S18: ^{13}C NMR spectrum of C_{15}N_9 in CDCl_3 .

Figure S19: IR and RAMAN spectra of solid C_1N_9 .

Figure S20: IR and RAMAN spectra of solid C_6N_{15} .

Figure S21: IR spectra of solid C_9N_{15} .

Figure S22: IR and RAMAN spectra of solid $C_{12}N_{15}$.

Figure S23: IR and RAMAN spectra of solid $C_{15}N_9$.

3. HRMS

Figure S24: Exact mass spectrum by direct introduction (APCI) for C_1N_9 .

Figure S25: Exact mass spectrum by direct introduction (APCI) for C_6N_{15} .

Figure S26: Exact mass spectrum by direct introduction (APCI) for C_9N_{15} .

Figure S27: Exact mass spectrum by direct introduction (APCI) for $C_{12}N_{15}$.

Figure S28: Exact mass spectrum by direct introduction (APCI) for $C_{15}N_9$.

4. PXRD

Figure S29 : Experimental powder XRD diffractograms of C_1N_9 at 25 °C (left) and 125 °C (right).

Figure S30: Experimental powder XRD diffractograms of C_6N_{15} at 25 °C (left) and 125 °C (right).

Figure S31: Experimental powder XRD diffractograms of C_9N_{15} at 25 °C (left) and 125 °C (right).

Figure S32: Experimental powder XRD diffractograms of $\text{C}_{12}\text{N}_{15}$ at 25 °C (left) and 125 °C (right).

Figure S33: Experimental powder XRD diffractograms of C₁₅N₉ at 25 °C (left) and 125 °C (right).

Figure S34: Hypothetical packing structure of solid C₁₅N₉ at 25 °C based on curve fitting of the powder XRD patterns.

5. DSC

Figure S35: DSC traces (exo up) of C_1N_9 , scan rate = 10 $^{\circ}C/min$.

Figure S36: DSC traces (exo up) of C_6N_{15} , scan rate = 10 $^{\circ}C/min$.

Figure S37: DSC traces (exo up) of C_9N_{15} , scan rate = 10 $^{\circ}C/min$.

Figure S38: DSC traces (exo up) of $C_{12}N_{15}$, scan rate = 10 $^{\circ}C/min$

Figure S39: DSC traces (exo up) of $C_{15}N_9$, scan rate = 10 $^{\circ}C/min$

6. TGA

Figure S40: Thermogravimetric analysis (black line) and corresponding first derivative (grey line) of C_1N_9 under argon atmosphere from 20 to 950 $^{\circ}C$.

Figure S41: Thermogravimetric analysis (black line) and corresponding first derivative (grey line) of C_6N_{15} under argon atmosphere from 20 to 950 $^{\circ}C$.

Figure S42: Thermogravimetric analysis (black line) and corresponding first derivative (grey line) of C_9N_{15} under argon atmosphere from 20 to 950 $^{\circ}C$.

Figure S43: Thermogravimetric analysis (black line) and corresponding first derivative (grey line) of $C_{12}N_{15}$ under argon atmosphere from 20 to 950 $^{\circ}C$.

Figure S44: Thermogravimetric analysis (black line) and corresponding first derivative (grey line) of C_{15}N_9 under argon atmosphere from 20 to 950 $^{\circ}\text{C}$.

Figure S45: TGA analysis of the residual at 950°C as a function of mass percent of carbon.

Figure S46: TGA analysis of the residual at 950°C as a function of number of carbon atoms.

7. Microscopy

Figure S47: Polarized light microscopy images of C_1N_9 at 298K (left), at 398K (middle) and at 408K (right). Note that the image with the yellow back ground is without polarized light.

Figure S48: Polarized light microscopy images of C_1N_9 upon cooling at 388K (left), at 383K (middle) and 298K (right).

Figure S49: Polarized light microscopy images of C_9N_{15} at 298K (left), heated at 403K (right) and cooled down to 392K (right). Note that the image with the yellow back ground is without polarized light.

Figure S50: Polarized light microscopy images of $\text{C}_{12}\text{N}_{15}$ at 298K (left), heated at 403K (right) and heated at to 418K (right). Note that the image with the yellow back ground is without polarized light.

Figure S51: Polarized light microscopy images of $\text{C}_{12}\text{N}_{15}$ cooled down to 298K. Note that the image with the yellow back ground is without polarized light.

8. DFT

Computational Details

C_1N_9 in a CH_2Cl_2 solvent field

Figure S52: Structure (optimized geometry) of C_1N_9 in the ground state in a CH_2Cl_2 solvent field.

Figure S53: Representations of the frontier MOs of C_1N_9 in the ground state in a CH_2Cl_2 solvent field.

Table S1: Atomic contributions of the frontier MOs of C_1N_9 in a CH_2Cl_2 solvent field. (H = HOMO; L = LUMO).

Fragment	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
Energy (eV)	-9.47	-9.05	-8.73	-8.46	-7.38	0.03	0.66	1.22	1.32	1.80
Au (%)	11.10	0.20	19.55	3.28	6.63	12.89	29.25	0.94	9.42	0.53
Ethynyl (%)	84.34	99.58	77.86	3.66	90.83	9.57	12.25	3.51	47.72	98.91
Isocyanide (%)	4.56	0.22	2.59	93.06	2.54	77.53	58.51	95.55	42.86	0.57

Figure S54: Optimized geometry of C_1N_9 in the triplet state in a CH_2Cl_2 solvent field.

Figure S55: Representation of the frontier MOs of C_1N_9 in the triplet state in a CH_2Cl_2 solvent field.

Phosphorescence position : $E_{\text{triplet}} - E_{\text{singlet}} = 3.07 \text{ eV} = 404 \text{ nm}$

Table S2: Atomic contributions of the frontier MOs of C_1N_9 in the triplet state in a CH_2Cl_2 solvent field.

Fragment	LSOMO	HSOMO
Energy (eV)	-7.88	-4.36
Au (%)	10.24	3.52
Ethynyl (%)	79.68	94.50
Isocyanide (%)	10.08	1.98

Figure S56 : Bar graph of the calculated positions of the spin-allowed electronic transition (blue) of C_1N_9 in a CH_2Cl_2 solvent field vs their oscillator strength (the simulated spectrum (black) is generated by assigning an arbitrary thickness of 1500 cm^{-1} for each bar).

Table S3: Calculated positions, oscillator strengths and major contributions of the 100 first spin-allowed electronic transitions of C_1N_9 in a CH_2Cl_2 solvent field.

Transition No.	λ (nm)	Osc. Str.	Major contribs (% ; - means no major contribution)
1	286.3952	1.4505	HOMO→LUMO (59%), HOMO→L+3 (22%)
2	266.0815	0	H-4→L+1 (11%), HOMO→L+1 (75%)
3	252.3731	0.1971	H-2→LUMO (30%), H-2→L+3 (13%), H-1→LUMO (38%)
4	251.5947	0.19	H-2→LUMO (34%), H-2→L+3 (12%), H-1→LUMO (32%)
5	249.8455	0.0748	HOMO→L+4 (74%)
6	241.6452	0.0272	H-6→LUMO (20%), H-1→L+2 (60%)
7	231.3467	0.2131	H-5→LUMO (87%)
8	226.247	1.0237	H-2→L+1 (47%), HOMO→L+3 (14%), HOMO→L+5 (16%)
9	225.9995	0.2495	H-5→L+1 (97%)
10	222.3478	0.0156	H-1→L+1 (69%)
11	214.6414	0.1263	H-2→L+1 (33%), HOMO→LUMO (23%), HOMO→L+3 (15%), HOMO→L+5 (12%)
12	202.6401	0.0005	H-2→LUMO (16%), H-2→L+3 (33%), H-2→L+5 (23%)
13	199.1636	0.4055	H-6→LUMO (62%), H-1→L+2 (25%)
14	197.6239	0.008	H-9→L+1 (14%), H-8→LUMO (73%)
15	197.6145	0.0083	H-9→LUMO (72%), H-8→L+1 (14%)
16	195.5049	0.3586	H-3→LUMO (25%), H-3→L+3 (33%), H-3→L+5 (10%), HOMO→L+4 (15%)
17	192.9401	0.0592	H-9→L+1 (35%), H-8→L+1 (48%)
18	192.9251	0.0691	H-9→L+1 (48%), H-8→L+1 (35%)
19	190.8993	0.2499	H-4→LUMO (11%), H-4→L+3 (17%), H-3→L+4 (16%), HOMO→L+5 (11%)
20	186.2003	0.1367	H-6→L+2 (38%)
21	183.3314	0.143	H-3→L+4 (16%), HOMO→L+3 (10%), HOMO→L+5 (43%)
22	182.9472	0.0047	H-2→L+4 (81%), HOMO→L+7 (10%)
23	182.5862	0.0236	H-2→L+4 (13%), HOMO→L+7 (65%), HOMO→L+10 (11%)
24	180.3656	0.5762	H-6→L+2 (10%), H-4→LUMO (18%), H-3→L+4 (47%)
25	179.317	0.0785	H-6→L+2 (16%), HOMO→L+9 (19%)
26	178.9185	0.0646	H-6→L+2 (16%), HOMO→L+9 (20%)
27	175.7706	0	H-4→L+1 (26%), HOMO→L+1 (14%), HOMO→L+6 (11%), HOMO→L+9 (14%)
28	175.5317	0.0021	H-19→LUMO (13%), H-17→LUMO (30%), H-2→L+5 (27%)
29	173.2046	0.0033	HOMO→L+2 (82%)
30	172.0891	0.0013	H-4→L+1 (12%), HOMO→L+6 (58%)
31	171.9746	0.0002	H-6→L+1 (85%)
32	171.665	0.1383	H-5→L+3 (65%)
33	170.0032	0.0523	H-4→L+4 (78%)

34	169.4989	0.1502	H-1→L+3 (24%)
35	166.7003	0.0007	H-3→L+1 (87%)
36	165.5429	0.0002	H-17→LUMO (11%), H-2→LUMO (11%), H-2→L+3 (22%), H-2→L+5 (35%)
37	163.9319	0.0139	H-3→LUMO (21%), H-2→L+7 (40%), H-2→L+10 (10%)
38	163.8712	0.2067	H-3→LUMO (26%), H-3→L+5 (11%), H-2→L+7 (31%)
39	163.683	0.0022	H-22→LUMO (18%), H-19→LUMO (33%)
40	162.4286	0.1716	H-19→L+1 (18%), H-17→L+1 (16%), H-2→L+6 (13%)
41	160.1314	0.0754	H-5→L+6 (73%)
42	159.898	0.0151	H-13→LUMO (22%)
43	158.1178	0.0009	H-14→LUMO (16%), H-14→L+3 (37%), H-14→L+5 (19%)
44	157.7537	0.0061	H-1→L+7 (18%), HOMO→L+10 (36%)
45	157.4532	0.0001	H-24→L+1 (16%), H-20→L+1 (18%), H-13→L+1 (12%), H-4→L+1 (20%), HOMO→L+9 (10%)
46	157.3792	0.0017	H-22→L+2 (15%), H-17→L+2 (35%), H-2→L+2 (20%)
47	155.146	0.0011	H-24→LUMO (12%), H-4→LUMO (12%), H-2→L+6 (27%)
48	154.5098	0.0254	H-4→LUMO (10%), H-2→L+6 (41%)
49	154.1583	0.0276	H-14→L+4 (51%), H-5→L+5 (10%)
50	154.0931	0.0155	H-23→LUMO (13%), H-14→L+4 (26%), H-5→L+5 (18%), H-1→L+7 (14%)
51	153.4523	0.0097	H-1→L+1 (10%), H-1→L+6 (36%)
52	153.2588	0.0225	H-2→L+9 (11%), HOMO→L+8 (24%), HOMO→L+13 (14%)
53	152.766	0.0249	H-1→L+7 (22%), HOMO→L+10 (20%)
54	152.4841	0.0251	H-6→L+3 (13%), H-2→L+2 (26%)
55	152.3474	0.0303	H-6→L+3 (14%), H-2→L+2 (23%)
56	151.8975	0.0006	H-32→LUMO (10%), H-28→LUMO (13%), H-26→LUMO (10%), H-2→L+2 (11%), H-1→L+6 (10%)
57	150.9709	0.0076	H-23→LUMO (23%), H-5→L+5 (28%), HOMO→L+15 (14%)
58	150.4086	0.0012	HOMO→L+15 (50%)
59	149.2714	0.0827	H-23→L+1 (55%), H-5→L+6 (10%)
60	148.92	0.002	H-9→L+3 (36%), H-8→L+3 (29%)
61	148.8842	0.0125	H-9→L+3 (29%), H-8→L+3 (36%)
62	148.6076	0.1466	H-13→L+2 (39%), H-6→L+3 (11%)
63	147.8315	0.1991	H-2→L+9 (26%), HOMO→L+8 (18%)
64	145.9623	0.0002	H-5→L+2 (90%)
65	145.1915	0.0031	H-5→L+7 (54%), H-1→L+8 (12%)
66	145.1099	0.0054	H-2→L+10 (51%)
67	145.0946	0.1237	H-5→L+7 (34%), H-1→L+8 (17%)
68	144.1415	0.0001	H-32→LUMO (11%), H-7→LUMO (45%)
69	142.2578	0.0142	H-18→L+3 (16%), H-5→L+10 (13%)
70	141.9971	0.0017	H-1→L+3 (12%), H-1→L+5 (46%)
71	141.0232	0.0001	H-3→L+7 (45%), H-3→L+10 (10%), H-3→L+15 (16%)

72	140.9574	0.0023	H-30→L+4 (11%), H-23→L+4 (14%), H-5→L+4 (39%)
73	140.7143	0.0014	H-1→L+7 (17%), H-1→L+12 (28%)
74	140.5962	0.0308	
75	140.3352	0.0003	H-5→L+4 (12%), H-2→L+8 (21%), H-2→L+13 (23%)
76	140.2352	0.0168	H-9→L+6 (39%), H-8→L+6 (46%)
77	140.2193	0.0158	H-9→L+6 (47%), H-8→L+6 (39%)
78	139.8335	0.0008	H-27→L+1 (11%), H-24→L+1 (13%), H-13→L+1 (14%), H-1→L+6 (15%)
79	139.709	0.005	H-3→L+3 (23%), H-3→L+5 (35%)
80	139.2539	0.0112	H-4→L+19 (11%), HOMO→L+19 (53%)
81	138.5769	0.1068	H-18→L+4 (29%), H-1→L+4 (23%)
82	138.4809	0.0117	H-1→L+8 (19%), HOMO→L+8 (17%)
83	138.2185	0.0026	H-28→L+2 (15%), H-26→L+2 (11%), H-19→L+2 (22%)
84	137.911	0.0008	H-23→L+3 (13%)
85	137.8159	0.0239	H-4→L+5 (24%), H-1→L+4 (15%)
86	136.9966	0.0009	H-6→L+7 (41%), H-6→L+10 (18%), H-6→L+12 (16%)
87	136.547	0.0024	H-3→L+2 (77%), H-3→L+3 (14%)
88	136.0182	0.0708	H-18→L+4 (26%), H-1→L+4 (44%)
89	135.7472	0	H-7→LUMO (28%)
90	135.3574	0.0032	H-30→L+4 (22%), H-25→L+4 (15%), H-23→L+4 (18%), H-5→L+4 (28%)
91	135.0802	0.1048	H-16→LUMO (18%), H-11→LUMO (17%)
92	134.9831	0.0011	H-5→L+9 (87%)
93	134.7718	0.0261	H-4→L+7 (52%)
94	134.5846	0.0017	H-9→L+10 (34%), H-8→L+10 (26%)
95	134.3964	0.0012	H-9→L+10 (27%), H-8→L+10 (35%)
96	134.2232	0.0155	H-4→L+2 (52%)
97	134.1796	0.0016	H-25→L+3 (17%)
98	133.0565	0.0006	H-19→L+3 (11%), H-17→L+3 (10%), H-4→L+6 (14%)
99	132.9965	0.0063	H-1→L+18 (12%)
100	132.7317	0.0249	H-1→L+16 (12%), H-1→L+18 (19%)

9. Photophysics

Table S4: Absorption maxima of the gold complexes

Sample	λ_{Abs} (CH ₂ Cl ₂)	λ_{Abs} (2-MeTHF)	λ_{Abs} (solid state)
	298K (nm)	77K (nm)	298K (nm)
C₁N₉	285	294	286
C₆N₁₅	281	290	298
C₉N₁₅	286	290	297
C₁₂N₁₅	286	286	297
C₁₅N₉	286	288	298

Solution 298K

Figure S57: **C₁N₉** in CH₂Cl₂ at 298K. Left, excitation (blue), absorption (black) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Multi-exponential analysis yields $\tau_e = 16.4 \mu\text{s}$ (100%), $\chi^2 = 1.040$.

Figure S58: **C₆N₁₅** in CH₂Cl₂ at 298K. Left, excitation (blue), absorption (black) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Multi-exponential analysis yields $\tau_e = 14.3\mu\text{s}$ (100 %), $\chi^2=1.00$.

Figure S59: **C₉N₁₅** in CH₂Cl₂ at 298K. Left, excitation (blue), absorption (black) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Exponential smoothing model (ESM) yields $\tau_e = 4.2\mu\text{s}$ (100 %), $\chi^2=1.10$.

Figure S60: **C₁₂N₁₅** in CH₂Cl₂ at 298K. Left, excitation (blue), absorption (black) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Exponential smoothing model (ESM) yields $\tau_e = 24.6\mu\text{s}$ (100 %), $\chi^2=1.00$.

Figure S61: $C_{15}N_9$ in CH_2Cl_2 at 298K. Left, excitation (blue), absorption (black) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Exponential smoothing model (ESM) yields $\tau_e = 9.1\mu\text{s}$ (100 %), $\chi^2=1.02$.

Solution 77K

Figure S62: C_1N_9 in 2-MeTHF at 77K. Left, excitation (blue), absorption (black) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Multi-exponential analysis yields $\tau_e = 0.3\mu\text{s}$ (0.6%), $5.9\mu\text{s}$ (1.1%) and $170\mu\text{s}$ (98.3%), $\chi^2= 1.06$.

Figure S63: C_6N_{15} in 2-MeTHF at 77K. Left, excitation (blue), absorption (black) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Multi-exponential analysis yields $\tau_e = 0.3\mu\text{s}$ (1.1%), $17.2\mu\text{s}$ (1.3%) and $150\mu\text{s}$ (97.6%), $\chi^2=1.10$.

Figure S64: C_9N_{15} in 2-MeTHF at 77K. Left, excitation (blue), absorption (black) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Multi-exponential analysis yields $\tau_e = 0.3\mu\text{s}$ (2.0%), $6.1\mu\text{s}$ (0.6%) and $160\mu\text{s}$ (97.4%), $\chi^2=1.09$.

Figure S65: $\text{C}_{12}\text{N}_{15}$ in 2-MeTHF at 77K. Left, excitation (blue), absorption (black) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Multi-exponential analysis yields $\tau_e = 0.3\mu\text{s}$ (2.1%), $14.1\mu\text{s}$ (0.6%), $67.4\mu\text{s}$ (5.2%) and $160\mu\text{s}$ (92.1%), $\chi^2=1.10$.

Figure S66: C_{15}N_9 in 2-MeTHF at 77K. Left, excitation (blue), absorption (black) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Multi-exponential analysis yields $\tau_e = 150\mu\text{s}$ (100%), $\chi^2=1.00$.

Solid state 298K

Figure S67: C_1N_9 in the solid state at 298K. Excitation (blue), absorption (black) and emission (red) spectra. The sharper peaks at 370 (blue), 475 (red) and 530 (red) nm are instrumental artifacts.

Figure S68: C_6N_{15} in the solid state at 298K. Excitation (blue), absorption (black) and emission (red) spectra.

Figure S69: C_9N_{15} in the solid state at 298K. Excitation (blue), absorption (black) and emission (red) spectra.

Figure S70: $\text{C}_{12}\text{N}_{15}$ in the solid state at 298K. Excitation (blue), absorption (black) and emission (red) spectra.

Figure S71: C_{15}N_9 in the solid state at 298K. Excitation (blue), absorption (black) and emission (red) spectra.

Solid state 77K

Figure S72: C_1N_9 in the solid state at 77K. Left, excitation (blue) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Multi-exponential analysis yields $\tau_P = 1.52 \mu\text{s}$ (10.18%), $7.56 \mu\text{s}$ (7.99%), $34.07 \mu\text{s}$ (81.83%), $\chi^2 = 1.07$. Inset, Multi-exponential analysis. $\lambda_{\text{ex}} = 300 \text{ nm}$, $\lambda_{\text{em}} = 425 \text{ nm}$.

Figure S73: C_6N_{15} in the solid state at 77K. Left, excitation (blue) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Multi-exponential analysis yields $\tau_p = 13.78 \mu\text{s}$ (16.42%), $69.34 \mu\text{s}$ (83.58%), $\chi^2 = 1.06$. Inset, Multi-exponential analysis. $\lambda_{\text{ex}} = 350 \text{ nm}$, $\lambda_{\text{em}} = 442 \text{ nm}$.

Figure S74: C_9N_{15} in the solid state at 77K. Left, excitation (blue) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Multi-exponential analysis yields $\tau_p = 5.08 \text{ ns}$ (26.13%), 1.81 ns (48.23%), 0.52 ns (18.51%), 0.07 ns (7.14%), $\chi^2 = 1.03$. Inset, Multi-exponential analysis. $\lambda_{\text{ex}} = 300 \text{ nm}$, $\lambda_{\text{em}} = 425 \text{ nm}$.

Figure S75: $\text{C}_{12}\text{N}_{15}$ in the solid state at 77K. Left, excitation (blue) and emission (red) spectra. Right, emission decay (black), IRF (blue), residuals (green) and best fit (red). Multi-exponential analysis yields $\tau_p = 2.23 \mu\text{s}$ (13.53%), $10.27 \mu\text{s}$ (31.80%), $20.10 \mu\text{s}$ (31.13%), $48.00 \mu\text{s}$ (23.54%), $\chi^2 = 1.00$. Inset, Multi-exponential analysis. $\lambda_{\text{ex}} = 350 \text{ nm}$, $\lambda_{\text{em}} = 434 \text{ nm}$.

Figure S76: C_{15}N_9 in the solid state at 77K. Excitation (blue), absorption (black) and emission (red) spectra. Multi-exponential analysis yields $\tau_p = 19.98 \mu\text{s}$ (80.15%), $13.19 \mu\text{s}$ (17.32%), $3.76 \mu\text{s}$ (2.52%), $\chi^2 = 1.01$. Inset, Multi-exponential analysis. $\lambda_{\text{ex}} = 300 \text{ nm}$, $\lambda_{\text{em}} = 425 \text{ nm}$.

10. Transient Absorption Spectroscopy

Figure S77: a) Time evolution of the fs-TAS of $C_{15}N_9$ in CH_2Cl_2 (295 K; $\lambda_{exc} = 266$ nm; pulse power = 0.2 mJ/cm^2). Note that in this scale the positive and negative responses represent the bleached and transient signals, respectively. Also note the presence of an isosbestic point at 585 nm. b) Corresponding decay associated spectra and the transient lifetimes (note that the lifetime indicated inside the frame are those directly issued from best fits. The uncertainties based on multiple measurements is $\pm 10\%$). c) and d) Decay traces monitored at different wavelengths.

Figure S78: a) Time evolution of the fs-TAS of C_6N_{15} in CH_2Cl_2 (295 K; $\lambda_{exc} = 266$ nm; pulse power = 0.2 mJ/cm²). Note that in this scale the positive and negative responses represent the bleached and transient signals, respectively. Also note the presence of an isosbestic point at 585 nm. b) Corresponding decay associated spectra and the transient lifetimes (note that the lifetime indicated inside the frame are those directly issued from best fits. The uncertainties based on multiple measurements is $\pm 10\%$). c) and d) Decay traces monitored at different wavelengths.

Figure S79: a) Time evolution of the fs-TAS of C_9N_{15} in CH_2Cl_2 (295 K; $\lambda_{exc} = 266$ nm; pulse power = 0.2 mJ/cm²). Note that in this scale the positive and negative responses represent the bleached and transient signals, respectively. Also note the presence of an isosbestic point at 585 nm. b) Corresponding decay associated spectra and the transient lifetimes (note that the lifetime indicated inside the frame are those directly issued from best fits. The uncertainties based on multiple measurements is $\pm 10\%$). c) and d) Decay traces monitored at different wavelengths.

Figure S80: a) Time evolution of the fs-TAS of $C_{12}N_{15}$ in CH_2Cl_2 (295 K; $\lambda_{exc} = 266$ nm; pulse power = 0.2 mJ/cm^2). Note that in this scale the positive and negative responses represent the bleached and transient signals, respectively. Also note the presence of an isosbestic point at 585 nm. b) Corresponding decay associated spectra and the transient lifetimes (note that the lifetime indicated inside the frame are those directly issued from best fits. The uncertainties based on multiple measurements is $\pm 10\%$). c) and d) Decay traces monitored at different wavelengths.

Figure S81: a) Time evolution of the fs-TAS of Au NPs generated upon the photodecomposition of C_{15}N_9 in CH_2Cl_2 (295 K; $\lambda_{\text{exc}} = 266 \text{ nm}$; pulse power = 0.2 mJ/cm^2). Note that in this scale the positive and negative responses represent the bleached and transient signals, respectively. b) Corresponding decay associated spectra and the transient lifetimes (note that the lifetime indicated inside the frame are those directly issued from best fits. The uncertainties based on multiple measurements is $\pm 10\%$). c) and d) Decay traces monitored at different wavelengths. The fs-TAS data for the other four complexes are placed in the SI.

Figure S82: a) Time evolution of the fs-TAS of Au NPs generated upon the photodecomposition of C_6N_{15} in CH_2Cl_2 (295 K; $\lambda_{\text{exc}} = 266 \text{ nm}$; pulse power = 0.2 mJ/cm^2). Note that in this scale the positive and negative responses represent the bleached and transient signals, respectively. b) Corresponding decay associated spectra and the transient lifetimes (note that the lifetime indicated inside the frame are those directly issued from best fits. The uncertainties based on multiple measurements is $\pm 10\%$). c) and d) Decay traces monitored at different wavelengths. The fs-TAS data for the other four complexes are placed in the SI.

Figure S83: a) Time evolution of the fs-TAS of Au NPs generated upon the photodecomposition of C_9N_{15} in CH_2Cl_2 (295 K; $\lambda_{\text{exc}} = 266 \text{ nm}$; pulse power = 0.2 mJ/cm^2). Note that in this scale the positive and negative responses represent the bleached and transient signals, respectively. b) Corresponding decay associated spectra and the transient lifetimes (note that the lifetime indicated inside the frame are those directly issued from best fits. The uncertainties based on multiple measurements is $\pm 10\%$). c) and d) Decay traces monitored at different wavelengths. The fs-TAS data for the other four complexes are placed in the SI.

Figure S84: a) Time evolution of the fs-TAS of Au NPs generated upon the photodecomposition of $\text{C}_{12}\text{N}_{15}$ in CH_2Cl_2 (295 K; $\lambda_{\text{exc}} = 266$ nm; pulse power = 0.2 mJ/cm^2). Note that in this scale the positive and negative responses represent the bleached and transient signals, respectively. b) Corresponding decay associated spectra and the transient lifetimes (note that the lifetime indicated inside the frame are those directly issued from best fits. The uncertainties based on multiple measurements is $\pm 10\%$). c) and d) Decay traces monitored at different wavelengths. The fs-TAS data for the other four complexes are placed in the SI.

11.Singlet Oxygen

Figure S85: Experimental setup for near-infrared singlet oxygen steady state detection and lifetime measurements.

Figure S86: Emission decay of singlet oxygen photosensitized by gold complexes upon excitation at 300 nm in CH_2Cl_2 (DCM) at 298K.

Figure S87: Emission decay of singlet oxygen photosensitized by gold complexes upon excitation at 300 nm in CH_2Cl_2 (DCM) at 298K.

12. Transmission electron microscopy

Figure S88: Setup for the irradiation of the gold complexes.

Figure S89: TEM images of C_1N_9 . Left: thermal decomposition at $130^{\circ}C$. Right: Photodecomposition at 405 nm.

Figure S90: TEM images of C_6N_{15} . Left: thermal decomposition at 130°C . Right: Photodecomposition at 365 nm.

Figure S91: TEM images of C_9N_{15} , photodecomposition at 405 nm.

Figure S92: TEM images of $\text{C}_{12}\text{N}_{15}$. Left: thermal decomposition at 130°C . Right: Photodecomposition at 365 nm.

Figure S93: Evolution of the absorption spectra of **C₁N₉** in the solid state upon photolysis ($\lambda_{\text{exc}} = 365$ nm). Note the appearance of the band at 560 nm witnessing the growth of the Au NPs. The setup for photolysis is shown in Figure S94.

Figure S95: Evolution of the absorption spectra of **C₁N₉** in CH_2Cl_2 upon photolysis ($\lambda_{\text{exc}} = 365$ nm). Note the absence of the band at 560 nm associated with the Au NPs. The setup for photolysis is shown in Figure S96.

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