Luminescence of a transition metal complex inside a metamaterial nanocavity

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Modification of the local density of optical states using metallic nanostructures leads to enhancement in the number of emitted quanta and photocatalytic turn-over of luminescent materials. In this work, we present the fabrication of a metamaterial that consists of a nanowire separated from a metallic mirror by a polymer thin film doped with a luminescent organometallic iridium(III) complex. The large spin-orbit coupling of the heavy metal atom results in an excited state with significant magnetic dipole character. The nanostructured architecture supports two distinct optical modes and their assignment achieved with the assistance of numerical simulations. The simulations show that one mode is characterized by strong confinement of the electric field and the other by strong confinement of the magnetic
field. These modes elicit drastic changes in the emitter’s photophysical properties, including dominant nano-cavity derived modes observable in the emission spectra along with significant increases in emission intensity and the total decay rate. A combination of simulations and momentum-resolved spectroscopy help explain the mechanism of the different interactions of each optical mode supported by the metamaterial with the excited state of the emitter.

1. Introduction
Cyclometalated iridium(III) complexes are versatile luminescent emitters with the ability to readily tune emission properties through control of their coordinated ligand environment. They also exhibit robust photophysics (large Stokes shifts, long emission lifetimes, high photostability) which has led to their widespread application in electrochemiluminescent sensors, photovoltaics and bioimaging.\[1\] These $d^6$ transition metal complexes (along with ruthenium(II) complexes) are also pivotal in the emerging field of photoredox catalysis; in the excited state they act as potent single electron donors or acceptors and facilitate a large number of chemical transformations.\[2\] A key limitation of these complexes is their relatively low molar absorptivity in the visible spectrum, which limits the total number of absorbed and emitted quanta in light-emitting applications or turn-over rates in photocatalysis. For catalysis, this limitation is typically overcome using high intensity light sources and long reaction times that may also reduce yields and increase unwanted reaction byproducts. An alternative approach is to modify the local density of optical states around the molecular species, achievable by exploiting the large electromagnetic field confinements and enhancements obtained with various metal nanostructures. By way of example, colloidal silver nanoparticles afford a two-fold emission enhancement of the common transition metal photoredox catalyst $[\text{Ru(bpy)}_3]^{2+}$, which in turn directly correlates to a greater turn-over for the photocatalytic oxidation of styrene derivatives.\[3\]
A promising architecture for optimizing the electromagnetic environment of molecular species is the ‘nanoparticle on mirror geometry’ (NPoM). These structures consist of a nanostructured metal layer and a metallic mirror, separated by a fixed distance, and support a variety of different optical modes.[4] When a suitable emitter (such as organic fluorophores, quantum dots or two-dimensional semiconductors) resides in this engineered cavity, significant emission enhancements arise as a consequence of the large electromagnetic field confinement.[5] Recently, the NPoM architecture has enabled the first observation of Rabi splitting (strong coupling) at room temperature.[6] Importantly, this sample geometry does not hinder catalytic processes as cadmium selenide nano-platelets situated in a NPoM cavity showed greatly enhanced photocatalytic water splitting ability.[7]

Emission enhancement using NPoM or other plasmonic structures has to date resulted from substantial enhancements in the electric near-fields, which significantly modify electric-dipole allowed (singlet) transitions. For cyclometalated iridium(III) emitters this primarily affects the absorption of light. Emission from these complexes occurs from a triplet state (Figure 1A), accessible due to extremely fast intersystem crossing (ISC) facilitated by the large spin-orbit coupling constant of the heavy metal center ($\zeta = 3909 \text{ cm}^{-1}$ for iridium(III)). Triplet state emission is often characterized by long lifetimes but is also readily identified by a strong magnetic-dipole character, making these transitions sensitive to local magnetic fields.[8] Spin-orbit coupling also leads to mixing of the singlet and triplet states, imparting the transition with a finite transition dipole moment.[9] It is possible to elicit strong confinement of both the electric and magnetic field using structures comprised of an optically-resonant (metallic) nanostructure suspended above a mirror, such as NPoM and other perfect-absorber metamaterials. By placing a layer of triplet-state emitters in the gap region between the resonant nanostructure and the mirror, it is therefore possible to modify their photophysical characteristics. In this work, we present an embodiment of this concept consisting of a nanowire grating separated from a mirror...
by a thin layer containing an iridium(III) complex. We demonstrate that the emission from these complexes has a magnetic dipole character and that it is drastically modified by the optical resonances of the nanowire-on-mirror metamaterial. In particular, we report the observation of changes to both the spectrum line-shape and spontaneous decay rates of the transition metal complex emission.

2. Results and Discussion

2.1. Iridium(III) complex characterization

The model cyclometalated iridium(III) complex 1 (Figure 1B) was synthesized via a modified procedure and characterized by NMR spectroscopy. Single crystals suitable for X-ray crystallography were grown and the solved structure (Figure 1C) showed the iridium atom occupying a distorted octahedral environment. Two bidentate cyclometalating ligands are coordinated to the metal atom with an overall N,N-trans geometry. The final two sites are occupied by the modified acetylacetonate ligand. Deprotonation of this ligand during synthesis resulted in an overall neutral complex. Electronic absorption spectroscopy showed strong bands below $\lambda = 400$ nm, assigned to $\pi-\pi^*$ transitions of the cyclometalating ligands and consistent with similar reported iridium(III) complexes, as well as several less intense bands in the visible region ($\lambda > 400$ nm). The lower energy transitions were assigned as either singlet or triplet metal-ligand charge transfer (MLCT) in character (Figure 1A). Emission spectra were measured both in solution (Figure 1D) and in a doped poly(methyl methacrylate) (PMMA) thin film. The emission spectrum showed a broad band with a maximum at $\lambda_{em} = 619$ nm and a long tail extending towards lower energy frequencies. The emission profile of 1 underwent a slight hypsochromic shift (~10 nm) when incorporated into a doped PMMA film relative to when in solution (Supporting information, Figure S1); this was attributed to differences in polarity of the medium surrounding the complex. Solvatochromic effects are common in phosphorescent
iridium(III) complexes and indicate a greater delocalization of charge in the triplet MLCT excited state.\cite{12}

2.2. Metamaterial fabrication

The architecture of the plasmonic metamaterial (Figure 2A) consisted of periodic arrays (450 nm fixed period) of silver nanowires (height 30 nm, length 100 μm) with varying widths (100 – 250 nm). Wire length on the micrometer scale ensured that any plasmonic features were attributed to the width of the wires. These dimensions were selected following Rigorous-coupled wave numerical calculations\cite{13} to achieve strong electromagnetic field confinement concomitant with the emission spectrum of 1. The nanowires were fabricated by means of standard lift-off electron beam lithography (representative SEM in Figure 2B) and supported on a glass substrate. The wires were spin-coated with thin films of PMMA (1% w/v in anisole, final thickness 20 nm thick) doped with complex 1 (100 μM). Concentration of the dopant was selected to minimize deleterious triplet-triplet interactions. Fabrication was completed by direct deposition of a silver mirror onto the PMMA film. The measured absorbance spectra of the metamaterial as a function of nanowire width (Figure 2C) was dominated by two bands. The position of these bands is sensitive to the distance between the nanowires and mirror and a theoretical distance of 7 nm closely correlated with the experimental absorption spectrum (Figure S2). Direction and polarization of the light-source restricted excitation to the lateral plane of the substrates. One of these bands showed absorbance of up to ~70 % of visible light ($\lambda_{\text{max}} = 596$ nm, nanowire width = 160 nm), a value that exceeds the 50% absorbance limit for a thin film.\cite{14} The strong absorption of these nanowire-on-mirror structures can be interpreted in three possible and equivalent ways: (i) critical coupling,\cite{15} (ii) destructive interference between the incident light and the multiply-reflected light between the mirror and nanowires\cite{16} and (iii) partial impedance matching due to a magnetic response that originates from anti-parallel charge–currents occurring on both the metal mirror and the nanowires.\cite{17} The high absorbance is postulated to translate into extreme confinement of electromagnetic energy by
the nanostructures and consequently facilitate a large Purcell effect.\cite{18} The two dominant bands underwent a bathochromic shift with increasing width of the nanowires. Experimental results also suggested the appearance of a third narrow absorption band ($\lambda \approx 650$ nm) beginning at nanowire widths of 200 nm that was subsequently assigned as an artifact arising from the finite angle of incidence of the experimental light source (Figure S4).

2.3. Optical spectroscopy

The emission spectra of the prepared metamaterials showed strong modification of the line shape and area (Figure 3A). For instance, a sample with wire width of 100 nm revealed the appearance of an emission band at $\lambda_{\text{em}} = 679$ nm which possessed a full-width at half-maximum of 24 nm and increased intensity of approximately 7.6 times relative to the control (doped PMMA thin film on glass, shaded blue area, Figure 3A). This luminescence enhancement results from the interaction of the excited state of complex \textit{1} and the resonance modes of the metamaterial (vide infra) and is expected to be sensitive to any mismatch between the frequency (and symmetry) of these states. A comparison of emission with changing nanowire width (Figure 3B) highlights that the narrow and intense bands bathochromically shift along with increments in width and the emission intensity varies as the metamaterial resonances traverse the emission band of complex \textit{1}.

The measured decay kinetics integrated for the entire emission spectra of the metamaterial nanocavities are highly non-exponential but well-described by stretched exponentials (Figure 3D).\cite{19} These decay functions allow for an estimation of the underlying distribution of decay rates (Figure 3E) and revealed a broad distribution of rates, relative to a control film. Confinement of the electromagnetic field occurs in close proximity to the nanowires and it is thus expected that strong emission modification will occur only in the area occupied by these wires. In all samples the total decay rates were higher than that estimated for the control film. Rate values in the top 5\% of the calculated distributions (dashed vertical line in Figure 3E) reveal average enhancements in the emission decay rate up to 100-fold (Figure 3F). Given the
intrinsic heterogeneity of the electromagnetic field distribution in the polymer film (vide infra), we attributed the distribution of decay rates to originate from this spatial heterogeneity. It is important to note that the proximity of complex 1 to the bare metal film resulted in quenching of the emission (Figure S4).\textsuperscript{[20]} Emission enhancements are thus only likely to occur when these emitters reside in the gap region between mirror and nanowire.

The observed modifications to both the emission spectra (Figure 3A-B) and spontaneous emission rates (Figure 3D-F) was rationalized as an interplay between (\textit{i}) an increase in the luminescence collection efficiency, which occurs due to increased directionality of the emission caused by coupling of complex 1’s emitted light to the resonances of the metamaterial and (\textit{ii}) changes in the local density of optical states: the Purcell effect.\textsuperscript{[21]} Photo-excitation that is non-resonant with the optical modes of the metamaterial excluded an increased excitation rate as a major pathway for the observed modification of emission.

\textbf{2.4. Numerical simulations}

Within a Purcell effect context, the emission rate is proportional to the local density of optical states, which need to be estimated. Numerical simulations of the two dominant bands in the absorption spectrum of the metamaterial enabled their assignment to optical excitation of modes characterized by strong confinement of electromagnetic energy (Figure 4A). The geometry of the metamaterial in these simulations is assumed to be perfect (sharp corners, abrupt interfaces) and this leads to narrow and intense spectral bands. Imperfections unintentionally introduced during the nanofabrication process lead to the broadening and decreased intensity observed experimentally. The simulations (calculated for nanowire width = 130 nm) reproduced (semi-quantitatively) the dominant peaks of the experimental spectrum; the additional short-wavelength band predicted by the simulations (\(\lambda \approx 480\) nm) occurs in a region of limited intensity for the light source used. Maps of the electromagnetic field (Figure 4B) indicated the sharp band at \(\lambda = 694\) nm was principally dipolar in character with strong confinement of the incident electric field at the edges of the nanowire. This mode was expected
to enhance electric-dipole radiation from molecules in a fashion similar to reported plasmonic ‘nanopatch’ antennas.\textsuperscript{[5b-e, 22]} Additionally, the symmetry of this mode is also expected to result in strong modifications of the emission pattern which subsequently leads to an increase in the luminescence collection efficiency (Figure S6.1). On the contrary, the band located at $\lambda = 544$ nm displayed a strong localization of the magnetic field in the gap between the nanowire and the mirror along with quadrupole-like character in the symmetry of its electric field distribution. The strong localization of the magnetic field (Figure 4) may lead to an increase in the emission of a magnetic dipole emitter (Figure S6.2).

The lowest excited state of transition metal complexes (including 1) often possesses significant triplet character (Figure 1A), therefore distinguished by a strong magnetic-dipole character. The magnetic nature of emitted light from 1 was quantified using wavelength- and momentum-resolved spectroscopy (Figure 5).\textsuperscript{[23]} From an image of the back-focal plane (BFP, momentum space) of emitted $s$-/$p$-polarized light (Figure 5A, D respectively), the wavelength- and momentum-resolved emission spectrum of 1 was obtained for either polarization (Figure 5B, E). Cross sections of the measured spectra were fitted to a previously described model,\textsuperscript{[23]} which ascertained predominantly magnetic-dipole (MD) character at the emission maxima ($\lambda_{em} = 623$ nm, Figure 5C). At longer wavelengths the emission was instead primarily of electric-dipole (ED) character (Figure 5F). The varying character of complex 1’s emission at different wavelengths leads to the unique interactions observed between emitter and the metamaterial.

The electric-dipole mode of the metamaterial (Figure 4B, $\lambda = 694$ nm when nanowire width = 130 nm) is expected to enhance the lower energy tail of complex 1’s emission spectrum and indeed, the emission spectra of the fabricated metamaterials agrees with this supposition.

Strong confinement of the magnetic field, as exhibited by the quadrupole-like mode, was therefore predicted to accelerate the MD dominated emission of 1 ($\lambda_{em} = 619$ nm). Experimentally, we see significant enhancement of emission where the quadrupole-like mode
overlaps with emission maxima, in particular where nanowire width ≈ 160-180 nm. As the frequency (wavelength) of the magnetic quadrupole-like mode of the metamaterial shifted away from the emission maximum of complex 1, it no longer accelerated the predominantly MD emission (Figure 3B). It has been shown that a metamaterial nanocavity supporting magnetic (electric) hot-spots strongly enhance the MD (ED) emission from europium(III) ions, which is in agreement with our interpretation.[24]

3. Conclusion
In summary, we have shown strong modification of the emission spectrum and decay rate of an organometallic complex when positioned in a metamaterial nanocavity. We have shown that the emission from this complex exhibits both magnetic and electric dipole character. The metamaterial nanocavity supports two optical resonances which show different degrees of interaction with the magnetic and electric dipole emission of the complex, and result in drastic modifications to its luminescence. The approach presented here paves the way for creating efficient opto-electronic devices with transition metal complexes. For instance, one can envisage a light-emitting device where the metal nanostructure and mirror act as the electrodes for charge injection into the active area located in the gap. Similarly, the structures presented here may also be engineered for applications in photocatalysis.

4. Experimental Section
*Synthesis of non-8-ene-2,4-dione:* Synthesized via modification of a previously reported procedure.[25] To a suspension of sodium hydride (60% dispersion in oil, 1.6 g, 40 mmol) in anhydrous tetrahydrofuran (100 mL) was added acetylacetonate (3.64 g, 36 mmol) and hexamethylphosphoramide (1.5 mL) at 0 °C and the suspension was stirred for 10 min. A solution of butyllithium in hexane (1.6 M, 25 mL, 40 mmol) was added dropwise to this suspension at 0 °C and stirred for a further 10 min. To this suspension 4-bromo-1-butene (5.4
g, 40 mmol) was added dropwise and stirred for 20 min. The solution was concentrated under reduced pressure, acidified with H₂SO₄ and separated between water and toluene. The product was extracted into the organic phase and washed with water and brine, while the aqueous phase was back extracted with toluene. The combined organic fractions were concentrated under reduced pressure and purified using silica gel chromatography with an eluent of 10:1 pentane/ethyl acetate to yield a colourless oil (3.56 g, 64%). ¹H NMR (500 MHz; CDCl₃): δ 1.71 (2H, quintet, acac-CH₂-CH₂), 2.05 (3H, s, acac-CH₃), 2.09 (2H, q, J = 7.1 Hz, acac-CH₂-CH₂-CH₂), 2.27 (2H, m, -CH=CH₂), 5.01 (2H, m, acac-CH₂-CH₂), 5.49 (1H, s, CO-CH=COH), 5.78 (1H, m, -CH=CH₂), 15.48 (1H, s, CO-CH=COH).

Synthesis of complex I: The iridium(III) dimer precursor was prepared according to a previously published procedure.[10] A solution of non-8-ene-2,4-dione (48 mg, 311 μmol) and triethylamine (50 μL, 361 μmol) in anhydrous methanol (5 mL) was sparged with nitrogen for 20 min. The dimer (144 mg, 97 μmol) was added and the suspension was heated at reflux in the dark for three hours. The solvent was removed under reduced pressure and the residue dissolved in dichloromethane and washed with water and brine then dried (Na₂SO₄). The solution was concentrated and the product purified via silica gel chromatography with an eluent of 8:1 pentane/ethyl acetate to yield a bright red solid (154 mg, 93%). ¹H NMR (500 MHz; CDCl₃): δ 1.04-1.35 (2H, m, acac-CH₂-CH₂), 1.57 (3H, s, acac-CH₃), 1.63 (2H, q, J = 7.4 Hz, acac-CH₂-CH₂-CH₂), 1.69-1.91 (2H, m, acac-CH₂-CH₂), 4.83 (2H, m, -CH=CH₂), 5.27 (1H, s, CO-CH-Co), 5.51 (1H, m, -CH=CH₂), 6.33 (1H, dd, J = 7.6, 0.7 Hz, phenyl-H), 6.36 (1H, dd, J = 7.6, 0.8 Hz, phenyl-H), 6.75 (2H, m, phenyl-H), 6.86 (2H, m, phenyl-H), 7.50 (4H, m, benzoyl-H), 7.56-7.69 (4H, m, pyridyl-H, benzoyl-H), 7.81 (2H, d, J = 7.2 Hz, benzoyl-H), 7.98 (2H, t, J = 7.9 Hz, pyridyl-H), 8.27 (2H, m, pyridyl-H), 8.87 (2H, m, pyridyl-H). ¹³C NMR (125 MHz, CDCl₃) 25.5, 28.3, 32.5, 40.4, 76.8, 99.8, 114.3, 117.6, 117.7, 120.8 (2C), 125.2,
Sample fabrication: Nanowire gratings were fabricated by electron beam lithography (Vistec EBPG 5000 plus ES, 10 nA, 100 keV, 450 \( \mu \)C/cm\(^2\)) on a glass substrate using a double layer positive resist consisting of 50 nm poly(methyl methacrylate) (Micro-Chem, 950k A4) on top of 110 nm of methyl methacrylate (Micro-Chem, MMA(8.5) MAA EL6).\(^{[26]}\) A 20 nm layer of chromium was deposited on top of the resist in order to provide a charge dissipation layer during the electron beam lithography step. After exposure, the chromium layer was chemically etched and the patterns on the positive resist layer were developed with a 1:3 methyl isobutyl ketone/isopropanol solution for 60 s, rinsed by ultrasonication with isopropanol, and dried with a nitrogen gun. Using electron beam evaporation, 2 nm of titanium, then 30 nm of silver were deposited at a rate of \( \sim 0.5 \) Å sec\(^{-1}\). A lift-off step with acetone completed the nanofabrication procedure. The structures were characterized by scanning electron microscopy (FEI, Nova NanoSEM 430) and had lateral extent of 100 \( \mu \)m x 100 \( \mu \)m. PMMA solutions (950k, 1% by weight) containing complex 1 (100 \( \mu \)M) were spin coated (Laurell, WS-400B-8NPP/LITE, 3000 rpm for 60 sec) directly onto the fabricated nanostructures. Resulting film thickness was measured with a profilometer (Veeco, DEKTAK 6) and the films were subsequently dried in a vacuum oven (ambient temperature). A silver film of 150 nm was later evaporated on the resulting structures.

Simulations: A Rigorous coupled-wave approximation (RCWA), as implemented in the MATLAB package RETICOLO,\(^{[13]}\) was employed to calculate the optical reflection spectra of the nanocavities and their electromagnetic field distributions. The refractive index data for
silver was obtained from a previously published report,[27] whereas the refractive index of the
doped polymer layer was obtained from a Cauchy fit to spectroscopic ellipsometry data (Figure
S3)

**Spectroscopy of metal complexes in solution.** All photophysical measurements were performed
in anisole in screw-capped quartz cuvettes. Absorbance spectra were obtained on a UV-
Vis/NIR spectrophotometer (Perkin Elmer Lambda 1050). The sample was measured at
different concentrations (5-25 μM) and extinction coefficients calculated using the Beer-
Lambert law. An emission spectrum was obtained using a fluorescence spectrophotometer
(Perkin Elmer LS-50) with the emission and excitation spectral bandwidth set to 10 nm. The
samples was measured at a concentration of 20 μM and the excitation wavelength set to 450
nm.

**Spectroscopy of thin films and nanostructures.** (i) Absorption/Reflectance: Samples were
illuminated through a 4x microscope objective (Numerical aperture 0.13) with unpolarized
white light. The reflected light was passed through a polarizer and directed to an imaging
spectrograph (PI Acton SP2300) equipped with a CCD (Princeton Instruments PIXIS 1024).
Reference measurements were made with respect to a silver mirror with known reflectance
over the visible spectrum (Thorlabs BB1-E02). The transmission (T) of light through the
nanocavities was independently measured to be well below the detection limit of our
instrument.[28] The absorbance (A) was therefore calculated (following conservation of energy)
as A = 1-R, where R is the measured reflectance (normalized with respect to the reference silver
mirror). (ii) Steady state emission: Light from a diode-pumped solid state continuous-wave 478
nm laser was directed to the samples through the microscope objective and the emission spectra
were acquired with the spectrograph. (iii) Time-correlated single photon counting: collimated
white light from a supercontinuum source (10 MHz repetition rate, Fianium, SC-450-pp) was spectrally filtered with a series of band-pass filters (Fianium Super-K) and directed through a filter cube (comprising a bandpass excitation filter 531/22, a dichroic mirror 532DM and a long pass filter 532 Razor edge, Semrock), to the back aperture of a microscope objective (20x/0.4 NA). The emission was sent to an avalanche photodiode (APD, Perkin Elmer). The luminescence decay curves were obtained with a PicoQuant TimeHarp 200.  

(iv) Momentum-space imaging: The 478 nm laser light was directed at the samples with an oil-immersion objective (100x/1.3 NA). Power measured at the back of the objective (900 nW) and the back-focal plane of the objective was imaged onto the entrance slit of the spectrograph with a Bertrand lens (50 mm focal length). Spectral measurements were carried out by placing a slit and using a polarizer (Thorlabs LPVISB050-MP2).

Crystallography: Intensity data was collected on a CCD diffractometer using Cu-Kα radiation (graphite crystal monochromator λ = 1.54184 Å). The temperature during data collection was maintained at 130.0(1) K. The structure was solved by direct methods and difference Fourier synthesis.[29] Thermal ellipsoid plots were generated using the program ORTEP-3[30] integrated within the WINGX[31] suite of programs.  

Crystal data for 1. IrC₄₅H₃₇N₂O₄, M = 861.96, T = 130.0(1) K, λ = 1.54184 Å, Orthorhombic, space group Pca2₁: a = 17.4028(2), b = 26.1446(3), c = 15.7845(2) Å, α = β = γ =90°, V = 7181.78(15) Å³, Z = 8, Dc = 1.594 Mg M⁻³ μ(Cu-Kα) = 7.578 mm⁻¹, F(000) = 3440, crystal size 0.35 x 0.09 x 0.04 mm. 55746 reflections measured, 12212 independent reflections (R_{int} = 0.043) the final R = 0.0381 [I > 2σ(I), 11200 data] and wR(F2) = 0.1029 (all data) GOOF = 1.043.
[CCDC 1516050 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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The acetylacetonate ancillary ligand was modified to incorporate a short alkyl chain ending with an alkene to allow for future installation of extra functionality.


Figure 1. Photophysics of an iridium(III) organometallic complex. A Representative Jablonski diagram of triplet-based emission in cyclometalated iridium(III) complexes. LC: ligand centered, MLCT: metal-ligand charge transfer, IC: internal conversion, ISC: inter-system crossing. B Representation of complex 1. C ORTEP representation of 1 with ellipsoids at 50% probability. Disorder around alkene in ligand and hydrogen atoms except for H85 omitted for clarity. D Solution (anisole, 20 μM) absorption and emission spectra of 1, $\lambda_{ex} = 450$ nm.
Figure 2. Metamaterial Nanocavities. A Schematic representation (not to scale) of the fabricated metamaterial. B Scanning electron micrograph of the top-view of the silver nanowires, sample is of width 160 nm. C Normalized absorption spectra (1-R) of nanocavities vs nanowire width illuminated with linearly polarized broadband light oriented perpendicular to the nanowire long axis.
Figure 3. Emission properties of fabricated metamaterials. Steady-state emission spectra of nanocavities of different nanowire widths presented as individual spectra (A) and a 2D plot representation (B). Wire widths are stated in nanometers as indicated in legend, λ_ex = 533 nm. The shaded area in A corresponds to the emission of 1 in a PMMA control film on glass. C Photo of luminescent enhancement of complex 1 in nanocavity of metamaterial structure. D Emission kinetics for 1 dispersed in PMMA on either a glass substrate or deposited on nanocavities of nanowire thicknesses as indicated in legend.32 E Distribution of the decay rates fitted according to stretched exponentials from the data in D. Emitters optimally situated in the nanocavity are expected to account for the decay rates > k_max. F The relative decay rates (k_max from nanocavities and k_o from 1 on glass) vs nanowire width.
Figure 4. Nanocavity modes. A Measured absorption spectrum (blue line) of a metamaterial structure (where nanowire width = 130 nm) along with the results of a numerical simulation (orange line). The dominant optical modes at $\lambda = 544$ and 594 nm are highlighted. B Electromagnetic maps showing intensity of the two dominant modes relative to the metamaterial configuration in space. The quadrupolar mode is characterized by strong confinement of the magnetic field in the gap region. The dipolar mode exhibits strong confinement of the electric field ($x$ and $z$ components) on the region of space away from the gap. The white lines indicate the boundaries of the mirror and nanowire. TM transverse magnetic polarization.
Figure 5. Wavelength- and momentum-resolved spectroscopy. Back-focal plane image of the emission of a thin PMMA film containing 1 with $s$- (A) and $p$-polarization (D), $\lambda_{ex} = 478$ nm. Momentum-wavelength spectra for $s$- (B) and $p$-polarization (E). Momentum cross-sections at $\lambda_{em} = 623$ nm (C) and 677 nm (F). Following a previous report, a theoretical analysis of these cross-sections (black lines) reveal that the emission at $\lambda_{em} = 623$ nm has a strong magnetic dipole character, whereas the one at $\lambda_{em} = 677$ nm has a strong electric dipole (ED) character.
The nanocavity of a novel metamaterial that supports several optical modes enables increased luminescence from an organometallic iridium(III) complex, a hybrid magnetic/electric dipole emitter. The mechanism for the strong modification to the emission spectrum and spontaneous decay rates is rationalized through analysis of momentum- and time-resolved spectroscopy experiments.

Plasmonics, photoluminescent enhancement, organometallic complexes, Purcell effect, metamaterial


Luminescence of a transition metal complex inside a metamaterial nanocavity
Supporting Information

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S1 Complex 1 emission in PMMA thin film

Thin films of 1 were spin-coated on glass microscope slides. Emission spectra were obtained using a fluorescence spectrophotometer (Perkin Elmer LS-50) with the emission and excitation spectral bandwidth set to 10 nm and excitation wavelength set to 450 nm.

Figure S1. Emission of complex 1 in solution (black) and in a doped PMMA film (red).
S2 Fit of film thickness

A Rigorous coupled-wave approximation (RCWA), as implemented in the MATLAB package RETICOLO,\cite{1} was employed to calculate the optical reflection spectra of the nanocavities and their electromagnetic field distributions. The refractive index data for silver was obtained from a previously published report,\cite{2} whereas the refractive index of the doped polymer layer was obtained from a Cauchy fit to spectroscopic ellipsometry data.

**Figure S2.** Absorbance of metamaterial sample where nanowire width = 110 nm (blue shaded, exp in legend) compared simulations with different distances between the wires and the mirror, as indicated in the legend (units in nm).
S3 Spectroscopic Ellipsometry

Thin films of 1 were spin-coated on silicon substrates. Spectroscopic ellipsometry measurements were carried out using a J.A. Woollam M-2000DI instrument. The data, along with a Cauchy model for the doped PMMA film are shown in Figure S2. The parameters obtained from analysis of these data (MSE = 3.318) are: Thickness of doped PMMA layer = (15.40 ± 0.063) nm, Cauchy parameters: $A = (1.468 ± 0.0057)$, $B = (0.00912 ± 0.00040605)$, $C = (-7.8752E-05 ± 1.3123E-05)$.

Figure S3. Spectroscopic Ellipsometry of PMMA films doped with complex 1. A: $\Psi$ and $\Delta$ along with fits (black dashed lines) to a Cauchy model for the doped-polymer layer. B: The Cauchy model results in a complex refractive shown in this panel.
S4 Simulated absorption of metamaterial nanocavities

The results of numerical simulations of the metamaterial nanocavity for the cases of normally incident light and light incident at 5 degrees with respect to the normal of the surface of the samples are shown in Figure S3 and agree qualitatively with the measured spectra. These simulations also reveal that the third absorption band observed experimentally (nanowire widths > 200 nm) is a consequence of the illumination of the sample with an angular spread that originates from the finite numerical aperture of the lenses utilised in the experiment. A Rigorous coupled-wave approximation (RCWA), as implemented in the Matlab package RETICOLO\textsuperscript{[1]} was employed to calculate the optical reflection spectra of the nano-cavities.

**Figure S4.** Simulated absorption spectra ($A_p = \text{absorbance for p-polarised light}$) of nanocavities vs nanowire width when excited by either normally-incident light (A) or light incident at 5 degrees with respect to the normal of the sample (B).
S5 Emission decay curves

Time-correlated single photon counting: collimated white light from a supercontinuum source (10 MHz repetition rate, Fianium, SC-450-pp) was spectrally filtered with a series of band-pass filters (Fianium Super-K) and directed through a filter cube (comprising a bandpass excitation filter 531/22, a dichroic mirror 532DM and a long pass filter 532 Razor edge, Semrock), to the back aperture of a microscope objective (20x/0.4 NA). The emission was sent to an avalanche photodiode (APD, Perkin Elmer). The luminescence decay curves were obtained with a PicoQuant TimeHarp 200.

Figure S5 Representative set of the measured decay curves for nanowire-on-mirror metamaterials with wires of different widths, as indicated in the legends (units are nm). For comparison, we also show a reference measurement on a region of the samples without nanowires, indicated in the legend with “mirror”.
Radiation patterns were calculated using a 2D simulation of the metamaterial. In this dimensionality the point dipole “emitter” is in actuality a line charge, a valid approximation due to the extent of the metamaterial relative to the emitter. This permitted a significantly increased simulation region to ensure the reliable calculation of the far-field pattern.

Figure S6.1. Calculated emission radiation patterns for a nanowire grating of width 100 nm and an emission wavelength of 600 nm (blue) and 678 nm (green). A Control dipole on glass with air as a superstrate. Emission radiation pattern for an electric dipole with an orientation perpendicular to the long axis of the metal nanowires (see diagram of Figure 2), vertically located half-way between the mirror and the nanowire but horizontally located: B in the middle of the nanowire, C on the edge of the nanowire, and D 50nm away from the edge of the nanowire. The shaded area represents the collection angle of the microscope objective.

The rf module of COMSOL Multiphysics was used to investigate the metamaterial’s influence on the emission of complex 1. A full-field 3D simulation was performed using either a magnetic/electric dipole as the excitation source using 3 periods of the grating elements. The emission of the dipole was integrated over the entire volume and by only the region defined by the collection objective for comparison. The identical simulation region was used with all volumes as vacuum (n=1), and the emission of the dipole in this volume was used to normalise that of the dipole in the periodic metamaterial to calculate the Purcell enhancement factor. Published materials data was used for the silver,[2] while n = 1.45 was used for the glass substrate and PMMA. The emitting dipole was placed 4 nm above the mirror surface, with its position translated perpendicularly to the grating elements. This position was selected as the midpoint between the mirror and grating element (8 nm separation).
Figure S6.2. Calculated average purcell factor ([PF_x+PF_y+PF_z]/3) for both the magnetic dipole at $\lambda = 600$ nm (A) and electric dipole at $\lambda = 678$ nm (B).
S7 Momentum–resolved spectroscopy

The analysis of the data shown in Figure 5 was carried out using the model described by Taminiau et al.[3] Briefly, the measured number of photon counts $N$ in Figures 1(G&H) were decomposed into contributions of electric dipole (ED) and magnetic dipole (MD) according to:

$$N^s,p(\lambda) = C [A_{ED}(\lambda)\rho_{ED}^s(\lambda, k||) + A_{MD}(\lambda)\rho_{MD}^s(\lambda, k||)]$$

where $C$ is an instrument–dependent parameter, independent of wavelength and momentum, which is determined by the collection/excitation efficiency of the experimental apparatus, $A_{ED}(\lambda)$ and $A_{MD}(\lambda)$ the spontaneous emission rates (Einstein coefficients) for ED and MD emitters and $\rho_{ED}^s(\lambda, k||)$ and $\rho_{MD}^s(\lambda, k||)$ are the normalised density of optical states in the multi–layer thin film structure. This structure is idealised to consist of three uniform and homogeneous layers (air/doped–PMMA film/glass substrate) which define the direction of the wave-vector into components parallel ($k||$) and perpendicular ($k_\perp$) with respect to the plane of light incidence.

Explicit expressions for these density of states are found in equations S8–S14 of Taminiau et al.[3] We have assumed a refractive index of 1.45 for the glass substrate and we have employed the data of Figure S3 for the one corresponding to the doped PMMA layer (including the thickness).

A non–linear least squares fit of cross-sections of the data of Figure 5B, E leads to the decomposition shown in Figure S4 which shows the evolution of the MD and ED character of the emission of 1. The same analysis leads to the black lines shown in Figure 5C, F. These fits were performed at each wavelength for both polarisations and over a momentum range of $|k||/k_o| \leq 0.96$ ($k_o$ is the incident wave-vector).

Figure S7. Decomposition of complex 1’s emission spectrum into ED and MD components
S8 References


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