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Breaking the Selection Rules of Spin-Forbidden Molecular Absorption in Plasmonic Nanocavities

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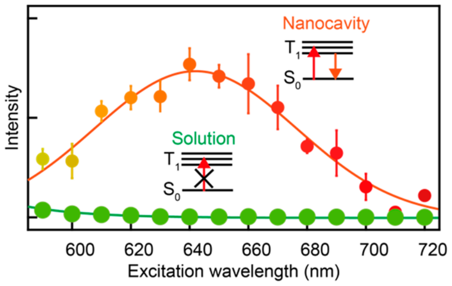
ABSTRACT: Controlling absorption and emission of organic molecules is crucial for efficient light-emitting diodes, organic solar cells, and single-molecule spectroscopy. Here, a new molecular absorption is activated inside a gold plasmonic nanocavity and found to break selection rules via spin−orbit coupling. Photoluminescence excitation scans reveal absorption from a normally spin-forbidden singlet to triplet state transition, while drastically enhancing the emission rate by several thousand fold. The experimental results are supported by density functional theory, revealing the manipulation of molecular absorption by nearby metallic gold atoms.



KEYWORDS: *spin mixing, plasmonic nanocavity, resonant Raman, photoluminescence, symmetry breaking*

Selection rules govern absorption and emission of light in atomic and molecular systems,[1] that stem from quantum mechanical symmetries dictating which atomic, electronic or vibrational transitions are allowed or forbidden.[1,2] Allowed transitions are desired for lasers and light emitting diodes, but forbidden transitions are typically inaccessible to optical excitation. Mechanisms that break these selection rules to allow forbidden transitions yield novel and efficient devices.[3−6]

Molecular light emission is typically limited to an internal quantum yield of only 25% through the singlet−singlet transitions, while 75% of pathways are spin forbidden singlet−triplet transitions (Figure 1a). To allow these forbidden transitions, spin−orbit coupling is induced by interacting the angular motion of electron spins with the magnetic dipole created by local massive atomic nuclei.[1,7] This is achieved in organo-transition-metal complexes[8−11] via internal heavy atom effects when a metal-to-ligand charge transfer state is formed, allowing intersystem crossing from the excited singlet state S_1 to excited triplet state T_1 (Figure 1b). External heavy-atom effects induce spin mixing by placing heavy atoms near an emitter without actual bond formation.[7] Heavy atom effects have been used to enhance emission rates,[12−14] thermally and optically activate "delayed" fluorescence,[15−18] reversibly control emission,[19−21] and activate light-emitting diodes (LEDs).[8,22,23] These approaches enhance triplet emission $T_1 \rightarrow S_0$ through exciting $S_0 \rightarrow S_1$, then followed by intersystem crossing $S_1 \rightarrow T_1$ (Figure 1b) in bulk ensembles of molecules. Due to weak spin−orbit coupling, directly accessing such forbidden singlet−triplet transition ($S_0 \rightarrow T_1$) has thus been inaccessible at the molecular level. Manipulating spin mixing to activate absorption and emission pathways at the nanoscale has, however, promising implications for nano-LEDs,[24] nanolasers,[25] nanosolar cells,[26] single molecule spectroscopy,[27,28] and opto-magnetism,[29,30] as well as single-photon quantum emitters.[31,32]

Here we activate a direct absorption from $S_0 \rightarrow T_1$ (a forbidden transition) using a nanophotonic construct that induces spin mixing to allow absorption from the forbidden transition (Figure 1c). Instead of organo-metallic complexes, we employ a nanoparticle-on-mirror (NPoM) plasmonic nanocavity that achieves an extreme optical field confinement below 25 nm[3],[33] with fields enhanced up to 300 times in these deeply subwavelength nanogaps (Figure 1d,e). The NPoM nanocavities each consist of an 80 nm Au nanoparticle on a Au film spaced by a monolayer of the molecular emitter Rubpy [tris(2,2′-bipyridine) ruthenium(II) hexafluorophosphate, typically denoted [Ru(bpy)_3]^{2+}], with ∼30 strongly emitting molecules under each Au nanoparticle[34] (for sample preparation, see Supporting Information, 1). Rubpy is a widely studied triplet emitter with a quantum yield of <3%,[8] absorbing in the ultraviolet ∼450 nm and has a large Stokes shift with a phosphorescence peak at 620 nm (Figure 1f). The tail of this broad emission is coupled here to the NPoM cavities which have a fundamental plasmon resonance in the near-infrared at

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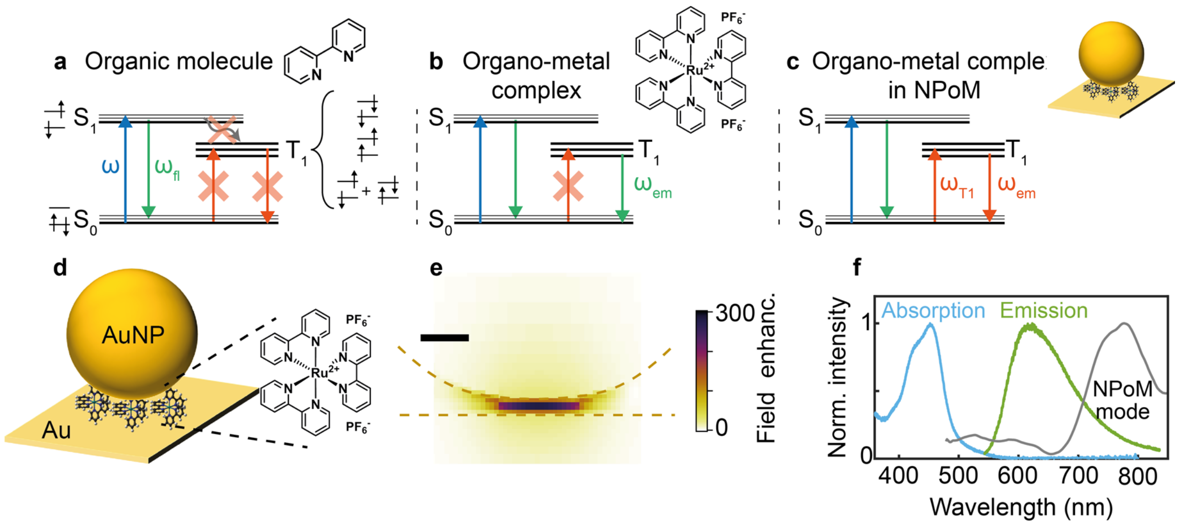

Figure 1. (a−c) Energy levels of allowed and forbidden transitions in molecular emitters embedded in different geometries, with (a) electron spin configurations of singlet S_0, S_1 (antiparallel electron spin pairs) and triplet T_1 (unpaired parallel electron spins) states. Excitation, fluorescence, emission, and triplet energies are denoted \omega, \omega_fl, \omega_em, and \omega_T1.(d) Nanoparticle-on-mirror (NPoM) construct with Rubpy spacer. (e) Finite-difference time domain simulation of field enhancement in the NPoM gap at λ = 750 nm. Dashed lines show boundaries of Au nanoparticle and Au film, scale bar is 10 nm. (f) Absorption (blue) and emission (green) curves of Rubpy in solution with 520 nm excitation. Gray curve is darkfield scattering showing dominant coupled mode of a NPoM.

830 ± 30 nm, set by the Rubpy monolayer height which creates a gap size ∼ 1 nm.[35]

■ RESULTS AND DISCUSSION

A single nanocavity is first irradiated at the forbidden transition $S_0 \rightarrow T_1$ with an excitation wavelength of 640 nm, close to the phosphorescence peak using 1 ps pulses (for experimental setup, see SI, 2). With average power of 1 μW on individual NPoMs, a broad spectral emission is seen with a maximum at ∼700 nm and a broad tail beyond 800 nm (Figure 2a). The broad emission has additional sharp peaks attributed to surface-enhanced resonant Raman scattering (SERRS). This emission is completely absent for Rubpy in solution (80 μM, Figure 2a, solid green) and for the Au mirror away from the NPoM (due to quenching). To check the nature of this emission from NPoMs, the total emission intensity is found to be linearly proportional to input power (Figure 2b). This confirms the emission comes from one-photon excitation rather than multiphoton excitation or other nonlinear processes, and no saturation is observed. Time-correlated single photon counting (TCSPC) gives the emission lifetime as τ_{rad} = 520 ± 10 ns in bulk, which is drastically shortened to <0.2 ± 0.1 ns in NPoMs (Figure 2c). While this NPoM Rubpy measurement is limited by the TCSPC instrument response, it shows over 3 orders of magnitude reduction in spontaneous lifetime due to the high optical density of states in these nanocavities. Finite-difference time domain (FDTD) simulations reveal that there is a Purcell factor of ∼10^6 for these 1 nm nanogaps, suggesting lifetimes ∼500 fs (for FDTD results, see SI, Figure S4). Moreover, the emission quantum yield increases more than 10-fold to 35% for Rubpy due to the resulting increase in radiative decay rate inside the nanocavity. Thus, there is an observable emission from NPoMs instead of quenching (as occurs for emitters close to an isolated single plasmonic nanoparticle[36,37]). Over long timescans of >1000 s at 0.1 μW excitation, we observe no significant reduction in intensity which implies that these emitters are stable in NPoMs and there is no observable bleaching (SI, Figure S6).

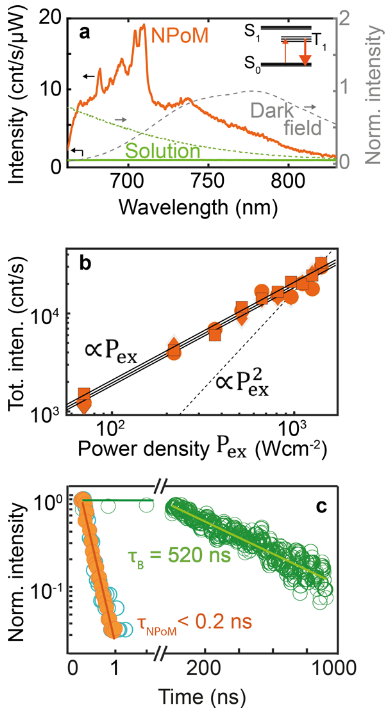

Figure 2. (a) Emission from Rubpy in NPoM gaps (orange) and in solution (solid green) with λ_{ex} = 640 nm excitation. For comparison, emission from solution with 520 nm excitation (dashed green) and darkfield scattering of NPoM (dashed gray) are shown. Inset gives energy levels of excitation and emission. (b) Power dependence of emission. (c) Time-resolved emission decay in NPoM (orange), and in solution (green), with instrumental response (blue).

To further probe the forbidden $S_0 \rightarrow T_1$ transition, photoluminescence excitation (PLE) pump wavelength scans are performed from λ_{ex} = 590−720 nm. At each λ_{ex}, the average laser power on the sample is set to 1 μW, precalibrated to account for power variations from wavelength-dependent transmission through the optical beamline. A consistent

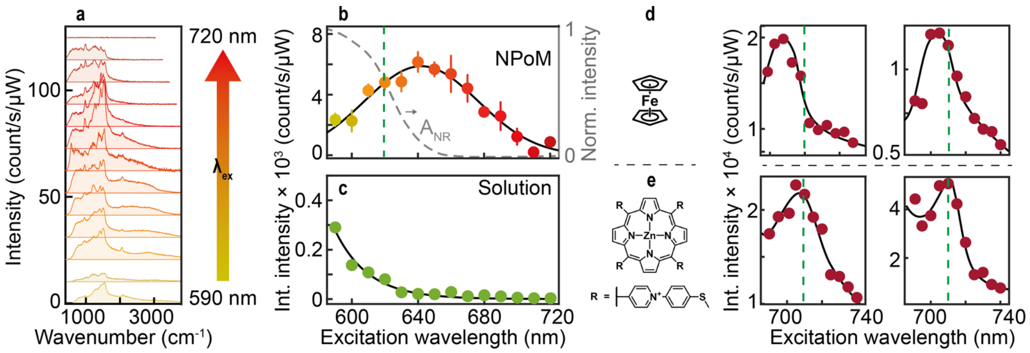

Figure 3. (a) Photoluminescence excitation (PLE) scan on singlet S_0 to triplet T_1 transition. (a) Emission spectra of Rubpy in NPoM vs energy shift from the pump for increasing λ_{ex} = 590−720 nm in 10 nm steps. (b, c) Integrated emission (PLE) spectra for NPoM vs Rubpy in solution, black curves are Gaussian fits. In (b), the gray dashed curve A_{NR} is the predicted absorption spectrum from near-field enhancement in the NPoM gap and the dashed vertical line is the expected triplet emission energy. (d, e) Chemical structures (left panel) of ferrocene and Zn porphyrin used as NPoM spacers to obtain the integrated emission (PLE) from two NPoMs for each (middle, right panels). Dashed vertical lines mark expected triplet state energies.

broad emission between 700 and 800 nm with additional SERRS peaks is seen for all λ_{ex} (Figure 3a), increasing and then decreasing as λ_{ex} is increased. This is unaffected when using the scattering resonance to normalize for NPoM outcoupling efficiencies (see SI, Figure S7). The resonant absorption in PLE from the integrated emission is maximum at 642 ± 2 nm and identical for different NPoMs (Figure 3b, average over 3 NPoMs), confirming it arises from the molecules in the gap. Note no emission is seen without Rubpy in the plasmonic gap. By contrast, the PLE of Rubpy in solution decreases steadily with λ_{ex} (Figure 3c), mapping the tail of the absorption line (Figure 1f). To further confirm the general nature of our observations, we show similar results for spacers of two other organo-metallic complexes, ferrocene and a Zn porphyrin, which also give a new excitation resonance at their $S_0 \rightarrow T_1$ transitions (Figure 3d,e and SI, 8).

In order to understand the new absorption line shape, we perform time-dependent density functional theory (TDDFT) on Au_2-Rubpy-Au_2 to model the NPoM environment and calculate the absorption spectra for different gap sizes d (Figure 4a, for TDDFT details, see SI, 10). The molecular orientation in Figure 4a is verified by structure optimization in the presence of an Au film and additional molecular orientations are also investigated. A new absorption peak appears with Au atoms close to the molecule that is absent in solution (Figure 4b) and this agrees with our measurements in Figure 3b,c, confirming that NPoMs switch on a new absorption state. The induced absorption is strongest at small gap sizes and decreases exponentially at larger d (Figure 4c). This dependence results from the atomic electron densities that decrease exponentially with distance and gives an exponential falloff of overlap between molecular and Au orbitals. By comparing the absorption curves, we find that the oscillator strength is enhanced by greater than 50-fold in NPoMs compared to solution. The shift of the absorption peak to higher energies at small d is due to an increased interaction of the molecule with the gold atoms, which results in mixed transitions at energies between that of the bright molecular transitions and gold transitions. The transitions responsible for this increase are mixed singlet−triplet transitions from electron exchange between the Au and Rubpy induced by spin−orbit coupling. For instance, at d = 9 Å, the band around 580 nm is built from four singlet transitions where the electron is excited from Ru and Au d orbitals and bpy π orbitals to Au sp and bpy π^* orbitals. At d = 14 Å, mixing of molecular and gold excitations is still noticeable, although the weight of transitions involving the molecule are smaller than at closer d (for more details, see SI, 10). The subnm proximity of Au atoms in both facets to the emitters induces spin−orbit coupling in the molecules, thus, modifying the electronic transitions and

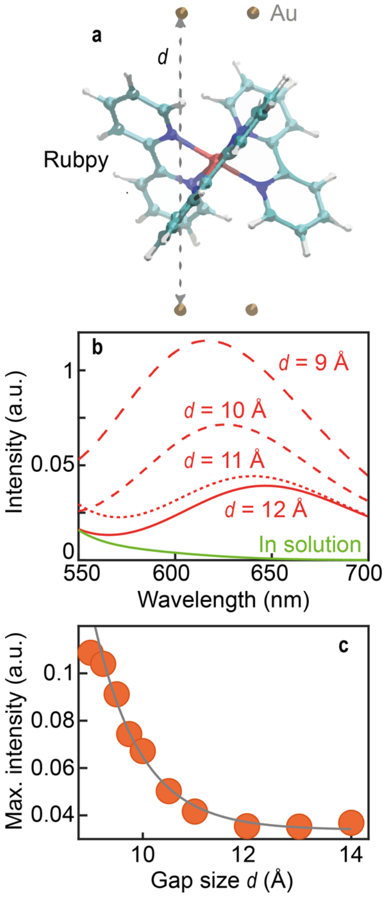

Figure 4. Time-dependent density functional theory simulation of the absorption of Rubpy. (a) Au_2-Rubpy-Au_2 system used for modeling the effect of the surrounding Au facets, at different gap sizes d. (b) Calculated absorption spectrum for solvated Rubpy and Au_2-Rubpy-Au_2 at different gap sizes d. (c) Maximum absorption intensity vs gap size d extracted from (b); gray curve is an exponential fit.

allowing direct absorption to the forbidden triplet state. At the same time, the nanocavity geometry gives efficient outcoupling without plasmonic quenching of the emission at such subnm distances.

Previous theoretical studies proposed that a high field gradient in a nanocavity can induce *ac* magnetic fields that break symmetry, allowing excitation of forbidden transitions.[30,38−43] To verify if this mechanism plays a role in our observations, we calculate the spatial distribution of the magnetic field component in NPoM gaps using FDTD simulations. The magnetic field is highest at the facet edges under the nanoparticle, but zero around the center of the gap, where molecules with the highest out-coupled emission are located (SI, Figure S5). This implies that the influence of the *ac* magnetic field on the bright molecules is minimal and thus the high field gradient effect is not responsible for the observed absorption peak. Moreover, enhanced near-field absorption (A_{NR}), which is calculated as the product of the absorption of Rubpy in solution and the near-field enhancement spectrum cannot explain the observed peak. The calculated A_{NR} deviates significantly from the observed absorption curve (gray dashed curve, Figure 3b). Furthermore, the charge density difference between the molecule and Au atoms reveals a dipole form of interaction rather than multipole interactions (Figure S13). We thus identify the external heavy atom effect as the mechanism that induces the new absorption transition in the molecules.

Because of its spectral position (Figure 3b), the observed emission at the $S_0 \rightarrow T_1$ excitation is attributed to mixed single-triplet electronic transitions that produce photoluminescence (PL) and resonant Raman (SERRS). For the bare molecule, the selection rules make this transition forbidden, which is why phosphorescence with a long lifetime is observed in solution (Figure 2c), through weak spin−orbit coupling. What is unexpected is the transformation from weak phosphorescence to strong photoluminescence, while at the same time as a new strong absorption line is observed at the triplet state, seen here at the few molecule level. For $S_0 \rightarrow T_1$ transitions to occur, a mechanism is required to break the electronic selection rule through spin mixing. We note that both PL and resonant Raman (or SERRS) require this same spin-mixing mechanism[44,45] to elicit the resonant lineshapes observed. Thus, the presence of SERRS in our observation is a further confirmation that selection rules have been broken.

CONCLUSIONS

In summary, we observe a strong singlet−triplet absorption and emission for molecules confined in these plasmonic nanocavities. The field enhancement inside the nanogaps speeds up the phosphorescence through the Purcell factor of several thousand when the mode volumes are so small compared to λ^3.[33,46] At the same time, the nanocavity induces absorption at singlet−triplet transitions by breaking the electronic selection rules via the sub-nm proximity of Au atoms. Typically, bulk metals so close to molecules quench their emission completely, but the NPoM system is different in that it enhances radiative emission. As a result, the effect is seen for the first time with metallic facets. The resulting effect is to convert the phosphorescent triplet emitter into an ultrafast (<1 ps) bright luminescent source (quantum yield ~ 35%). Since NPoMs allow spin-forbidden transitions to become optically accessible, this opens development of more efficient organic light-emitting diodes and solar cells, optically detected magnetic resonance, as well as directly accessing triplet states for fundamental spin interactions in quantum chemistry and nanophotonics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsphotonics.0c00732. Source data can be found at https://doi.org/10.17863/CAM.56210.

Supplementary Note 1: Sample preparation; Supplementary Note 2: Optical setup; Supplementary Note 3: CW measurements; Supplementary Note 4: finite-difference time domain (FDTD) simulations; Supplementary Note 5: Magnetic field component in NPoM; Supplementary Note 6: Stability of emission; Supplementary Note 7: Effect of darkfield scattering; Supplementary Note 8: Energy levels of ferrocene and Zn porphyrin; Supplementary Note 9: Raman spectrum; Supplementary Note 10: Simulation of the absorption spectrum of Rubpy (PDF)

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Notes

The authors declare no competing financial interest.

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