Electrical Control of Lifetime-Limited Quantum Emitters Using 2D **Materials**

Kevin G. Schädler,[†] Carlotta Ciancico,[†] Sofia Pazzagli,^{‡,§} Pietro Lombardi,[‡] Adrian Bachtold,[†][©] Costanza Toninelli,^{‡,||}[©] Antoine Reserbat-Plantey,[†] and Frank H. L. Koppens^{*,†,⊥}[©]

[†]ICFO - Institut de Ciencies Fotoniques, The Barcelona Institute of Science and Technology, 08860 Castelldefels, Spain [‡]LENS and CNR-INO, Via Nello Carrara 1, 50019 Sesto Fiorentino, Italy

[§]Dipartimento di Fisica ed Astronomia, Università di Firenze, Via Sansone 1, 50019 Sesto Fiorentino, Italy

^{II}QSTAR, Largo Fermi 2, 50125 Firenze, Italy

¹ICREA - Institució Catalana de Recerça i Estudis Avancats, 08010 Barcelona, Spain

Supporting Information



ABSTRACT: Solid-state quantum emitters are a mainstay of quantum nanophotonics as integrated single-photon sources (SPS) and optical nanoprobes. Integrating such emitters with active nanophotonic elements is desirable in order to attain efficient control of their optical properties, but it typically degrades the photostability of the emitter itself. Here, we demonstrate a tunable hybrid device that integrates state of the art lifetime-limited single emitters (line width ~40 MHz) and 2D materials at subwavelength separation without degradation of the emission properties. Our device's nanoscale dimensions enable ultrabroadband tuning (tuning range >400 GHz) and fast modulation (frequency ~100 MHz) of the emission energy, which renders it an integrated, ultracompact tunable SPS. Conversely, this offers a novel approach to optical sensing of 2D material properties using a single emitter as a nanoprobe.

KEYWORDS: Single molecules, 2D materials, electrical control, single photon source, Stark effect, lifetime-limited line width

ybrid nanophotonic systems blend the strengths of distinct photonic elements to strongly enhance lightmatter interactions¹ in integrated photonic circuits. In these systems, narrow-line width quantum light emitters play a key role as single-photon sources (SPS) which interact with their nanoscale environment.^{2,3} Controlling these interactions provides versatile SPS tuning⁴ required for coupling quantum resources.⁵⁻⁷ Integrating nanoscale light emitters with twodimensional (2D) materials is motivated by the rich physics of near-field interactions⁸ and new hybrid light-matter states.^{9,10} This approach unites integrated solid-state SPS such as nitrogen vacancy centers,¹¹ quantum dots,¹² and single molecules¹³ with the diverse optoelectronic properties of 2D materials that facilitate emitting,14 controlling,15-17 and detecting¹⁸ light at the nanoscale. In such hybrid devices, quantum emitters can be integrated at subwavelength separation to the 2D interface to achieve efficient near-field coupling,⁸ which modifies the emitter's radiative decay rate¹⁹⁻²¹ or transition energy.^{22,23} Recent experimental studies integrated 2D materials with ensembles of broadband emitters to demonstrate $electrical^{24-26}$ and $electromechanical^{27}$ tuning of the decay rate by controlling nonradiative energy transfer (nRET) or the energy flow to confined electromagnetic modes such as 2D polaritons.^{26,28} Therefore, hybrids of 2D materials and SPS have the potential for in situ control of the conversion and channelling of single photons at the nanoscale. So far, these studies have been limited to ensembles and broad line width emitters. Integrating bright and narrow quantum emitters in such systems paves the way toward a tunable quantum light-matter interface, which is an essential ingredient for integrated quantum networks.

Here, we demonstrate hybrid integration of 2D materials (semimetallic graphene or semiconducting MoS_2) with single, lifetime-limited quantum emitters in nanocrystals to provide active emission control. Using the 2D materials as transparent electrodes, we show broadband Stark tuning of the emission energy over 40 000 times the emitter line width and fast modulation of the emitter's optical resonance on the time scale

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Figure 1. Single molecules integrated with 2D materials. (a) Hybrid device schematic. Atomically thin layers of graphene and MoS₂ cover fluorescent molecules embedded in a PVA film ($h_{PVA} = 300 \text{ nm}$) on SiO₂ ($h_{SiO2} = 285 \text{ nm}$). Single molecules are resonantly excited (inset) and their red-shifted fluorescence detected with a single-photon counting module (SPCM). Electric fields are controlled by applying DC (V_g) and AC (δV_g) potentials to the Si⁺⁺ backgate. (b) Top to bottom: optical micrograph, AFM topography, and DBT emission map for MoS₂ (left column) and bilayer graphene (right column) devices. White dashed lines outline the flakes. Scale bars are 20 μ m. (c) Top panel: fluorescence excitation spectrum of an ensemble of single molecules in an uncovered nanocrystal at 3 K. Bottom panel: detail of two emission peaks with Lorentzian line shape (solid line), the narrower peak shows a fwhm of 43 ± 7 MHz. (d) Antibunching measurement for resonant excitation of a single peak as shown in part c. The solid line is a fit to the data using a second-order correlation function.

of its radiative lifetime. Such tuning can mitigate inhomogeneous broadening in solid-state environments to enable resonant and synchronized interaction between distinct quantum systems⁵ and allows for controlled coupling of narrowband quantum emitters to broadband nanophotonic circuitry.²⁹ Our approach is particularly suited for making integrated devices: although the 2D material is just tens of nanometers from the quantum emitter, we observe only weak emission line width broadening and spectral diffusion. In contrast, emitters close to bulk transparent electrodes³⁰ such as ultrathin metal films suffer strong emission quenching,³¹ which hampers nanoscale integration. Furthermore, we find that the deposition process required to integrate a transparent conducting oxide inhibits molecular fluorescence, which highlights the potential of 2D materials for integration with ultrasensitive quantum emitters. At the same time, we show that a single quantum emitter can be used as a transducer of the 2D materials' electronic properties.

We chose single dibenzoterrylene (DBT) molecules as bright, photostable single-photon sources^{32,33} emitting at 785 nm (1.58 eV) with lifetime-limited line width³⁴ (~40 MHz) at 3 K even when hosted in a submicron environment.³⁵ Experimentally, we perform scanning laser spectroscopy to address individual DBT molecules at subwavelength separation to a 2D metallic or semiconducting interface. The device comprises DBT molecules embedded in anthracene nanocrystals (see Supporting Information, section S1), interspersed in a thin poly(vinyl alcohol) (PVA) film on a Si⁺⁺/SiO₂ substrate (Figure 1a). MoS_2 or graphene flakes are placed on top of the polymer film by a dry transfer technique and electrically contacted by gold electrodes. This transfer process is performed at room temperature and without other nanofabrication steps, which could potentially degrade emission.³⁶ Spatial maps of DBT ensemble fluorescence (see Methods) at 3 K show bright, localized emission beneath both 2D materials (Figure 1b).

A simplified DBT energy level scheme is shown in the inset of Figure 1a. The transition of interest is the zero-phonon line (ZPL) between the ground vibrational levels ($\nu = 0$) of the electronic ground and excited states. Upon resonant excitation of this transition, the molecule relaxes either to the electronic ground state (30-40% of emission³⁷) or to a higher vibrational state ($\nu \neq 0$), thereby emitting a red-shifted photon. Scanning laser spectroscopy (see Methods) on a pristine nanocrystal (Figure 1c) at 3 K reveals a series of sharp peaks from a DBT ensemble. This peak dispersion arises from local variations of strain and charge and enables spectrally addressing a single molecule.³⁸ The narrowest peaks in such ensembles display a typical line width of $\Gamma/2\pi = 43 \pm 7$ MHz. To confirm that we can address single molecules in a nanocrystal, we measure statistics of photon emission in Hanbury-Brown and Twiss (HBT) configuration (Figure 1d) and fit the normalized data with the second-order intensity autocorrelation function³⁹ $g^{(2)}(\tau) = 1 - Ce^{-1\tau + 1/\tau_{DBT}}$, where *C* is the contrast. At zero delay time, we find $g^{(2)}(0) = 0.04 \pm 0.02 < 0.5$, which is signature of a single-photon source. We extract an excited state lifetime³⁹ of $\tau_{DBT} = 4.7 \pm 0.5$ ns, implying a lifetime-limited line width $\Gamma_0/2\pi = 1/2\pi\tau_{DBT} = 34 \pm 5$ MHz, comparable to values observed in bulk anthracene crystals.³⁷ Therefore, single molecules in our device can exhibit lifetime-limited line width within the measurement error. In a solid state environment, this line width can be broadened by dephasing and near-field interactions, which can hamper the performance of emitters in nanostructured devices.^{36,40}

In our device, a 2D material is placed in the near-field of a single emitter (separation $d \ll \lambda$). In this regime, near-field interactions such as nonradiative energy transfer (nRET) from the molecule to the 2D material⁴¹ and Casimir–Polder (CP) energy level shifts⁸ are expected to occur. Both interactions scale divergently with separation as d^{-4} , in contrast to d^{-3} for bulk interfaces.²² The nRET process leads to a line width broadening, while the CP energy level shift is a quantum effect related to the modification of vacuum fluctuations by the 2D interface. At fixed emitter–2D material separations, we can quantify the nRET contribution due to the presence of the 2D material by its impact on the emission line width. The CP contributions are difficult to quantify because for one specific emitter, the emission energy with and without the 2D material cannot be measured independently.

By measuring the emission line widths of over 500 molecules (Figure 2) in three different configurations (uncovered, covered by bilayer graphene (BLG)/MoS₂) in different samples, we quantify the effect of proximity to 2D materials on emission line width. We quantify the most probable line width $\tilde{\Gamma}$ in each case by fitting the line width histogram with a Smirnov distribution,⁴² which describes single molecule line



Figure 2. Emission broadening and time stability in the presence of 2D materials. (a) Line width distribution for uncovered DBT (green), DBT covered by monolayer MoS_2 (red), and bilayer graphene (gray). Solid lines are fits to the data as described in the main text. (b) Time trace of single DBT molecule emission (3 s/line) for uncovered DBT (bottom) and DBT covered by monolayer MoS_2 (middle) and bilayer graphene (top).

width distributions perturbed by long-range coupling to twolevel fluctuators, e.g., in polymers.^{43,44} For uncovered nanocrystals, we obtain $\tilde{\Gamma}_{uncov.}/2\pi = 62$ MHz, which is comparable to Γ_0 . This implies that the anthracene nanocrystal is a highly stable and crystalline environment,³⁵ and most molecules within it do not experience significant spectral diffusion due to defects or proximity to the surface.³⁵ While emitters covered by MoS₂ experience extremely weak spectral broadening $(\tilde{\Gamma}_{MoS,}/2\pi = 65$ MHz), they are significantly broadened when covered by BLG ($\tilde{\Gamma}_{BLG}/2\pi = 108$ MHz) and their line width distributed over a larger range. We attribute this broadening to higher nRET efficiency to gapless graphene as electronic transitions can be optically excited over a large range of energies and in particular at $\hbar\omega_{ZPL}$. In contrast, MoS₂ has bandgap and excitonic resonances at energies > $\hbar \omega_{ZPL}$, resulting in weak nRET, which preserves the narrow line width. These results show that neither the presence nor the integration process of 2D materials have a strong detrimental impact on the emission properties. In contrast, we find that the deposition of a commonly used transparent electrode material such as ITO results in the complete disappearance of DBT emission (see Supporting Information, section S2), most likely due to thermal damage to the nanocrystal during deposition. This highlights the weakly invasive nature of 2D material integration, which makes it particularly suitable for fragile quantum emitters.

To confirm that emission stability in time is preserved after 2D material integration, we measure DBT spectra over time for the three configurations (uncovered, covered by graphene/ MoS_2) as shown in Figure 2b. In each case, we observe stable emission intensity and fluctuations of ZPL frequency and line width below 42 MHz (see Supporting Information, section S3). Slightly higher fluctuations of ω_{ZPL} —possibly induced by charge fluctuations—are resolved in the case of MoS_2 . Overall, these results show that 2D semiconductors are particularly suitable for integration with sensitive quantum emitters at nanoscale proximity, introducing negligible perturbation in the photostability.

We now turn to electrical manipulation of single emitters. To achieve Stark⁴⁵ tuning of DBT emission energy, we apply an electric potential V_g over the capacitor formed by the 2D electrode and the Si⁺⁺ back-gate, separated by a PVA/SiO₂ layer (see Figure 1a). We reach comparatively large^{46,47} field strengths above 2 MV cm⁻¹ before dielectric breakdown takes place. DBT ensemble spectra below BLG at different V_{o} (Figure 3a) show a large, dominantly quadratic shift of the emitters in the whole ensemble on the order of hundreds of GHz (~10⁴ $\Gamma_0/2\pi$), comparable to the inhomogeneous broadening of the entire ensemble.³⁵ While this tuning range is comparable to state-of-the-art devices employing semiconductor quantum dots 47 and diamond defects, 48,49 we highlight that our device displays emission line widths within a smaller footprint, which is attractive for nanophotonic integration. We also verify that DBT emission energy remains stable under large applied electric fields by repeating stability measurements as shown in Figure 2b up to large values of V_g (see Supporting Information, section S3). We find small, gatedependent emission energy drifts (<3 MHz/s), likely due to small leakage currents in the device, which can be reduced by using a smaller 2D electrode area or by active feedback.²

For a centrosymmetric molecule such as DBT, we expect a quadratic Stark shift with linear contributions arising from



Figure 3. Stark tuning of a single molecule with a 2D electrode. (a) Spectral map showing the Stark shift of an ensemble of single molecules under BLG with back-gate voltage V_{g} (b) Gate-induced line shift of a single molecule under BLG (gray circles) and monolayer MoS₂ (red circles). Solid lines are parabolic fits (see main text). (c) Back-gate dependence of MoS₂ photoluminescence (PL) spectra at 532 nm (2.33 eV) excitation. (d) PL intensity of neutral exciton (X⁰, 1.96 eV, blue), negatively charged trion (X⁻,1.93 eV, green), and defect band (1.7 eV, red) with V_{g} . (e) Emission line width for a single molecule under BLG (gray) and monolayer MoS₂ (red).



Figure 4. Dynamical emission control of quantum emitters. (a) Single molecule emission as a function of AC amplitude δV_g for (left to right) sinusoidal, square and pulsed modulation ($f_{AC} = 1$ kHz), and for pink noise (100 kHz bandwidth). (b) Single DBT emission spectra vs f_{AC} ($V_g + \delta V_g = 20 + 1$ V) under MoS₂ (upper panel) and monolayer graphene (lower panel). (c) Transmission function $T(f_{AC})$ for a single molecule at different V_g under MoS₂ (filled circles) and graphene (open circles). (d) Back-gate dependence of MoS₂ cutoff frequency f_{-3dB} . (e) Transmission T (10 kHz) as a function of V_g for MoS₂ (red) and graphene (grey). (f) Histogram of time-resolved single molecule emission intensity modulation at $f_{AC} = 100$ MHz. The transition energy ω_{ZPL} is modulated electrically while the excitation energy ω_{exc} is kept constant, leading to a periodic emission modulation.

dipole moments induced by distortion of the molecule's insertion site.⁴⁶ The Stark shift is modeled as $\Delta \omega_{ZPL} = a |\vec{E}| + b |\vec{E}|^2$, where *a* and *b* are the linear and quadratic Stark coefficients, and functions of the dipole moment and

polarizability change, respectively, between ground and excited state. Here, $\vec{E} = L\vec{E}_{ext} - \vec{E}_0$ is the net local electric field experienced by the molecule upon application of an external field $|\vec{E}_{ext}| = V_g/h_{tot}$ ($h_{tot} = h_{PVA} + h_{SiO_2} \sim 600$ nm) with a

correction \tilde{E}_0 that accounts for intrinsic electric fields, e.g., due to trapped charges and work function differences.⁵⁰ We also include a local field correction factor $L = \frac{\overline{e}+2}{3} = 1.7$, derived from anthracene's averaged isotropic permittivity⁵¹ $\overline{e} = 3.1$. Fitting detuning data for different emitters, we extract typical Stark coefficients of $a \sim 300$ MHz/(kV cm⁻¹) and $b \sim -0.15$ MHz/(kV cm⁻¹)² (see Supporting Information, section S4), comparable to reported results.³⁴ The observed quadratic stark shift shows that E_{ext} is linear in V_{g} , as is expected for a metallic electrode such as BLG (Figure 3b).

In contrast, emitters under MoS₂ deviate from the parabolic detuning below $V_{q,0} \sim -30$ V (Figure 3b), where the detuning flattens and $\Delta \omega_{ZPL}$ is almost independent of V_g . We attribute this deviation to a gate-induced change of resistivity:⁵² as the charge carrier density in a semiconductor changes more abruptly with $V_{g'}$ we expect a sublinear dependence of $E_{ext}(V_g)$ as excess charge carriers are depleted in MoS2. Electrostatic doping of the MoS_2 electrode is independently confirmed by gate-dependent photoluminescence (Figure 3c,d). The ratio of charged (X^{-}) to neutral (X^{0}) exciton PL intensities increases with V_g due to n-doping of the MoS₂ electrode. We also observe a broad emission peak at lower energy for negative V_{g} —associated with emission from defects in MoS₂⁵³—which overlaps with $\hbar\omega_{ZPL}$. With the appearance of this defect band, we observe a line width broadening Γ_{DBT} below $V_{g,0}$ for some emitters, which is absent in the case of a metallic BLG electrode (Figure 3e). This suggests that defects could act as n-RET acceptors, leading to emission line width broadening of emitters close to MoS₂.

Our system combines large Stark tuning with lifetimelimited emitters that potentially enable adiabatic control up to a frequency set by their natural line width Γ_0 . We investigate the range of this dynamical control by applying oscillating potentials $V_{tot} = V_g + \delta V_g(f_{AC})$ to graphene and MoS₂ electrodes. For fast modulation frequencies compared to the spectral acquisition time $(f_{AC} \gg t_{meas}^{-1} \sim 0.1 \text{ Hz})$, DBT emission peaks show a splitting $\sigma(f_{AC})$ (Figure 4a) proportional to the modulation amplitude δV_g and the local Stark slope $\frac{\partial \omega_{ZPL}}{\partial V_g}$:

$$\sigma = \frac{\partial \omega_{ZPL}}{\partial V_g} \delta V_g T \tag{1}$$

Here, $T(f_{AC})$ is the transmission of the RC-low-pass filter governed by the effective device resistance R which includes contact resistance as well as the sheet resistance of the 2D material and backgate capacitance C (see Supporting Information, section S5). At fixed V_g and f_{AC} , the DBT emission spectra reflect the oscillation turning points of the modulating waveform (Figure 4a). Under square modulation with a fixed amplitude $\delta V_{g'}$ the splitting vanishes with increasing f_{AC} for both MoS₂ and graphene electrodes (Figure 4b), albeit at a lower frequency for MoS₂. From this measurement, we extract $T(f_{AC})$ (eq 1) and confirm low-pass behavior with a characteristic cutoff frequency f_{-3dB} (Figure 4c). Interestingly, $T(f_{AC})$ shows a strong gate voltage V_g dependence for MoS₂ electrode, which is not observed for graphene. This dependence is quantified by f_{-3dB} , which increases with V_g and saturates at ~5 kHz $\ll \Gamma_0$ for $V_g > 0$ V (Figure 4d). We attribute this behavior to a change of sheet resistivity and contact resistance due to gate-induced electrostatic n-doping⁵² of the MoS₂, consistent with PL measurements (Figure 3c,d). As a result, $f_{-3dB} \propto (RC)^{-1}$ increases as we sweep V_q from negative to positive values.

To capture the gating efficiency of our 2D electrodes, we extract transmission T at fixed f_{AC} = 10 kHz varying V_g (Figure 4e, and Supporting Information). The strong reduction of Tfor $V_g < 0$ V is consistent with a large gate-induced change of resistance in the semiconducting MoS₂ device, while graphene's metallicity maintains $T \sim 1$ over the full V_g range. Therefore, graphene enables Stark tuning of emitters over a large energy range and at high frequency at the expense of weak line width broadening. To extend this modulation bandwidth, we reduce the gate capacitance C by using a thicker PVA dielectric (h_{PVA} = 800 nm). Then, we modulate $\hbar \omega_{ZPL}$ around a fixed excitation energy by applying δV_g at f_{AC} = 100 MHz ~ $\Gamma_0/2\pi$ to a graphene electrode. Using a time-correlated single-photon counter synchronized to the modulation δV_{g} , we observe a periodic oscillation of emission intensity (Figure 4f) with a modulation depth of \sim 50 % (measurement time 30 s). This oscillation is a signature of the excitation laser periodically exploring a fraction of the emitter's absorption line. These measurements show that the dynamical modulation bandwidth of our devices, determined by the 2D electrode material and device geometry, approaches Γ_0 . Conversely, single emitters act as local nanoprobes of the 2D material's electronic properties.

In conclusion, we demonstrate a hybrid device where 2D materials are integrated with lifetime-limited single-photon emitters to achieve broadband and fast emission energy tuning. Our results highlight the potential of atomically thin electrodes for integration with sensitive quantum emitters in a nanoscale device without perturbing narrow emission line width, in contrast to commonly employed bulk transparent electrodes. At high frequencies, Stark modulation reveals low-pass transmission behavior related to the 2D materials' sheet resistivity. Using a graphene electrode, we show emission energy modulation at frequencies approaching the emitters' line width. Our device thus provides resonant tuning and highfrequency modulation of SPS on chip, required for obtaining indistinguishable and synchronized single photons. Finally, our device is a platform for studying novel forms of light-matter interaction such as plasmon-polaritons in graphene⁹ and exciton-polaritons in TMDs¹⁰ at the single excitation level. Conversely, strong coupling to such excitations could allow the observation of normally forbidden higher order transitions of the emitter.54

Methods. Device Fabrication. We make a suspension of anthracene nanocrystals hosting DBT molecules in PVA by reprecipitation. The suspension is spin-cast onto a p-doped Si wafer coated with 285 nm thermally grown SiO₂. Electrodes are deposited onto the coated chip by thermal evaporation of 100 nm Au through a shadow mask. Nanocrystals close to the electrode displaying DBT fluorescence are localized at room temperature using off-resonant wide-field illumination. Bulk MoS_2 and graphite are exfoliated mechanically using commercial polydimethylsiloxane (PDMS) sheets. Mono-and bilayer flakes of both materials are identified optically by absorption contrast (see Supporting Information, section S6) and transferred onto anthracene nanocrystals in PVA by dry stamp transfer.

Electrical Device Actuation and Optical Readout. Measurements are performed under vacuum in a cryostat at 3 K. Our hybrid devices are actuated electrically using a lownoise voltage source and an arbitrary waveform generator to

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provide DC and AC voltages. Using a custom-built confocal microscope to locally illuminate the device, we excite single molecules with a tunable 785 nm laser with circular polarization at 5 nW, well below the saturation power of ~ 20 nW (see Supporting Information, section S7). Red-shifted single photon emission is detected with a single-photon counting module (SPCM) combined with spectral ZPL filtering by a long-pass filter. Emission maps are made using pseudobroadband excitation of DBT ensemble fluorescence by fast modulation (200 Hz) of the laser detuning compared to the SPCM integration time (~ 10 ms). MoS₂ photoluminescence is excited using a S32 nm laser and detected with a spectrometer (10 s integration time).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.9b00916.

Nanocrystal characterization, impact of ITO deposition on molecular emission, emission stability, Stark coefficients, electrical low-pass model of the device, 2D material identification, and emission saturation behavior (PDF)

AUTHOR INFORMATION

Corresponding Author

*(F.H.L.K.) E-mail: Frank.Koppens@icfo.eu.

ORCID ®

Adrian Bachtold: 0000-0002-6145-2479 Costanza Toninelli: 0000-0002-6843-058X Frank H. L. Koppens: 0000-0001-9764-6120

Author Contributions

K.G.S., A.R.-P., C.T., and F.H.L.K. conceived the experiment. K.G.S. and C.C. made the samples with the support of S.P., P.L., and C.T. Measurements and analysis were performed by K.G.S., C.C., and A.R.-P. K.G.S, A.R.-P. and F.H.L.K. wrote the manuscript with critical comments from all authors.

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Notes

The authors declare no competing financial interest.

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