Accidental Contamination of Substrates and Polymer Films by Organic Quantum Emitters

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ABSTRACT: We report the observation of ubiquitous contamination of dielectric substrates and poly(methyl methacrylate) matrices by organic molecules with optical transitions in the visible spectral range. Contamination sites of individual solvent-related fluorophores in thin films of poly(methyl methacrylate) constitute fluorescence hotspots with quantum emission statistics and quantum yields approaching 30% at cryogenic temperatures. Our findings not only resolve prevalent puzzles in the assignment of spectral features to various nanoemitters on bare dielectric substrates or in polymer matrices but also identify the means for the simple and cost-efficient realization of single-photon sources in the visible spectral range.

KEYWORDS: Photoluminescence spectroscopy, fluorescence spectroscopy, single-molecule spectroscopy, contamination of substrates and polymer matrices, organic fluorophores, single-photon emitters

Embedding quantum emitters within chemically and electrostatically inert polymer matrices such as poly(methyl methacrylate) (PMMA) is a common approach to reduce the fluorescence (FL) intermittency encountered by a broad class of photoactive nanoparticles and molecular dyes under ambient conditions, thus promoting stable and enhanced FL. However, contamination of the polymer matrix by fluorescent constituents can result in controversial assignment of spectral features. An early example of such unintentional contamination by bright impurity molecules is the single-molecule study of laser dye molecule rhodamine 640 in polymer matrices. In some of the more recent spectroscopy studies, it has proven difficult to distinguish between the FL stemming from quantum emitters, the polymer matrix, or the underlying dielectric support. This is not surprising given the challenge of unambiguous assignment of the FL to its actual source for photoactive systems with low quantum yields or individual quantum emitters with high quantum yields but inherently low absolute FL intensities.

In the visible spectral range, the realm of photoactive nanoemitters includes single molecules, fluorescent nanodiamonds, colloidal quantum dots and nanoplatelets, transition-metal dichalcogenide quantum dots, or perovskite nanoplatelets. The range of related potential applications in light-emitting, light-detecting, and light-harvesting devices is as diverse as the specific details of the photophysics of the underlying emitters. In absolute terms, however, and depending on the radiative lifetime, some of these systems feature low FL intensities despite high quantum yields, while others suffer from reduced quantum yields due to optically inactive lowest-lying dark states with strongly inhibited FL at cryogenic temperatures. Irrespective of the actual reason for low intensity, any contamination of the relevant FL by photoemissive substrates or matrices is clearly detrimental to both fundamental studies of nanoemitters and their related applications.

In the following, we present a comprehensive study targeting a quantitative analysis of the FL in the visible spectral range arising from thin films of PMMA and dielectric substrates. Surprisingly, we find that PMMA films prepared by standard solution-deposition procedures exhibit optical transitions in the visible at both room and cryogenic temperatures. However, the FL is not a characteristic feature of the PMMA itself. It, rather, stems from fluorescent contaminants in the PMMA matrix that we ascribe to solvent residuals with specific FL intensity and spectra. For individual fluorescent contaminants, pronounced and spectrally stable zero-phonon lines (ZPLs) with red-shifted vibronic satellites and highly non-classical emission statistics emerge as a generic feature at cryogenic temperatures. At room temperature, thermal broadening of...
both the ZPL and the vibrational sidebands give rise to a characteristic three-peak spectrum that is suspiciously similar to the spectra reported for color centers in bulk silica and silicon or silica nanoparticles or can be subject to other interpretations.

The basics of our experiment are illustrated in Figure 1a. We performed FL spectroscopy in a home-built optical microscope with confocal raster-scan imaging and spectroscopy. Raster-scan fluorescence intensity maps (normalized to 10 kW/cm² excitation power density) of the surface of fused silica after (b) sonication in acetone and isopropanol, (c) additional sonication in deionized water, and (d) oxygen plasma treatment. (e) Fluorescence image of plasma-cleaned fused silica with a thin film of PMMA formulated in anisole. All maps were recorded with laser excitation at 532 nm and 130 kW/cm² (scale bars: 3 μm). (f) Fluorescence spectrum of a typical hotspot in PMMA with a fit by 3 Gaussian peaks with full-width at half-maximum line widths of 90 meV and equidistant energy spacings of 155 meV.

Figure 1. (a) Schematic of the experiment: fluorescence from dielectric substrates coated with a thin film of PMMA was studied with confocal raster-scan imaging and spectroscopy. Raster-scan fluorescence intensity maps (normalized to 10 kW/cm² excitation power density) of the surface of fused silica after (b) sonication in acetone and isopropanol, (c) additional sonication in deionized water, and (d) oxygen plasma treatment. (e) Fluorescence image of plasma-cleaned fused silica with a thin film of PMMA formulated in anisole. All maps were recorded with laser excitation at 532 nm and 130 kW/cm² (scale bars: 3 μm). (f) Fluorescence spectrum of a typical hotspot in PMMA with a fit by 3 Gaussian peaks with full-width at half-maximum line widths of 90 meV and equidistant energy spacings of 155 meV.

to study sample-specific emission in the spectral range of 560–770 nm excited with a continuous-wave laser at 532 nm, a wavelength frequently used to excite FL in the visible. By raster-scanning the sample with respect to fixed diffraction-limited confocal excitation and collection spots, we acquired maps of FL intensity as in Figure 1b–e with a single-photon counting avalanche photodiode (APD) and hyperspectral maps with spectrally dispersed FL as in Figure 1f recorded at each raster-scan pixel for spectral analysis of individual emission hotspots. The studies were complemented by time-correlated FL, second-order FL coherence, and FL excitation spectroscopy experiments performed either at room temperature or at the cryogenic temperature of 3.1 K.

In the first stage of the experiments, we studied the FL characteristics of bare dielectric substrates. It has been argued recently that silica-based substrates host intrinsic fluorescent centers with sizable FL intensity in the visible. Therefore, we first investigated the FL from the surface of bare fused silica substrates exposed to different cleaning procedures (see the Methods section for details on cleaning protocols). Under ambient conditions and 250 μW irradiation in a full-width at half-maximum (fwhm) spot of 0.5 μm diameter, we acquired raster-scan FL maps shown in Figure 1b–d. The color-coded FL intensity in these maps as well as in all following maps was normalized to an excitation power density of 10 kW/cm² to facilitate direct quantitative comparison. For fused silica sonicated subsequently in acetone and isopropanol according to a common cleaning procedure, we observed FL from the entire sample surface with inhomogeneous intensity and an average APD count rate of ~0.3 kcts/s (Figure 1b). After an additional sonication step in deionized water the level of FL decreased to an average of ~0.2 kcts/s away from hotspot emission with ~0.3 kcts/s (Figure 1c). Most remarkably, additional treatment with oxygen plasma suppressed the FL from the silica surface below the dark count rate of the APD (Figure 1d). This set of data, consistently observed for quartz and sapphire substrates subjected to oxygen plasma treatment (see the Supporting Information for substrate-specific FL maps), clearly establishes the absence of intrinsic FL defects on silica substrates. Moreover, it provides a first hint at the source of the FL as stemming from organic surface contaminants that do not withstand oxygen plasma treatment.

For the second experimental stage, we prepared substrates free of FL background and covered them by spin-coating with PMMA dissolved in anisole. On a silica substrate with 200 nm of PMMA, we observed the reappearance of fluorescent hotspots with intensities of up to ~0.5 kcts/s on a background close to the detection limit of the APD (Figure 1e) under measurement conditions identical to those of Figure 1b–d. Similar results were found for as-deposited and thermally cross-linked PMMA films fabricated from anisole solutions (see the Methods section for sample details). For most hotspots, the FL was spatially localized to the diffraction-limited spot and characterized by room-temperature spectra as in Figure 1f. The spectrum with maximum FL at 2.02 eV (614 nm) can be reproduced with some success by three overlapping Gaussian peaks with fwhm line widths of 90 meV, equidistant separations of 155 meV, and intensities that reduce with decreasing emission energy (gray solid lines in Figure 1f). Pending an explanation for the mismatch between this simplistic model fit and the actual spectrum, we point out its striking similarity to the spectra ascribed earlier to various sources. Providing a second hint to hydrocarbon molecules as a source for misinterpretation and establishing a link to the visionary association made between the spectra of nonblinking colloidal quantum dots and organic dyes.

To elucidate the correspondence between the FL hotspots found at room temperature in thin films of PMMA and the spectral signatures of organic molecules, we carried out spectroscopy studies at the cryogenic temperature of 3.1 K. Figure 2a,b shows representative cryogenic FL maps of PMMA films on a fused silica substrate and a perforated silicon nitride membrane, respectively. Both maps were acquired in the hyperspectral mode by recording spectrally dispersed FL with a nitrogen-cooled CCD and color-coding its maximum intensity at each raster-scan pixel. Note the conceptual difference to the
The Gaussian resonance condition with a scanning Fabry-Perot etalon (gray line) suggests that spectral wandering broadens the ZPL on minute time scale to an inhomogeneous peak with a fwhm of 13.1 ± 0.5 μeV (Figure 2f). These spectral signatures find their correspondence in the studies of hydrocarbon fluorophores embedded in a polymer host matrix.31–33 Within this framework, low-temperature FL of single molecules is characterized by a spectrally narrow ZPL associated with the principal electronic transition34 and sidebands stemming from Franck-Condon transitions between vibronically dressed molecular electronic states.35,36 Stabilized in PMMA, single molecules exhibit FL with low intermittency and ZPLs limited by spectral diffusion to ~5 μeV.37–39 The red-shifted satellites of the ZPL are equally well-pronounced in vibronic spectroscopy39 of molecules with characteristic vibrational degrees of aromatic hydrocarbons. Even though the natural zero-phonon lineshapes were out of reach in our experiments, their studies with resonant FL excitation would yield information about macroscopic properties of the local host environment surrounding the emitters.40,41

The set of data in Figure 3 further substantiates the correspondence. With polarization-resolved measurements shown in Figure 3a, we confirmed the dipolar character associated with the molecular transition of the ZPL.28 The orientation of the absorption and emission axes measured with linearly polarized excitation and detection, respectively, were determined as collinear within our experimental precision. Furthermore, time-correlated measurements of Figure 3b revealed the characteristic FL decay dynamics of molecules on nanoseconds time scale.52 The single-exponential lifetimes of 3.8 and 3.6 ns for the ZPL within a spectral window of 60 meV and the total FL emission, respectively, were the same within the temporal resolution of ~0.3 ns in our experiments, identifying red-shifted sidebands as vibronic ZPL replicas. Finally, single-photon emission statistics as a hallmark of single-molecule FL43,44 are presented in Figure 3c,d. With photon correlation spectroscopy, we observed pronounced photon anti-bunching in the normalized second-order coherence function g(2)(t) at zero time delay for both the FL within a band-pass interval of 60 meV around the ZPL (with g(2)(0) = 0.24 ± 0.05 in Figure 3c) and the full FL spectrum without spectral filtering (g(2)(0) = 0.32 ± 0.04 in Figure 3d). Thus, within the uncertainty of our measurement, we can rule out simultaneous photon emission into the ZPL.
and the sideband spectrum associated with the vibronic ZPL satellites.

Having identified the hotspots in PMMA as single fluorescent molecules, we utilized vibrationally resolved FL spectroscopy to shed light on their chemical nature. Figure 4a shows a spectrum of a hotspot that is representative for fluorescent contaminants in PMMA prepared with anisole as solvent. A series of low-frequency vibrational modes contributes to the sidebands below 80 meV (645 cm⁻¹) followed by a group of replicas around 173 meV (1395 cm⁻¹) and a weaker satellite group around 346 meV (2790 cm⁻¹). The latter is, in fact, a second harmonic of the preceding group as confirmed by correlation analysis between all individual peaks of the two groups upon a spectral shift by 173 meV. All main vibrational features in emission have their broadened counterpart resonances in absorption, as demonstrated by the FL excitation spectra in Figure 4b recorded for two typical emitters with different ZPL energies as a function of laser energy detuning at constant excitation power. For both quantum emitters of Figure 4b, the absorption is enhanced whenever the laser detuning with respect to the ZPL matches the energy of the vibronic sidebands (the dashed lines in Figure 4 emphasize the correspondence between the resonances in emission and absorption).

The vibrationally resolved spectrum of Figure 4a is typical for fluorescent molecules in PMMA films from anisole-based solutions. It exhibits a striking similarity with the cryogenic FL of anthracene characterized by a ZPL in the ultraviolet (around 3 eV) and a pronounced vibronic satellite group red-shifted by around 1400 cm⁻¹. The corresponding vibrational degrees of freedom are related to the intramolecular stretching of adjacent carbon bonds in polycyclic aromatic hydrocarbons. The observation of the ZPL emission in the visible (around 2 eV) from anisole-based PMMA suggests that the optical transitions of solvent-related contaminants in such films stems from polycenes such as pentacene or from anthracene-derived dyes such as alizarin. Moreover, we note that these emitters are not a particularity of PMMA hosts because similar spectra have been reported for individual impurities (termed “molecules X”) found in n-hexadecane and polyethylene matrices (see the Supporting Information for details).

To shed light on the nature and possible distinctions of the FL hotspots, we applied vibrational FL spectroscopy to PMMA films derived from other solvents (see the Methods section for sample preparation details). As highlighted by the raster-scan maps of Figure 5, the areal density and the FL intensity of hotspots in PMMA films formed with chlorobenzene, methyl isobutyl ketone, and toluene were similar to anisole-based PMMA characteristics (Figures 1e and 2a) but, however, not without differences in vibronic signatures. Figure 5g shows normalized average spectra of 25 brightest fluorophore contaminants in PMMA films prepared with different solvents (see the Supporting Information for FL maps corresponding to the average spectrum of anisole-based PMMA). The dissimilarities in the spectra most probably result from different synthesis chemistry and manufacturing processes of the solvents.

The spectrum of a typical hotspot in chlorobenzene-based PMMA (green trace) shows a pronounced vibronic band at 250 cm⁻¹ (indicated by the rhomb), additional features around 548 cm⁻¹ (tip-up triangle), and a very weak high-frequency band around 1400 cm⁻¹, as discussed earlier (indicated by the hexagon). In contrast, the vibronic FL characteristics of hotspots in PMMA films formed with methyl isobutyl ketone and toluene solutions (orange and brown traces, respectively) exhibit vibrational signatures around 318 cm⁻¹ (labeled by the square) as well as a band at 757 cm⁻¹ (tip-down triangle). The

**Figure 3.** (a) Polarization characteristics of the zero-phonon line: normalized intensity as a function of the rotation angle of a linear polarizer in excitation and detection (top and bottom panels, respectively; the gray lines represent the same functional form of the fits to the data). (b) Time-correlated decay of the zero-phonon line and the total fluorescence (gray traces) of a single hotspot and corresponding mono-exponential fits with decay constants of 3.8 and 3.6 ns (blue and purple traces). The plots were offset for clarity. (c, d) Second-order coherence function $g^{(2)}(\tau)$ recorded with and without spectral selection of the zero-phonon line, respectively. The blue and purple lines are fits to the data with multiphoton probabilities of 0.24 ± 0.05 and 0.32 ± 0.04, respectively. All data were recorded at 3.1 K with excitation at 532 nm.

**Figure 4.** (a) Normalized fluorescence spectrum of a typical hotspot recorded with excitation at 532 nm and plotted as a function of spectral redshift from the zero-phonon line at 2.134 eV. The intensity was magnified by a factor of 4 (20) above 7 meV (280 meV) redshift to highlight two groups of phonon sidebands with a spacing of 173 meV. (b) Normalized zero-phonon line intensity as a function of excitation laser detuning for two quantum emitters (QE1 and QE2) with spectral features as in panel a recorded within excitation wavelength intervals of 538–583 and 485–555 nm (solid and open circles, respectively). All data were recorded at 3.1 K.

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The symbols indicate specific vibronic modes of hydrocarbon-based molecular dyes. All data were recorded at 3.1 K on thermally annealed PMMA films of 200 nm thickness on oxygen plasma-cleaned fused silica with laser excitation at 532 nm and 52 kW/cm² excitation power density; the fluorescence intensities in panels a–f were scaled to 10 kW/cm².

vibronic modes, labeled by the rhomb and tip-up and tip-down triangles in Figure 5g are characteristic of rylene dyes composed of naphthalenes. While the low-frequency mode (rhomb) is close to that of the long axis stretch of a terylene molecule, the higher-frequency modes (tip-up and tip-down triangles) are consistent with the short axis stretch and ring deformation of outer naphthalenes, respectively. Note that naphthalene-related bands of rylene dyes are only very weakly expressed in the averaged vibronic FL spectra observed in anisole- and chlorobenzene-based PMMA films (blue and green traces in Figure 5g, respectively). The normal mode labeled by the square in Figure 5g, and most-pronounced for emitters in anisole-based PMMA, is distinctive for skeletal distortion of short acene molecules such as tetracene and complements our assignment of stretching vibrations to their carbon bonds (hexagon). Interestingly, the mode related to distortion of the acene skeleton was also weakly visible for hotspots in PMMA matrices based on methyl isobutyl ketone and toluene.

In addition to solvent-specific differences in the spectra of fluorescent hotspots in PMMA, vibrationally resolved FL spectroscopy identifies the normal modes of aromatic hydrocarbons in the region between 1200 and 1600 cm⁻¹ (strongest for anisole-based PMMA) as a common feature of FL contaminants at low temperatures. At elevated temperatures, these modes develop into broad vibronic satellites (see the Supporting Information for FL spectra at different temperatures) that accompany the FL from the thermally broadened principal molecular transition. With this in mind, the interpretation of the three-peak structure of the room-temperature FL spectrum in Figure 1f as stemming from an organic fluorophore is straightforward. For an adequate modeling, in which the fit with three Gaussians most significantly deviates from the actual spectrum, the contributions of all other vibrational modes must be taken into account. The main corrections to the thermally broadened spectral profile of the ZPL appear on the low-energy side of the peak stemming from vibronic modes red-shifted by up to ~85 meV (690 cm⁻¹). The second resonance peaking at 155 meV (1250 cm⁻¹) in Figure 1f stems from the overlap of the ZPL tail with the aggregate of vibrational bands describing aromatic carbon bond stretching (1200–1600 cm⁻¹ in Figure 5g). Note that the room-temperature redshift of this peak is dependent on the low-temperature vibrational signature of the strongest normal modes for the molecule in question. In agreement with Figure 4a, the third resonance is correlated to the second peak as its higher harmonic.

In concise terms, our comprehensive study of fluorescent spots, ubiquitously present in PMMA films and on contaminated dielectric substrates, leads to the conclusion that organic fluorophores are the actual source of misinterpreted FL signatures. We estimate the quantum yield of such organic quantum emitters to range from ~5% at room temperature up to 30% at 3.1 K (see the Supporting Information for the estimate of the quantum yield). These values are not remarkably high; however, the corresponding FL intensity can be significant in studies of photoactive systems with reduced quantum yields in cryogenic or ambient environments. In fact, we found the FL intensity of PMMA hotspots to be roughly a third of the emission intensity of individual terylenediimide (TDI) molecules at cryogenic temperatures (see the Supporting Information for the optical spectroscopy of TDI molecules embedded in PMMA) and, in many instances, even more intense than commercial radiant dyes at ambient conditions. Given the present technological limitations to solvent purity, it seems unlikely that contamination of PMMA and other polymer matrices can be completely avoided in future experiments. However, the abundance of stable quantum emitters in polymer films could facilitate a range of fundamental studies and technological developments relying on simple and cheap sources of nonclassical light.

Methods. The sample with TDI molecules in a PMMA matrix was prepared in the group of Thomas Basché in Mainz. All other samples were prepared in the clean room at LMU Munich. Unless stated otherwise, substrates were cleaned by initial sonication in acetone (Technich, acetone Micropur VLSI) for 5 min, followed by isopropanol (Technich, propan-2-ol Micropur VLSI) for 5 min, and finally exposed for 1 min to oxygen plasma. Polymer covered samples were prepared by...
spin-coating ~10 μL of PMMA onto oxygen plasma-treated fused silica (CrysTec) and other dielectric substrates (quartz and sapphire). An ellipsometer was used to adjust the spin-coating parameters for a film thickness of 200 nm. The films were obtained from commercial PMMA formulated in anisole with a molecular weight of 950 K (MicroChem, 905PMMA A4 resist for electron-beam lithography). The spin-coated PMMA film was left to dry at ambient conditions. Optionally, the samples were baked at 180 °C for 90 s on a hot plate. The PMMA film on the perforated silicon nitride membrane (PELCO) of Figure 2b was drop-cast and baked to ensure mechanical stability of freely suspended PMMA. Control experiments were carried out with 4% of 450 K PMMA resin (DuPont, Elvacite 2041) diluted in 96% of chlorobenzene (Merck, 801791), methyl isobutyl ketone (Technic, MIBK Micropur VLSI), or toluene (Sigma-Aldrich, 79418). Additional studies were conducted on films prepared with 6% of the 450 K PMMA resin mixed with 94% of anisole (Merck, 801452).

FL imaging and spectroscopy measurements were performed with a home-built confocal microscope coupled to single-mode fibers. Room-temperature experiments were conducted with an apochromatic objective with numerical aperture (NA) of 0.8 (Attocube Systems, LT-APO/VISIR/0.82) and an oil-immersion objective (Olympus, UPLFLN 100XO12) with a NA of 1.30 for the data in Figure 1f. Cryogenic experiments were carried out in a helium bath cryostat or a low-vibration closed-cycle cryostat (Attocube Systems, attoDRIY1000) with a base temperatures of 4.2 and 3 K, respectively, using low-temperature apochromatic objectives with NA of 0.65 (Attocube Systems, LT-APO/VIS/0.65) and 0.82 (Attocube Systems, LT-APO/VISIR/0.82).

Continuous-wave excitation with a solid-state laser at 532 nm (CNI, MILL-III-532-501) was used in all experiments except for the measurements of data in Figures 3b, 4b, and S6. All FL maps were recorded with circularly polarized excitation except for Figures 2b and S1, where linearly polarized excitation was used. Time-resolved FL data in Figure 3b were measured with picosecond excitation at 532 nm. The FL excitation experiments of Figure 4b were performed with an optical parametric oscillator (Coherent, Mira-OPO with a fwhm spectral bandwidth of 0.5 nm) or a spectrally filtered supercontinuum laser (NKT Photonics, SuperK EXW-12 with a fwhm spectral bandwidth of 0.5 nm). Single-photon counting emission intermittency in quantum dots, nanorods and nanowires. Nat. Phys. 2008, 4, 519–522.

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Additional details on sample fabrication, the experimental setup, the characterization of substrates and PMMA films, the characteristics of quantum emitters in films, and the quantum yield of fluorescent contaminants (PDF)

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**Notes**
The authors declare no competing financial interest.

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