

Wide-Range Spectral Diffusion in Single Mg-Tetraazaporphyrin Molecules in a Polymer Matrix at Cryogenic Temperatures

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Zero-phonon spectral lines of single Mg-tetraazaporphyrin molecules in a polymer matrix and their spectral trails are recorded using cryogenic fluorescence nanoscopy at a temperature of 6 K. Spectral diffusion (stochastic jumps of zero-phonon lines) in an anomalously wide spectral range up to several tens of inverse centimeters is revealed. The structure of the vibronic band in the fluorescence excitation spectrum of single molecules, including both a narrow zero-phonon line and a broad phonon shoulder, is directly observed.

Fluorescence spectroscopy of single molecules at cryogenic temperatures has proven itself in numerous studies as a unique tool for investigating the internal dynamics of doped solids at the microscopic level (see, for example, [1, 2] and references therein). The ability to probe the local dynamics of the medium with the help of single impurity molecules results from the very high sensitivity of zero-phonon spectral lines (ZPLs) to the parameters of the nearest environment (a few to a few tens of nanometers) [3, 4]. For example, the tunneling transitions of matrix atomic groups in two-level systems (TLSs) lead to spectral diffusion, i.e., stochastic jumps of ZPLs [5], and the interaction of the electronic transition in a single molecule with phonon excitations in the medium causes the homogeneous broadening and shift of ZPLs [6, 7]. The parameters of ZPLs also depend significantly on the temperature and other thermodynamic parameters and external fields. Thus, with increasing temperature, the relative intensity of the ZPL decreases owing to a rapid decrease in the Debye–Waller factor [7, 8], and there appears additional broadening caused by the interaction of the single-molecule electronic transition with excitations of the tunneling and phonon types [1, 2].

One of the most informative methods for investigating the internal local dynamics of complex molecular systems is the repetitive detection of the fluorescence excitation spectra of single impurity

molecules using a wide-field luminescence microscope, since the analysis of time evolution is combined in this case with nanometer-accuracy control over the position of the spectral probe [9].

By analyzing, within appropriate models, the spectral trails of single-molecule ZPLs in time and their dependence on external parameters, it is possible to measure the individual characteristics of tunneling TLSs and phonon-type quasi-localized low-frequency modes of the matrix; i.e., one can directly investigate the microscopic nature of these excitations and their relation to the structure of the material, which in itself is a very important task in modern solid-state physics [10]. In addition, data can be obtained on the dynamics of the excited state of the impurity molecule itself, the effect of local fields on luminescence kinetics, photoinduced processes, and various photochemical and photophysical transformations.

One of the strategically important areas in selective spectroscopy and microscopy of single luminescent quantum objects and nanostructures is the search for new efficient luminophors with desired properties.

Among the huge diversity of possible luminescent materials, conjugated heterocyclic chlorophyll-like compounds (porphyrins) and, in particular, metal complexes of porphyrins and their analogs are of special importance [11]. These compounds are widespread in nature (chlorophyll, heme, petroleum pigments), and, as a result, they are ideal model media for studying oxygenation processes in photosynthesis, light-harvesting processes, and energy conversion in biological objects, as well as for the development of new drugs for phototherapy and theranostics and as the basis for a new generation of catalytic systems. New luminophors are of particular interest in the context of making efficient sources of nonclassical light for quantum informatics.

Metalloporphines have become one of the most popular model objects in impurity-center spectroscopy, since the compounds of this series exhibit a high quantum yield of zero-phonon luminescence in a wide range of low temperatures and allow direct investigation of intra- and intermolecular processes, as well as the processes of molecule–matrix interaction. Of particular interest are the issues of photosensitization of singlet oxygen upon the transition of molecular complexes into triplet states and of the possibility of detecting ZPL at relatively high temperatures (above liquid-nitrogen temperatures).

Meanwhile, the detection of the luminescence of single molecular complexes of this class was reported only in a few publications, although such experiments allow direct observation/control of quantum

processes at the single-molecule level. For example, direct fluorescent visualization of the tautomerization process in single porphyrin complexes was carried out in a recent study [12] (appraised as one of the most promising advances in single-molecule spectroscopy). In [13], scanning tunneling microscopy with submolecular resolution was used to investigate the native oscillatory dynamics of the Zn-phthalocyanine molecule. Zero-phonon lines from single porphyrin molecules at cryogenic temperatures were detected only in one experiment [14], where the impurity molecules were embedded in an isotropic ordered matrix of condensed xenon.

The spectroscopy of single impurity molecules in solid matrices is of particular interest for studying the microscopic nature of dynamic processes in disordered solids, since the question of the microscopic nature of low-energy elementary excitations of tunnelling and vibrational types in glasses and polymers remains of much interest to date [15]. The observation of the temporal dynamics of the spectra of probe single molecules makes it possible to directly characterize processes involving tunneling systems and quasilocalized phonon states.

Here, we report on the first experiments on the recording of fluorescence excitation spectra of single Mg-tetraazaporphyrin (Mg-TAP) molecules in a thin polymer film of polyisobutylene (PIB) in a wide spectral range (up to several nanometers) at a temperature of 6 K. The time evolution of ZPLs of single molecules is analyzed.

Mg-tetraazaporphyrin was synthesized according to the modified procedure proposed in [16] and thoroughly purified chromatographically. The structure of the product was determined by NMR spectroscopy, and its purity was confirmed by infrared, absorption, and fluorescence spectroscopy. Polyisobutylene produced by Aldrich was used as the polymer matrix. To make the polymer films, the solution of Mg-TAP molecules in 2-methyltetrahydrofuran was diluted with a solution of PIB in 2-methyltetrahydrofuran and then applied onto a microscope cover glass by standard spin coating technique. The concentration of Mg-TAP was adjusted in such a way that there were a small number (several to several tens) of emitting molecules at a given temperature in the field of view of the microscope for the entire scanning range of the excitation laser. In addition, it was necessary to ensure that the luminescence of only one molecule was excited within any diffraction-limited volume in the sample for each laser frequency.

The experimental setup [9] is a cryogenic luminescence microscope–spectrometer that allows recording fluorescence excitation spectra of single molecules and obtaining their images in the field of view of the microscope (μm). The sample under study (a thin polymer film with a thickness of about several hundred nanometers deposited on a cover glass) was attached to a holder and placed in the focal plane of a Melles Griot wide-aperture microobjective (40x, 0.65 NA). The holder, sample, and microobjective were mounted on a specially designed optomechanical stage that allows focusing the microscope on the sample during measurements. This stage (with the mounted sample and objective) was placed inside a He-4 temperature controlled optical cryostat (RTI, Chernogolovka, Russia) allowing measurements in a wide temperature range from room to 4.2 K. A Lakeshore 93C temperature controller was used to measure the temperature in the cryostat. Single-molecule fluorescence was excited by a Coherent CR-599 tunable dye laser (Rhodamine 6G) with an effective line width of 10 GHz ($\sim 0.3\text{ cm}^{-1}$). Laser wavelength tuning was performed using an intracavity birefringent filter. The wavelength was scanned in a wide spectral range (570– 595 nm) corresponding to the Q-band absorption of Mg-TAP molecules in 2-methyltetrahydrofuran. The scan step was 0.0055 nm ($\sim 5\text{ GHz}/\sim 0.15\text{ cm}^{-1}$ in the 580 nm region).

To automate laser wavelength tuning, the birefringent filter assembly was fitted with a micrometer linear translator with a stepper motor. Wavelength scanning was carried out under the control of an Arduino card. To determine the spectral trails of single molecules, the procedure of repetitive scanning over the same spectral range was performed synchronously with the measurement of the Stokes component of single-molecule luminescence. The calibration of the automated laser wavelength scanning system and the control of the laser wavelength during the experiment were carried out using a portable echelle spectrometer (MORS, Russia).

The laser power was monitored using a Newport 2930C power meter. The intensity of laser radiation focused on the sample into a $\sim 30 \times 30\text{-}\mu\text{m}$ spot was 100–200 W/cm^2 (depending on the spectral range).

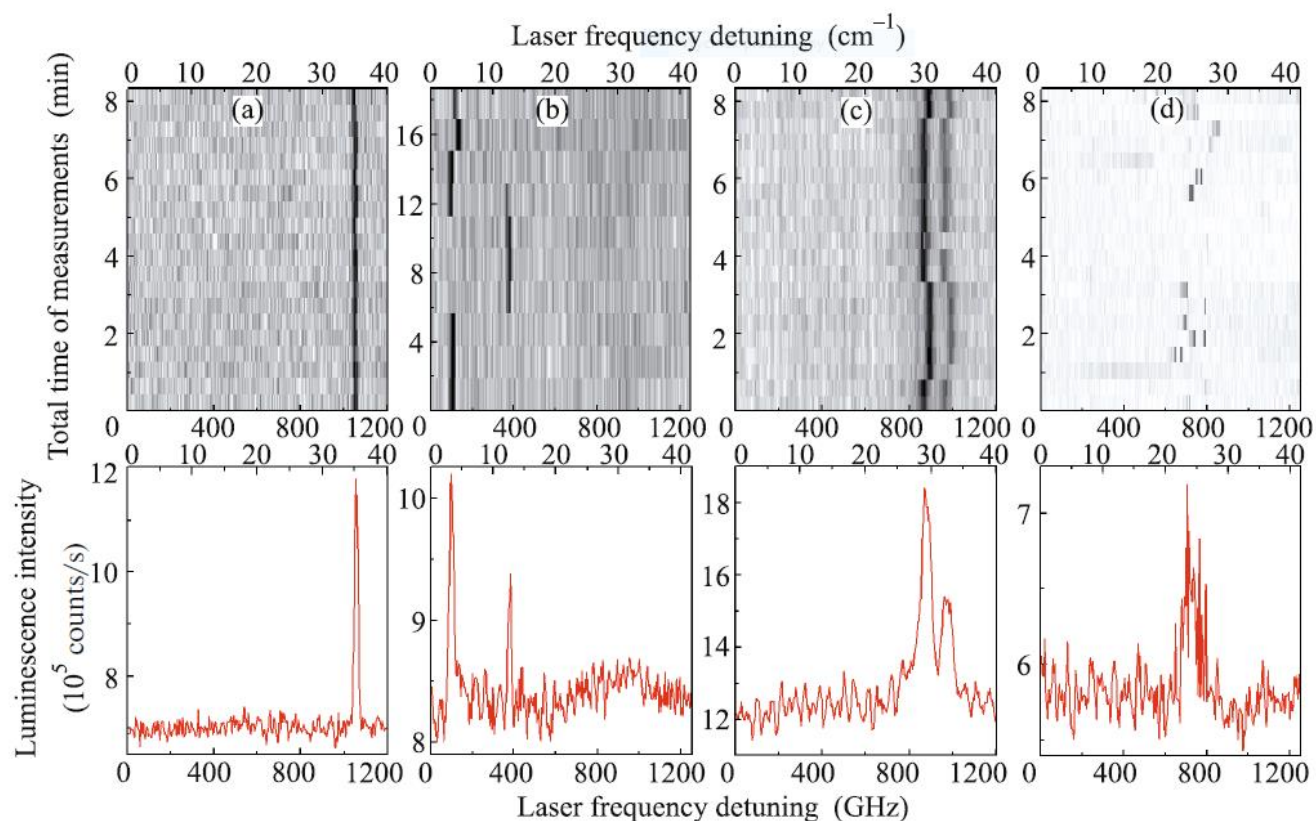


Fig. 1. (Color online) Spectral trails and corresponding integrated fluorescence excitation spectra (upper and lower panels, respectively) for three single Mg-TAP molecules in PIB measured at $T = 6$ K. The molecules exhibit different spectral dynamics: (a) absence of noticeable spectral jumps, (b) jumps between two spectral positions, (c) correlated jumps between four spectral positions, and (d) chaotic irreproducible jumps between multiple spectral positions.

The luminescent images of single molecules obtained in the cryogenic microscope were recorded with a high-sensitivity camera (Andor Ixon Ultra, $QE > 90\%$) with a cooled (-80°C) electron multiplying CCD matrix. The Stokes component of single-molecule luminescence was recorded in the wavelength range from 612 to 644 nm upon scanning the wavelength of excitation laser radiation. To isolate the luminescence of single molecules and to remove scattered laser radiation as well as unwanted luminescence of the sample, we used a set of filters including a Thorlabs DMLP605 dichroic mirror and a Semrock SR628/32 bandpass interference filter. The frequency of the excitation laser was repetitively scanned with the signal accumulation time per frame of 100 ms.

The processing and recognition of fluorescent images of individual molecules and identification and analysis of their spectral trails were carried out using specially developed original software [3]. The spectral trails of several dozen single Mg-TAP molecules in PIB at $T = 6$ K were recorded in this way.

Figure 1 shows typical spectral trails for three single Mg-TAP molecules in PIB, manifesting different temporal dynamics. The spectrum of the first molecule (Fig. 1a) exhibits no measurable jumps. This behavior is of considerable interest in the context of the development of nonclassical light sources based on single molecules, molecular complexes, and/or other quantum emitters. Indeed, a single molecule is by its nature an ideal source of single photons, since the probability of two-photon transitions is very small for most compounds. It is also possible to select compounds with a low efficiency of nonradiative transitions, i.e., with a high luminescence quantum yield. In the case of zero-phonon luminescence, high spectral selectivity can be attained, since ZPLs can be extremely narrow. However, several hindering factors have typically been encountered on the way. These are the occurrence of luminescence blinking and/or spectral diffusion, as well as the need to work at low (cryogenic) temperatures, required for ZPL observation. Zero-phonon lines extremely stable in time were already observed at a temperature of 1.5 K for polyethylene terephthalate molecules in a 1,2-ortho-dichlorobenzene molecular crystal [17]. Here, we see that temporally stable ZPLs can be observed for molecules of metalloporphyrins, in particular, those embedded in a polymer matrix. In addition, the potential for observing single-molecule ZPLs at relatively high temperatures makes these metalloorganic complexes promising for the development of single-photon emitters.

Zero-phonon luminescence from the second molecule (see Fig. 1b) exhibits jumps between two positions, which is indicative of tunneling transitions in an effective TLS with characteristic dwelling times in both states exceeding the laser frequency tuning time in a scan.

Zero-phonon luminescence of the third molecule (Fig. 1c) exhibits correlated jumps between four positions, indicating tunneling transitions in two TLSs. In the first TLS, the rate of tunneling transitions at the temperature of the experiment is much higher than the laser scanning speed; thus, this leads to the splitting of the spectrum into two components. Jumps in the second TLS occur on a time scale considerably longer than the laser scanning time. The interaction of the electronic transition with these two TLSs leads to the observation of a spectral trail featuring repeated “jumps” of the doublet.

Finally, several single molecules exhibited anomalous dynamics manifested in chaotic irreproducible jumps between multiple spectral positions (see Fig. 1d). The absence of spectral dynamics is characteristic of well-ordered crystalline media; reproducible jumps between certain spectral positions correspond to

the conventional model of noninteracting tunneling TLSs and are observed in doped polymers and a number of Shpolskii matrices; and anomalous chaotic dynamics is typical of low-molecular-weight organic glasses and oligomers, as well as impurity molecules located in the surface layers of the material or in ultra-thin films [9, 18].

In the model of noninteracting tunneling TLSs and the stochastic model of random jumps, each transition in the j th TLS interacting with the electronic transition of the impurity molecule leads to a shift in the frequency of the electronic transition of the impurity center by ν_j . Thus, the electronic-transition frequency of the impurity center at time t is determined by the set of independent transitions in all surrounding TLSs and can be written as [19]

$$\omega(t) = \omega_0 + \sum_j \zeta_j(t) \nu_j, \quad (1)$$

where $\zeta_j(t) = 0$ or 1 when the j th TLS is in the ground or excited state, respectively, and ω_0 is the 0–0 transition frequency in the single molecule when all TLSs interacting with this molecule are in the ground state. The frequency shift ν_j can be expressed in the dipole–dipole approximation as

$$\nu_j = 2\pi \Lambda \frac{A_j \varepsilon_j}{E_j r_j^3} \quad (2)$$

where the constant Λ describes the strength of interaction between the chromophore and the TLS, ε_j is the orientation parameter, r_j is the distance between the TLS and the molecule, A_j is the TLS asymmetry parameter, and E_j is the TLS energy.

Numerous studies with impurity molecules (mainly rylene dyes) in solid matrices with different degrees of structural disorder (Shpolskii matrices, polymers, organic glasses) have shown that, at temperatures of liquid He-4 to a few kelvin, the amplitudes of jumps and splittings in electron spectra rarely exceed several gigahertz. The order of magnitude of such jumps can be estimated by calculating the moments of single-molecule spectra measured over a given period of time: the first and second moments will reflect the spectral range of jumps [20].

Scenarios of spectral diffusion processes (reproducibility of spectral positions, the occurrence of drifts, statistical and correlation characteristics) depend on the type of matrix. In well-ordered molecular

crystals, spectral diffusion may be absent; in long- chain polymers, repeated jumps between a fixed set of spectral positions take place (which corresponds to the standard TLS model); and in short-chain oligomers and molecular glasses, irreproducible ZPL dynamics is observed [21].

Analysis of single-molecule spectra for a number of doped polymers and glasses shows that the cited values correspond to TLS energies from a fraction of to a few inverse centimeters, while the distance from TLSs to the molecule varies from a few to a few tens of nanometers [22]. The microscopic nature of TLSs is associated with the existence of groups of matrix atoms for which tunneling transitions between two localized potential minima separated by a potential barrier are possible. The impact on spectral diffusion of isomeric conformational changes of the impurity molecule itself is rarely discussed [23]. At the same time, it should be noted that, in most of the measurements of this kind, continuous laser frequency scanning was carried out in a range not exceeding 30 GHz (owing to the technical characteristics of laser sources used). In this case, the diffusion of ZPL beyond the scanning range will look like the effect of luminescence blinking [5].

The recorded spectra of single Mg-TAP molecules in PIB presented above indicate that ZPLs can exhibit spectral jumps in a significantly wider range, even up to hundreds of gigahertz. The histogram in Fig. 2 shows the distribution of the amplitudes of 120 spectral shifts of ZPLs for single Mg-TAP molecules in PIB. One can see that the peak of this distribution is in the range of 20–30 GHz, which exceeds the typical values for similar measurements for ZPLs of single rylene molecules in PIB under similar conditions [20]. It should be noted that the number of jumps with amplitudes exceeding 30 GHz will increase at higher temperatures because of local structural relaxation processes [24].

Especially intriguing is the tail of the distribution, which is a manifestation of wide-range spectral diffusion. The amplitude of the largest experimentally observed jump was 950 GHz, which corresponds to 32 cm^{-1} or 1 nm in this spectral range.

In the dipole–dipole approximation (see Eq. (2)), such a jump at a temperature of 6 K will correspond to a characteristic distance between the TLS and the single molecule noticeably shorter than 1 nm. This estimate suggests that the observed spectral diffusion is caused by transformations in the Mg-TAP molecule itself. Among the possible mechanisms are conformational isomeric transformations and/or tautomerization, which is typical of porphyrin compounds. The internal dynamics of large molecular

complexes leading to wide-range spectral diffusion has been observed in macromolecules; for example, it was investigated in LH2 light-harvesting macromolecular complexes [25]. It is the internal dynamics of macromolecular systems that can lead to spectral diffusion in an anomalously wide spectral range.

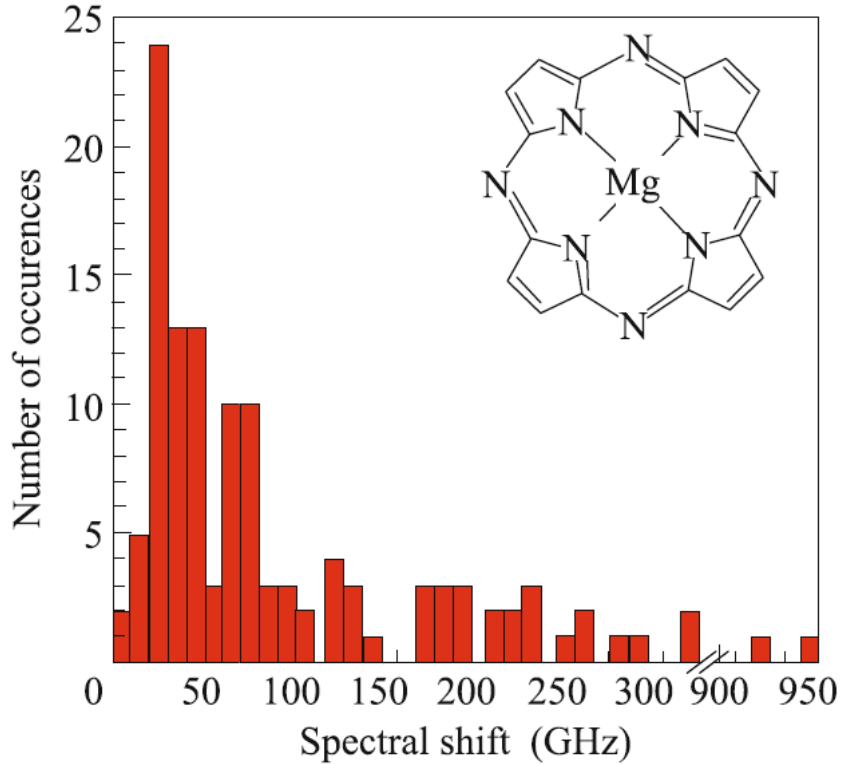


Fig. 2. (Color online) Histogram of the distribution of the amplitudes of 120 ZPL spectral shifts observed in the spectral trails (repetitively recorded fluorescence excitation spectra) of single Mg-TAP molecules in PIB at a temperature of 6 K.

Let us consider in more detail the spectral trail of the Mg-TAP single molecule whose ZPL exhibits the largest spectral jumps of $\nu_j \approx 950$ GHz (Fig. 3). In addition to the fact that wide-range jumps are possible only in the case of small distances between the single molecule and the TLS, as discussed above, this trail demonstrates that the single-molecule spectrum includes not only the narrow ZPL but also a broad higher energy peak, which can be interpreted as the phonon wing.

The ratio of the integrated intensity of the ZPL to the total intensity of the spectral band (Debye–Waller factor) is determined by electron–phonon interaction and is generally expressed as

$$\alpha_{\text{DW}}(T) = \frac{I_{\text{ZPL}}}{I_{\text{ZPL}} + I_{\text{PW}}} = \exp\left(-\int_0^{\infty} g(\nu) \left[\frac{2}{\exp(h\nu/kT) - 1} + 1 \right] d\nu\right) \quad (3)$$

where $g(\nu)$ is the phonon density of states in the matrix. Studies of disordered solids (see [26] and references therein) show that, at low temperatures (from a few to several tens of kelvin), $g(\nu)$ features an anomalous peak (so-called “boson peak”) in the range from several to several tens of inverse centimeters. The methods of selective spectroscopy make it possible to experimentally determine $g(\nu)$ by detecting the phonon wing observed in a homogeneous vibronic band of a selectively excited molecular ensemble [27].

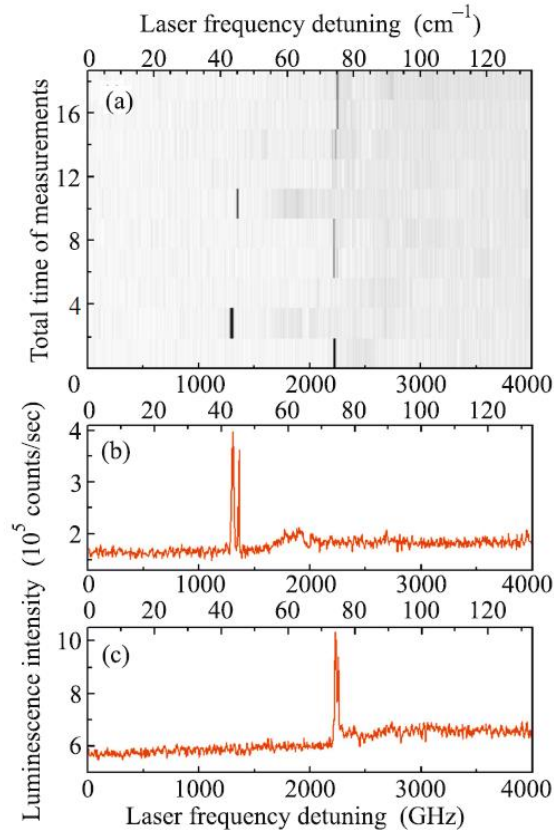


Fig. 3. (Color online) (a) Spectral trail of a single Mg-TAP molecule in PIB at a temperature of 6 K, exhibiting spectral jumps of anomalously large amplitude (950 cm^{-1}). (b, c) Vibronic band consisting of a narrow ZPL and a broad phonon wing for two spectral positions of the ZPL.

Here, we managed for the first time to detect a homogeneous vibronic band for a single molecule in a polymer matrix. The observed phonon wing is an inherent part of the spectrum and exhibits jumps simultaneously with the ZPL. Furthermore, the maximum of the phonon wing is separated by $\omega_{\text{PW}} \approx 15 \text{ cm}^{-1}$ from the ZPL; i.e., it corresponds to the position of the maximum of the boson peak, which determines the phonon density of states in PIB, measured in separate experiments [26]. It is noteworthy that a spectral jump leads to noticeable changes both in the Debye–Waller factor, i.e., in the efficiency of linear electron–phonon interaction in the system, and in the shape of the phonon wing. Apparently, the significant conformational rearrangement of the Mg-TAP molecule and its local environment, leading to the widerange

shift of the ZPL, causes a noticeable change in the parameters of electron–phonon interaction and/or in the local phonon density of states.

In summary, we have for the first time detected zero-phonon spectral lines of single Mg-tetraazaporphyrin molecules in amorphous polyisobutylene at a cryogenic temperature (6 K). Single-molecule fluorescence excitation spectra have been repeatedly recorded in a spectral range as wide as 4000 GHz. Spectral diffusion in an anomalously wide range (up to 950 GHz) has been observed. Apparently, this indicates the occurrence of intramolecular conformational rearrangements of the impurity molecule. Histograms of the distributions of the amplitudes of ZPL spectral shifts give evidence of anomalous tunneling dynamics in the impurity system under study at the level of a single porphyrin molecule and its nearest environment. The observation of time-stable single-molecule ZPLs, i.e., single-molecule spectral trails with no noticeable spectral dynamics, is of considerable interest for applications in the context of the development of nonclassical light (single-photon) sources. The phonon wing has been identified for the first time in the vibronic band of one of the Mg-TAP molecules; the position of this wing with respect to the ZPL corresponds to the position of the maximum of the boson peak in the phonon density of states of PIB (15 cm^{-1}).

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