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The intrinsic non-radiative decay (internal conversion) from the triplet excited state in phosphorescent dyes can be described by a multi-phonon emission process. Since non-radiative decay of triplet excitons can be a significant process in organic light-emitting diodes, a detailed understanding of this decay mechanism is important if the overall device efficiency is to be controlled. We compare a deuterated Pt(II)-containing phenylene ethynylene with its non-deuterated counterpart in order to investigate which phonon modes control to the non-radiative decay path. We observe that deuteration does not decrease the non-radiative decay rate. A Franck-Condon analysis of the phosphorescence spectra shows that the electronic excitation is coupled strongly to the breathing mode of the phenyl ring and the C≡C carbon stretching modes, while high-energy C-H or C-D stretching modes play an insignificant role. We, therefore, associate the internal conversion process with the carbon-carbon stretching vibrations. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3691105]

I. INTRODUCTION

A successful approach to high-performance organic light-emitting diodes (OLEDs) consists in employing efficient phosphorescent organometallic emitters that may be embedded in an organic host matrix.[1] The luminescence efficiency of such a phosphorescent dye depends on ratio between its radiative decay rate, k_r, and the sum $(k_r + \Sigma k_{nr})$ of all decay rates, radiative and non-radiative. Consequently, the phosphorescence efficiency can be increased (i) by enhancing the radiative decay rate, for example, by using π-conjugated ligands with high oscillator strength, (ii) by eliminating sources of extrinsic non-radiative decay, and (iii) by reducing the intrinsic non-radiative decay. When the extrinsic factors such as diffusion to quenching sites (defects, excimers, or other triplets) are eliminated[2,3] and the radiative rate cannot be enhanced further, the intrinsic decay mechanism can become the efficiency-limiting factor. It is also referred to as internal conversion, and it has been studied intensively for aromatic molecules and metal complexes.[4–11]

This non-radiative decay path is usually attributed to a multiphonon emission process described by the energy gap law, $k_{nr} \propto \exp(-\gamma \Delta E/\hbar \omega_M)$. It states that the non-radiative decay rate increases exponentially with decreasing energy ΔE of the excited state and with increasing energy $\hbar \omega_M$ of the highest available energy-accepting phonon mode. γ can be expressed in terms of molecular parameters.[4,5,8] As a result of the energy gap law, fluorescence, which results from singlet states with a high-radiative decay rate and a high energy,

is not limited by internal conversion while the efficiency of phosphorescence, arising from triplet states that have a lower energy and a much lower radiative decay rate, is very much controlled by the internal conversion process, even for complexes containing heavy metals such as Ir, Ru, or Pt.[12] For example, in Pt(II)-complexes, the radiative and the intrinsic non-radiative decay rates are equal for green emitters, yet for red emitters of very similar chemical structure, the non-radiative decay rate can already be three orders of magnitude larger.[13]

A good understanding of the factors controlling the intrinsic non-radiative decay rate of the triplet exciton is therefore an important prerequisite for the design of efficient phosphorescent OLEDs. For aromatic molecules such as benzene, naphthalene, and related phenylene-containing compounds, the high-energy C-H stretching mode at about 3000 cm^{-1} (0.372 eV) has been identified as the main sink of energy in the non-radiative decay process.[4,5,10] Experimental evidence for this assignment was provided by the observation of a reduction of the non-radiative decay rate when replacing C-H by C-D, which reduces the frequency of the vibration from 0.38 eV to 0.28 eV (the isotope) effect.[7,14] In contrast, lower energy phonons from the ring-stretching modes at 0.16 eV have been assigned to the dominant acceptor modes in biphenylene, bipyridine, and phenanthrene complexes of Pt(II), Os(II), or Ru(II) on the basis of the vibronic progression in the 77 K emission profile.[11,15,16]

Here, we have investigated which vibrational modes are involved in the internal conversion of a model phosphorescent conjugated Pt(II)-di-nuclear complex that contains a phenylene ethynylene in its conjugated ligand as shown in Fig. 1. This phosphorescent compound was chosen as model

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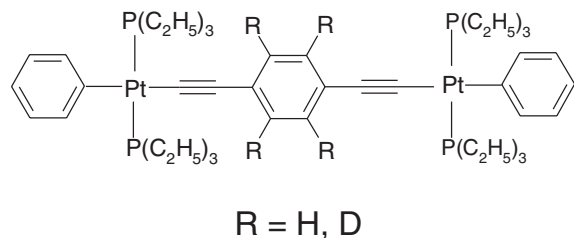
FIG. 1. The chemical structures of the Pt-TBT monomer and its deuterated counterpart.

compound since it is well-characterized and since it has a very clear, well-resolved vibronic progression that allows for a detailed Franck-Condon analysis.[13,17–23] The triplet state in this compound is largely based on the $\pi\pi^*$ transition of the conjugated bridging ligand, implying that the excited state properties essentially reflect the electronic structure of the organic bridging ligand, except for the larger spin-orbit coupling that is due to the metal. Following the methods of Meyer[11,16] and Siebrand[5,7,9,10] we use an approach consisting of Raman measurements, a Franck-Condon analysis of the phosphoresce spectra and a comparison of the non-radiative decay rates in analogous deuterated and non-deuterated compounds.

II. EXPERIMENTAL METHODS

A. Synthesis

All reactions were performed under a dry argon atmosphere using standard Schlenk or glove box techniques. Solvents were pre-dried and distilled before use by standard procedures.[24] All chemicals, except where stated otherwise, were obtained from Sigma Aldrich and checked for purity by GC/MS prior to use. *Trans*-[(Ph)(PEt$_3$)$_2$PtCl] (Ref. 25) was prepared by literature procedures. 1,4-dibromophenylene-d_4 was prepared by catalytic deuteration.[26] Phenylene-1,4-diethynylene and phenylene-1,4-diethynylene-d_4 were synthesized by a sequence of coupling and protodesilylation reactions (Scheme 1).[27] The platinum-containing polymers and monomers[28] were synthesized by the CuI-catalyzed dehydrohalogenation and polycondensation reactions (Scheme 2). The NMR spectra were recorded on a Bruker WM-250 or AM-400 spectrometer in CDCl$_3$. The ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to solvent resonances and ^{31}P{^{1}H}NMR spectra were referenced to external trimethylphosphite. IR spectra were recorded as CH$_2$Cl$_2$ solutions, in a NaCl cell, on a Perkin-Elmer 1710 Fourier transform infrared (FTIR) spectrometer. Mass spectra were measured on a Kratos MS 890 spectrometer by the electron impact and fast atom bombardment techniques. Microanalyses were performed in the Department of Chemistry, University of Cambridge, UK. Preparative thin layer chromatography (TLC) was carried out on commercial Merck plates with a 0.25 mm layer of silica. Column chromatography was performed either on Kieselgel 60 (230–400 mesh) silica gel or alumina (Brockman Grade II–III).
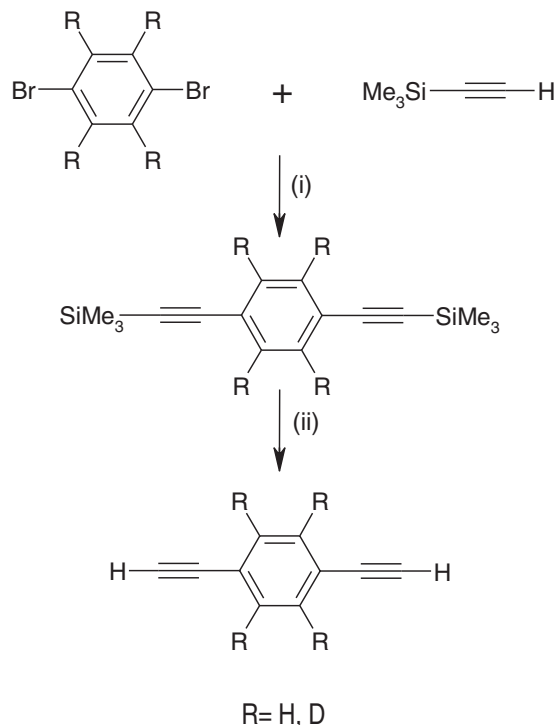
(i) Pd(OAc)$_2$, PPh$_3$, CuI, ^{i}Pr$_2$NH, THF

(ii) OH$^-$, MeOH/THF

SCHEME 1.

B. Photophysical measurements

For measurements in solution or glass, samples were prepared in deoxygenated 2-methyl-tetrahydrofuoran at a concentration of 1×10^{-5} M per monomer in 5×5 mm quartz cells. For thin film measurement, films with a typical thickness of 100–150 nm were spun onto quartz substrates from dichloromethane solutions using a photoresist spin-coater.

Excitation for the Raman scattering measurement was provided by the 1064 nm line of a diode pumped Nd:YAG
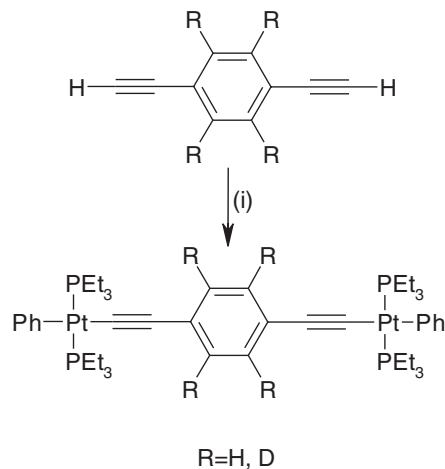
(i) 2[Pt(PEt$_3$)$_2$(Ph)Cl], CuI, ^{i}Pr$_2$NH, CH$_2$Cl$_2$;

SCHEME 2.

laser at an intensity of 1.0 W. A Nexus FTIR/Raman spectrometer (Thermo Nicolet) was used to record the Raman spectra from 250 cm^{-1} onwards. The Raman samples were provided as solids in quartz capillaries. Agreement with thin film spectra was checked using the 633 nm line of a He-Ne laser at an intensity of 10 mW for excitation and a Renishaw Raman Microprobe 1000$^{©}$ microscope which allows detection from 600 cm^{-1} onwards. For the FTIR measurements the polymers or monomers were pressed into KBr pellets with a polymer or monomer content of 0.5% by weight. FTIR spectra were taken using Nicolet 5SXB FTIR spectrometer with a hot filament source for IR radiation.

Thin films were used for ellipsometry and steady-state absorption and emission spectroscopy. Refractive indices were determined with a rotating compensator ellipsometer (J. A. Woollam M2000) using a uniaxial model fitting procedure.[29] The model fit was shown to be Kramer-Kronig consistent. The optical absorption was measured with a Hewlett-Packard ultraviolet-visible (UV-VIS) spectrometer. Measurements of photoluminescence spectra (PL) were made with the sample in a continuous-flow helium cryostat. For the PL spectra, excitation was provided by the UV lines (334–365 nm) of a continuous wave argon ion laser. Typical intensities used were a few mW/mm^2. The emission spectra were recorded using a spectrograph with an optical fiber input coupled to a cooled charge coupled device array (Oriel Instaspect IV) and displayed after background correction.

For lifetime measurements in glassy phase, a nitrogen laser (Spectra Physics) was used with an output of 20 μJ at 337 nm (20 Hz, ~500 ps pulses). The emission was recorded using a FLS920 spectrofluorimeter (Edinburgh Instruments) in multi-channel-scaling mode. The temporal resolution of this setup was found to be around 100 ns. The samples were cooled to 80 K in a nitrogen cryostat (Oxford Instruments).

III. FRANCK-CONDON ANALYSIS

Luminescence and absorption spectra show vibronic peaks that arise from electron-phonon coupling in conjugated polymers. These peaks are a signature of the vibrational normal modes which couple to the electronic excitation during a transition. Therefore, the analysis of these spectra can indicate the magnitude and nature of the distortion of the excited states in such materials. For a particular vibrational mode i, the probability of the transition from the 0th vibrational level of the excited state to the mth vibrational level of the ground state is given by the Franck-Condon factor for a displaced oscillator and is denoted here by I_{0-m_i}:[30]

$$I_{0-m_i} = \frac{e^{-S_i} S_i^{m_i}}{m_i!}, \tag{1}$$

where m ($m = 0, 1, 2, 3, \dots$) indicates the vibrational transition and S_i is the Huang-Rhys factor for the vibrational mode i. The Huang-Rhys parameter is related to the horizontal displacement, ΔQ_i, of vibrational mode i in the excited state relative to the ground state by

$$S_i = \frac{M_i \omega_i}{2\hbar} (\Delta Q_i)^2, \tag{2}$$

where M_i is the reduced mass and ω_i is the angular frequency of the vibrational mode. The phosphorescence can then be modeled by Eq. (3),[31]

$$P(\hbar\omega) \propto (n\hbar\omega)^3 \sum_{m_i=0} \prod_i I_{0-m_i} \Gamma\delta[\hbar\omega - (\hbar\omega_0 - m_i\hbar\omega_i)], \tag{3}$$

where the cubed product of the refractive index n with the energy $\hbar\omega$ gives the influence of the photon density-of-states in the medium surrounding the emitter on its emission rate. In this equation, for each mode i, and each vibrational level m_i, a Gaussian with intensity I_{0-m_i} is centred at the phonon energy $\hbar\omega_i$ away from the 0-0 peak of the electronic transition at $\hbar\omega_0$. In the Franck-Condon analysis presented here, the Gaussians were kept at a fixed full-width-at-half-maximum for all the vibronic components. The energies $\hbar\omega_i$ of the phonon modes were taken from the Raman spectra, and the refractive index n was determined by ellipsometry. Eight vibrational modes i and four vibronic transitions m_i were used to fit the spectra. The only free fitting parameters were the I_{0-1_i} intensities of the eight vibrational modes i, the other parameters are fixed by Eqs. (1)–(3). From the fit, we obtain the Huang-Rhys parameters S_i for the individual modes. They can be used to calculate the relaxation energy associated with the distortion of each mode by $E_{rel_i} = S_i\hbar\omega_i$. The total relaxation energy of the molecule is than given by $\sum E_{rel_i} = \sum S_i\hbar\omega_i$.

IV. RESULTS

A. Synthesis

The platinum-containing polymers and monomers were synthesized by adaptation of the synthetic route reported by Hagihara *et al.*[32] The reaction products were fully characterized by analytical and spectroscopic methods (IR, ^{1}H, ^{13}C, and ^{31}P NMR) and molecular weight determination; some of the important results are shown in Table I. The spectroscopic data confirm the formulations illustrated in Fig. 1 and Scheme 2. The IR, ^{13}C, and ^{31}P NMR data are consistent with those observed for other platinum-containing arylene-ethynylene polymers and monomers reported previously.[19, 28, 33] Deuteration shows no significant effect on the ν(C≡C) stretching frequency.

B. Spectroscopy

The vibrational normal modes $\hbar\omega_i$ of the materials were obtained using FTIR and Raman spectroscopy. The FTIR measurements were undertaken in order to assess the effect of deuteration. The Raman and FTIR spectra of the non-deuterated and deuterated compunds are shown in Figure 2. The assignment and labeling of the peaks are described in Table II together with their approximate wavenumbers and energies. The FTIR spectra are dominated by the strong modes centered around the 2900 cm^{-1} region associated with the C-H stretches in the alkyl side chains b. The carbon triple bond stretch (C≡C) 7 is observed at 2100 cm^{-1} and the modes below 1500 cm^{-1} are associated with the benzene ring. A high energy C-H stretching mode a at 3050 cm^{-1} of low intensity is observed in the FTIR spectra. Upon deuteration of the

TABLE I. Synthetic and spectroscopic data for the Pt-containing non-deuterated (Pt-TBT H) and deuterated (Pt-TBT D) monomer.

Compound	Yield (%)	M^+/M_w (gmol^{-1})	ν(C≡C) (cm^{-1})	^{13}C(C≡C) (ppm)	^{31}P{^{1}H} (ppm)
Pt TBT H	78	1141.19	2096	106.73, 106.56	−131.17, $^1J_{Pt-P}$ = 2643 Hz
Pt TBT D	72	1145.19	2097	107.23, 107.06	−131.17, $^1J_{Pt-P}$ = 2639 Hz

bridging ligand, this peak disappears and a lower energy C-D peak *c* appears at 2255 cm^{-1}. This is a result of the isotope effect which dictates that the C-D modes in the deuterated compounds will have their energies reduced by a factor of 0.74 from those of the C-H modes in the non-deuterated compounds as a result of the increased mass of D compared to H.[34] The peak *a* still exists in the deuterated compound as the benzene ring end caps have not been deuterated. From the above analysis it is evident that deuteration of the bridging ligand has been successful.

The Raman spectra indicate which modes couple to the electronic transitions. In fact, under certain conditions, the intensities of the Raman peaks scale with the square of the normal mode displacements.[35,36] For our compounds, the Raman spectra show a group of very weak peaks at 3020–3070 cm^{-1} (labeled a in Fig. 2) that is a characteristic range for the C-H stretching mode on the benzene rings of the phenylene ethynylene bridging ligand and the phenyl end caps of the monomer compound, respectively. The latter cause a characteristic group of bands at 3020–3040 cm^{-1}. The bridging ligand causes two bands at 3050 and 3065 cm^{-1} which are only visible in the non-deuterated compound. In the

region around 3000 cm^{-1}, there is also another, only slightly more intense band at 2900 cm^{-1} (labeled b in Fig. 2), which is associated to the many C-H stretching vibrations of the alkyl substituents of the phosphine ligand. The high energy modes that are prominent and of high intensity in the Raman spectra are the C≡C stretching mode 7, the benzene breathing mode 6, and, for the non-deuterated compound, the C-H in plane bending mode 4 at 1170 cm^{-1} that is on the benzene ring. Upon deuteration this peak disappears and a lower energy C-D in-plane mode 2 is observed in the Raman spectra at 860 cm^{-1} instead.

For an accurate Franck-Condon analysis of the thin film phosphorescence spectra, the refractive index *n* of the compound was measured. The refractive index was determined by spectroscopic ellipsometry measurements as described by Ramsdale and Greenham [29] and is shown in Figure 3 together with the absorption spectra (dashed lines) for the deuterated monomer. As expected, dispersion is strong near the optical gap while it is weak near the triplet energy of around 2.5 eV. This makes the refractive index correction less significant for phosphorescence than for fluorescence.

The coupling of the electronically excited state to the vibrations of the molecule is also manifested in the vibrational progression observed in the emission spectrum. Figure 4 shows the phosphorescence spectra of the deuterated and non-deuterated compounds (dotted lines) measured from thin films at 10 K. The emission from the non-deuterated compounds agrees well with thin film or frozen solution (glass) spectra reported earlier.[21,22] The phosphorescence spectra taken with these samples diluted into 2-methyl-tetrahydrofuran (MeTHF) glass were found to be identical. Also shown are the fits (solid lines) obtained using Eq. (3) with the modes 0–7 determined from Figure 2 and with the refractive index
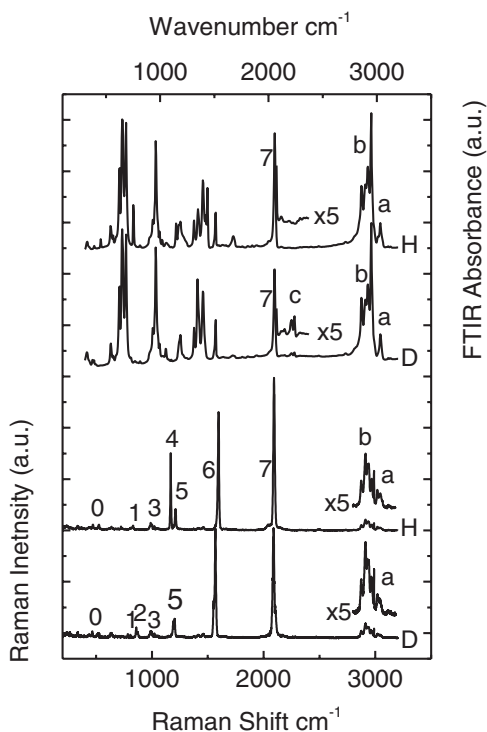

FIG. 2. The FTIR and Raman spectra of non-deuterated (H) and deuterated (D) Pt-monomer. The assignments of the peaks are discussed in detail in Table II.

TABLE II. Approximate wavenumbers and energies of Raman (0–7) and FTIR (a)–(c) peaks as shown in Figure 2 and their assignments.

| Vibrational modes *i* and Assignment		Wavenumber (cm^{-1})	Energy (meV)
0	Pt-C stretch	470	61
1	C-C-C quadrant in plane stretch	840	104
2	C-D in plane bend on benzene ring	860	107
3	Not assigned	1055	131
4	C-H in plane bend on benzene ring	1170	145
5	C-C/C = C stretch in benzene ring	1200	148
6	Benzene breathing mode	1600	198
7	C≡C stretch	2100	260
a	C-H stretch on benzene ring	3050	378
b	C-H stretch on the alkyl side chains	2900	360
c	C-D stretch on benzene ring	2255	280
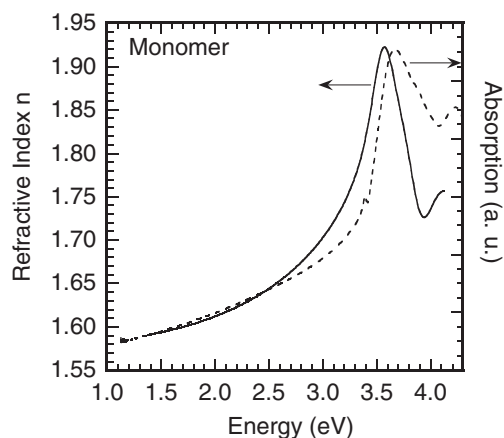
FIG. 3. The refractive index (solid lines) and absorption spectra (dashed lines) of the deuterated Pt-containing monomer. The non-deuterated analogues have very similar refractive index dispersions.
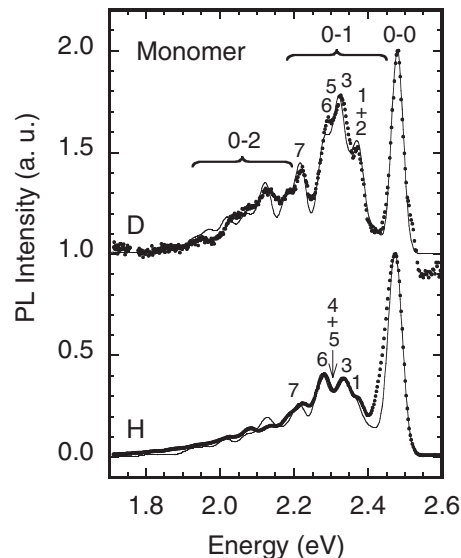

FIG. 4. Thin film phosphorescence spectra of the deuterated and non-deuterated compounds at 10 K (dotted lines) and the Franck-Condon fit (solid lines).

of Figure 3. The effect of including the C-H or C-D stretching modes labeled a or c was checked but their intensity was found to be indiscernible. The values extracted from the fit for the Huang-Rhys parameters are given in Table III. Our results are in general agreement with earlier work by Beljonne *et al*. on the non-deuterated systems.[18] We find an overall Huang-Rhys parameter of 1.1 and a corresponding relaxation energy of 180 meV. This relatively low value of the lattice relaxation may be attributed to the stiffness of the carbon-carbon triple bond. As can be seen from the table, the carbon triple bond 7 takes up only about a quarter of the lattice relaxation energy, while bulk of the lattice distortion occurs across the phenyl ring (modes 6, 5, and 4). The modes that couple most strongly to the electronic transition are the phenyl ring breathing mode 6 ($S = 0.35$) and the CC triple bond stretching mode 7 ($S = 0.17$). Upon deuteration, the higher mass of the deuterium causes a slightly larger overall geometric distortion and, notably, a significantly larger distortion of the C-C/C $=$ C stretching mode 5 in the benzene ring (on which the deuterium is attached), as evidenced by the triple value of the Huang-Rhys parameter. Obviously there is some degree of coupling between the in-plane bending and the C-C/C $=$ C streching modes on the phenyl ring for the monomer.

Having considered the effect of deuteration on the vibronic coupling by Raman, FTIR and phosphorescence spectra, we now consider the effect of deuteration has on the non-radiative decay rate by measuring the triplet lifetimes. Figure 5 shows the decay of the phosphorescence signal in the non-deuterated and deuterated compounds, measured at a concentration of 10^{-5} M (per repeat unit) in a MeTHF glass at 80 K. The low concentration in glass ensures an absence of non-radiative decay channels by inter-molecular interactions such as diffusion to excimer sites, defect sites or triplets on other molecules. A monoexponential fit to the phosphorescence decay yields lifetimes of about 140 μs, consistent with earlier measurements made on thin films.[13] Upon deuteration, we do not observe any noticeable change of the decay lifetimes.

V. DISCUSSION

The aim of this study is to find out whether carbon-carbon or carbon-hydrogen stretching modes are responsible for the non-radiative deactivation of an excited triplet state in Pt-containing phenylene etynylenes. Following the work of Meyer on organometallic complexes[11,16] and Siebrand on aromatic hydrocarbons,[4–10] we have used a threefold approach

TABLE III. The phonon energies ($\hbar\omega_i$) of the different vibronic modes as determined from Figure 2 and the Huang-Rhys parameters S_i calculated from the phosphorescence spectra (Figure 4). The relaxation energy associated with each mode $E_{rel, i} = S_i \hbar\omega_i$ is also shown along with the total relaxation energies of the individual materials $E_{rel} = \sum_i E_{rel,i}$.

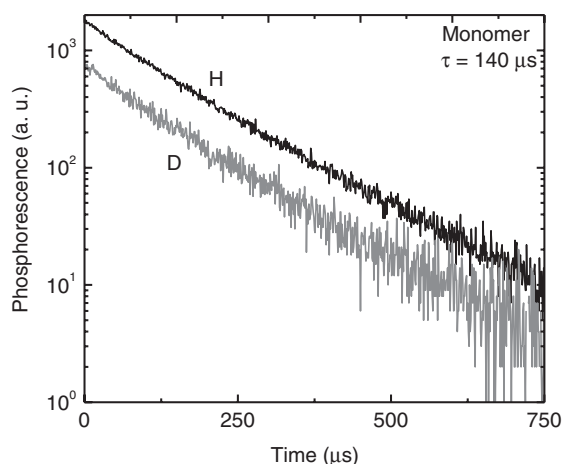| Vibrational Modes i	0	1	2	3	4	5	6	7	
				Monomer Pt-TBTH					
$\hbar\omega_i$	0.061	0.104	…	0.131	0.145	0.152	0.198	0.261	
S_i	0.12	0.11	…	0.08	0.14	0.14	0.35	0.17	$\sum S_i = 1.11$
E_{rel_i}	0.007	0.011	…	0.011	0.020	0.021	0.070	0.044	$\sum E_{rel_i} = 0.18$
				Monomer Pt-TBT D					
$\hbar\omega_i$	0.061	0.103	0.108	0.130	…	0.158	0.195	0.261	
S_i	0.10	0.14	0.09	0.11	…	0.42	0.34	0.18	$\sum S_i = 1.38$
E_{rel_i}	0.006	0.014	0.010	0.014	…	0.028	0.066	0.047	$\sum E_{rel_i} = 0.19$

FIG. 5. The decay of the phosphorescence measured at 10-5 M (per repeat unit) in MeTHF at 80 K. The laser pulse occurs at 0 μs.

based on Raman measurements, an analysis of the phosphorescence spectra and lifetime measurements of the deuterated compounds. We will first address the lifetime measurements. Deuteration can only have an effect on the experimentally measured lifetime $\tau = (k_r + \sum k_{nr})^{-1}$ when the intrinsic non-radiative decay by multiphonon emission takes place with a rate that is at least comparable to the radiative decay or other non-radiative decay processes. We will assess whether this condition is fulfilled for our material. In general, sources for non-radiative decay are internal conversion with k_{nr}^0 and diffusion to all kinds of quenching sites (including other triplets) with k_{nr}^q, i.e., $\sum k_{nr} = k_{nr}^0 + k_{nr}^q$.

We measured a lifetime of about 140 μs, similar to the value of 125 μs reported for thin films at 10 K.[13] The Pt-monomer has a radiative lifetime of about 2×10^3 s^{-1},[13,23] implying that $\sum k_{nr} = 5 \times 10^3$ s^{-1}. This is very similar to the 10 K thin film value of 6×10^3 s^{-1}.[13] Recent studies on triplet diffusion in short oligomers have shown that even in thin films at 10 K, triplet diffusion between oligomers is negligible,[3] and thus for a well-dispersed Pt-monomer at 10^{-5} M in a MeTHF glass at 80 K, one can also safely conclude that there are no diffusion-controlled non-radiative decay processes present. Thus, the value of 5×10^3 s^{-1} derived for the non-radiative decay rate corresponds to the intrinsic decay by internal conversion, k_{nr}^0. The lack on any lifetime changes upon deuteration of the central phenyl ring thus pertains to an unchanged internal conversion rate.

In addition to the Pt-monomer, we have also investigated the associated Pt-polymer. For the polymer, however, triplet diffusion takes place along the polymer chain,[20,22,37] leading to a high non-radiative decay rate due to triplet diffusion of $k_{nr}^q = 17 \times 10^3$ s^{-1}. This large extrinsic decay rate obscures any effect of deuteration on the intrinsic decay rate, implying that the Pt-polymer is not suitable to investigate what is the source for the intrinsic non-radiative decay. For reference, the data obtained on the Pt-polymer are deposited as supplementary material.[38]

While we were able to replace C-H by C-D in the central phenyl ring of the monomer, the phenyl ring end caps could not be deuterated as the synthetic approach taken does not al-

low for this. This is not ideal and requires a brief discussion of the role of the C-H on the phenyl end caps. We point out that for the Pt-monomer, the $\pi\pi^*$ triplet excited state is largely localized on the central phenyl ring, with minor contributions reaching into the adjacent carbon-carbon triple bonds. This is well established through quantum chemical calculations by Beljonne *et al.*[18] and by Glusac *et al.*[21] who show that bond length distortions between S_0 and T_1 are restraint to the section between two platinum atoms. Since the triplet excited state of the Pt-monomer does not extend beyond the platinum into the phenyl end caps, it can also not be affected by any C-H bonds there. This is well known from partial deuteration experiments on acenes, where it was shown that C-H bonds only affect the internal conversion when the excited state has some electron density there.[39] In a similar way, the C-H bonds on the butyl side groups are irrelevant to the non-radiative decay, as the excited state is not located on them. We, therefore, come to the conclusion that the absence of any change in the phosphorescence lifetime upon deuteration of the central phenyl ring in the Pt-monomer suggests that C-H stretching modes are not involved in the radiationless deactivation of the triplet excited state.

To understand this experimental observation, it is useful to recall that the rate for internal conversion, derived from a Fermi-golden rule expression, depends on the product of several terms,[40]

$$k_{nr}^0 = \frac{2\pi}{\hbar} \varrho_n \langle \Lambda_n | \Lambda_m \rangle^2 \sum_k c_k, \qquad (4)$$

where ϱ_n is the density of states (DOS) in the final electronic state manifold, Λ_i is the total vibrational function of the electronic state i and c_k is an electronic coupling term containing the vibronic coupling integral associated with the vibrational mode k. The final DOS is of no concern for our study. The Franck-Condon term $\langle \Lambda_n | \Lambda_m \rangle^2$ essentially quantifies how efficiently energy is dissipated by vibrations (that are then referred as "acceptor" modes). The $\sum_k c_k$ term is a measure for the vibrationally induced, non-Born-Oppenheimer coupling between two electronic states. It contains contributions from spin-orbit interactions and, importantly, from nuclear momentum integrals $\langle \Phi_n | \partial/\partial Q_k | \Phi_m \rangle$. Modes which are effective in the vibronic coupling process are called "promoter" modes. From Eq. (4), it is obvious that the intrinsic non-radiative decay rate will depend on both the acceptor modes and the promoting modes.

When Eq. (4) is evaluated, the theory of non-radiative decay distinguishes between the strong coupling limit, i.e., the case of strong molecular distortion upon excitation ($S > 2$), and the weak coupling limit given for $S < 1$.[8,41] In the strong coupling regime, the non-radiative decay can take place by all vibrational modes, and thus a weighted average vibrational frequency, often dominated by C-C stretching modes, controls the non-radiative decay. Consequently, deuteration has little effect on the non-radiative decay rate. While this regime sometimes applies to heavy metal complexes, the Franck-Condon analysis of the Pt-monomer used here yields an overall Huang-Rhys factor of 1.1. Therefore, the strong coupling regime cannot be invoked to account for the lack of deuteration effect.

In the weak coupling limit that thus applies to our compound, evaluation of the Franck-Condon term $\langle \Lambda_n | \Lambda_m \rangle^2$ in Eq. (4) results in the exponential energy dependence of k_{nr}^0 known as energy gap law, and its domination by the vibration with the highest frequency. The chemical structure of the Pt-monomer contains a number of normal modes. The mode with the highest frequency is the C-H stretching vibration, and this should thus be the acceptor mode, that is, most efficient in dissipating the excited state energy. The fact that we do not observe any change in lifetime upon deuteration suggest therefore that the vibronic coupling term for the C-H stretching mode must be very small. This conclusion is further supported by the Raman measurement and by the Franck-Condon analysis. The intensity of the Raman peaks is related to the normal mode displacement upon electronic excitation. The C-H and C-D stretching modes have very low Raman intensities, while the C-C triple bond and the phenyl ring breathing modes both feature prominently. Equally, explicit inclusion of the C-H and C-D stretching vibrations in the Franck-Condon fits results in them having zero intensity, while the C-C triple bond stretching vibration and in particular modes associated with phenyl ring show up strongly. This is consistent with the calculations by Beljonne *et al.*[18] and Glusac *et al.*,[21] that indicate a strong distortion, associated with a more quinoid character, across the central phenyl ring. From these data it seems that the optical excitation couples well to the phenyl ring breathing mode 6 and to the carbon-carbon triple bond stretching mode 7, while coupling to C-H stretching modes is poor. Therefore, modes 6 and 7 can be considered as efficient promoters for the intrinsic non-radiative decay in the Pt-monomer. This raises the question which mode may be the dominant acceptor mode that controls the non-radiative decay according to the energy gap law. Despite its high energy, the C-H stretching mode cannot act as an accepting mode as it is poorly coupled to the electronic excited state. After the C-H stretch, the next highest frequencies are given by the C-C triple bond and stretching mode and by the phenyl ring breathing mode. While both modes couple efficiently to the electronic excitation, we note that due to the exponential dependence on the frequency, even a rough estimate quickly shows that the triple bond vibration clearly dominates.

We, therefore, come to the conclusion that the dominant modes promoting the intrinsic non-radiative decay in the Pt-monomer are the C-C triple bond stretching mode and the phenyl ring breathing mode. As dominant acceptor mode we consider the C-C triple bond vibration. Our results are consistent with the body of work established by Meyer and co-workers[11,15,16] who find the triplet energy in organometallic complexes with bipyridine ligands to be dissipated by carbon-carbon skeletal stretching modes. We feel our work also agrees with Henry *et al.*, McClanahan *et al.*, Maruszewski *et al.* and others who by partial deuteration experiments and by the detailed quantitative analysis highlighted the crucial role of the promoting mode.[39–41] Finally, as the electronic structure of the triplet excited state in our compound is controlled by the π-conjugated system on the phenylene ethynylene ligand while the influence of the metal d orbital is essentially reduced to providing the spin-orbit coupling, we conjecture that our result may also be applicable to related analogous organic compounds, as long as the internal non-radiative decay is not limited by spin-orbit coupling.

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