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Picosecond Studies of Energy Transfer in Photoexcited Mixed Organometal Chelates

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Energy transfer in a single crystal of $[\text{Rh}(\text{phpy})_2\text{bpy}]\text{PF}_6$, substitutionally doped with 0.9% $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ ($\text{phpy}^- = 2\text{-phenylpyridine}$, $\text{bpy} = 2,2'\text{-bipyridine}$, and $\text{thpy}^- = 2,2'\text{-thienylpyridine}$), is studied from picosecond transient phosphorescence measurements in the temperature range from 130 up to 290 K. The cation complexes of host and guest compounds both exhibit a lowest excited $^3\pi\pi^*$ state, localized on one phpy^- or thpy^- ligand, respectively. The emission spectrum of the undoped crystal is characterized by luminescence from an A trap, 98 cm^{-1} below the origin of the host absorption. In the mixed crystal, the emission spectrum is dominated by luminescence from the deep Ir^{3+} trap (3200 cm^{-1} below the host band). After picosecond pulsed laser excitation, a decay of the phosphorescence intensity of the A trap within about 100 ns is observed; the decay of the A-trap emission is accompanied by a rise in the intensity of the Ir^{3+} -trap phosphorescence on the same time scale. The A-trap luminescence decay is attributed to intermolecular energy transfer, and its time behavior can be simulated using a 3D-exchange interaction model. In addition, it is found that, upon increasing the temperature, the characteristic time for hopping between nearest donor species is increased. It is argued that, at higher temperatures, the excitation hopping is among spatially extended donor states, characteristic of eigenstates of donor clusters. Due to the longer lifetime of these cluster eigenstates intercluster energy transfer is effectively slowed down.

Introduction

Dynamical studies of intra- and intermolecular electronic energy transport in solids are of great importance for the understanding of the details of energy-transfer mechanisms in many different systems.^{1,2} Much focus has been on organic mixed molecular crystals exhibiting orientational and substitutional disorder.³ For instance, site-selective phosphorescence studies concerning the dimensionality and the dynamics of the spectral diffusion processes (representative of the spread out of photo-excitations from energetically higher-lying donor molecules to energetically lower-lying acceptor molecules) have been reported for orientationally disordered crystals of 1-bromo-4-chloronaphthalene (BCN)⁴ and BCN doped in 1,4-dibromonaphthalene (DBN).⁵ From a theoretical point of view, ever since the seminal contributions by Förster⁶ and Dexter,⁷ the analysis of energy transfer has been further developed, e.g., in the case of three-dimensional exchange interactions by Inokuti and Hirayama,⁸ whereas the formalism was generalized to all dimensions, including multipolar interactions, by Blumen et al.⁹

The influence of cluster formation on the effective energy-transfer rate constant has been extensively studied. For substitutionally disordered naphthalene crystals, a significant decrease in the trap-to-supertrap energy-transfer rate constant was found when the trap concentration was increased from 4% to 8%.¹⁰ The effect was attributed to the formation of clusters of the trap molecules, from which long-range energy transport to other clusters and supertraps is suppressed. These findings were supported by Monte Carlo simulations of the distribution of trap sites in the crystal lattice as a function of the trap concentration.¹⁰ The role of dopant-induced energy funnels of host molecules has also been discussed. For singlet exciton transfer in a β -methylnaphthalene (BMN) doped naphthalene crystal, the sequential nature of the exciton trapping process

via the BMN-induced X-traps was experimentally observed by picosecond time-resolved fluorescence.^{11a} In the case of DCB (*p*-dichlorobenzene) doped DBB (*p*-dibromobenzene) crystals, the experimentally determined stretched exponential decay behavior of the monomer phosphorescence intensity has been attributed to hopping to guest aggregates by tunneling via the host sites in the energy funnels below the host exciton band.^{11b,c} Numerical simulations of this process revealed the contribution of different mechanisms at distinct intervals of length and time during energy transport.^{11d} Using a model with exponential hopping rates between donor sites and an energy staircase of guest states, the simulations are in agreement with the experiments for a doping concentration above 3%.^{11e}

Relatively few studies of electronic energy transport have been reported for molecular crystals of organometal chelates. For example, for TMMC (tetramethylammonium manganese(II) trichloride)¹² and $\text{Pd}^{\text{II}}(\text{phbpy})\text{Cl}$,¹³ the crystals are characterized by one-dimensional stacks of molecules predominantly leading to one-dimensional, intrachain energy transfer by way of exchange interactions, with only a minor contribution of interchain transfer.

In this paper, we examine the transfer of photoexcitations in a neat crystal of $[\text{Rh}(\text{phpy})_2\text{bpy}]\text{PF}_6$, substitutionally doped with 0.9% $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$, where the ligands are $\text{phpy}^- = 2\text{-phenylpyridine}$, $\text{bpy} = 2,2'\text{-bipyridine}$, and $\text{thpy}^- = 2,2'\text{-thienylpyridine}$. Recent experiments by Zilian et al.¹⁴ performed on a 1% $[\text{Rh}(\text{thpy})_2\text{bpy}]^+$ -doped $[\text{Rh}(\text{phpy})_2\text{bpy}]\text{PF}_6$ crystal yielded an estimate for the rate of molecular host-to-host energy transfer of $\geq 10^9\text{ s}^{-1}$. The $[\text{Rh}(\text{phpy})_2\text{bpy}]\text{PF}_6$ crystal has orthorhombic symmetry, and the complex cations form two sets of four cations each per unit cell; the two sets are related to each other by inversion symmetry.¹⁵ In the crystal, the lowest excited state of the Rh^{3+} and Ir^{3+} chelates was previously determined to be a $^3\pi\pi^*$ state, where the triplet excitation is localized on one of the cyclometalating ligands thpy^- or phpy^- .^{14–17} The dopant $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ complex acts as a deep energy trap, about 3200

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cm^{-1} below the origin of the host-complex emission at 22128 cm^{-1} . Moreover, the host crystal contains A traps (with a lowest excited level of about 100 cm^{-1} below the host band), these traps probably being a distorted host cation or a host cation with a defect ligand. In this paper, we study by means of picosecond optical emission spectroscopy energy migration from A traps to deep Ir traps. We will show that the energy transfer is a thermally activated hopping process involving excitations localized at the organic ligand sites in the molecular crystal. It is found that upon raising the temperature, energy transfer slows down. To interpret the phenomenon, it is proposed that at higher temperatures, energy transport develops via clusters of donor sites with relatively long lifetimes. Eventually, the excitation is transferred from the clusters to the deep trap sites, and thus, the overall trapping rate is found to decrease.

Experimental Section

Phosphorescence transients of the shallow A trap and deep $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ trap were measured using picosecond laser excitation of the crystal in combination with the single-photon-counting detection technique. Single crystals of $[\text{Rh}(\text{phpy})_2\text{bpy}]\text{PF}_6$ doped with 0.9% $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ were placed inside a Suprasil quartz tube, which was mounted inside a home-built small-size liquid nitrogen flow cryostat. By means of a Cryoson 17-90B/1 temperature regulator, attached to the liquid nitrogen supply, the temperature was varied in the range 130–290 K, with intervals of 20 K. The temperature was stabilized to within 1 deg. For the measurements below 10 K, the sample was placed inside a Dewar Suprasil flow tube and cooled by the controlled boil-off from a liquid helium container.

A Coherent Innova 200-15 Ar^+ ion laser was used as a pumping source, operating at a wavelength of 514 nm and mode-locked with a repetition frequency of about 74 MHz by a Coherent 468 mode locker. With this laser, a Coherent 700 dye laser was pumped, using DCM Spezial as a dye, outfitted with a Coherent 7200 cavity dumper, which selected 1 in 10 pulses. To match the lifetime of the compounds under investigation, the repetition frequency was lowered to 188 kHz. The laser wavelength near 630 nm (with typical power of 100 mW) was frequency-doubled using a BBO frequency-doubling crystal, yielding UV light with a wavelength of 317 nm and power of $300 \mu\text{W}$. The shape of the picosecond pulses delivered by the laser was determined using a home-built autocorrelator connected to a Tektronix B081341 oscilloscope. Gaussian-shaped pulses with a typical pulse duration of 8 ps were obtained. To avoid damage of the crystals, the laser beam for exciting the crystals was slightly defocused and its power was attenuated down to about $100 \mu\text{W}$ in the UV. Detection of the emission light was at an angle of 90° to the excitation beam, using a Zeiss M20 monochromator outfitted with a Hamamatsu R3809 CT13 GaAs photomultiplier tube. The detection wavelength was fixed at the emission maxima of 454 nm of the A trap or 533 nm for the $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ emission, respectively. The photomultiplier tube, operating in the single-photon-counting mode, was connected to an EG&G Ortec 918 multi-channel buffer, a Tennelec TC 486 TAC/biased amplifier, and Tennelec TC454 and TC455 Quad constant fraction discriminators (CFDs). A personal computer was used for data storage and analysis. The time resolution of the picosecond emission setup is better than 25 ps. The time span for the phosphorescent transients described below is 1 μs .

Results

The low-temperature emission and absorption spectra of a single crystal of $[\text{Rh}(\text{phpy})_2\text{bpy}]\text{PF}_6$ are shown in Figure 1. The

Figure 1. Origin region of the electronic absorption and emission spectra of a single crystal of $[\text{Rh}(\text{phpy})_2\text{bpy}]\text{PF}_6$ at low temperatures.¹⁴ Lines A–D in the absorption spectrum refer to the different observed electronic zero-phonon lines, as discussed in the Results section.

Figure 2. Luminescence spectrum of a 0.9% $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ -doped single crystal of $[\text{Rh}(\text{phpy})_2\text{bpy}]\text{PF}_6$ at 5 K,¹⁶ after excitation with the 364-nm Ar^+ ion laser line.

spectra are identical to those reported previously.¹⁴ The zero-phonon line at 453.9 nm (22030 cm^{-1}) of the luminescence spectrum is slightly red-shifted with respect to the origin of the absorption spectrum at 451.9 nm (22128 cm^{-1}), marked as line C in Figure 1. It coincides, however, with the less intense line A in the absorption spectrum. Comparison of the vibrational structure of the luminescence spectrum of the single $[\text{Rh}(\text{phpy})_2\text{bpy}]\text{PF}_6$ crystal with that for the $[\text{Rh}(\text{phpy})_2\text{bpy}]^+$ cation in various environments has previously led to the conclusion that in the pure crystal, the luminescence at 453.9 nm is not intrinsic but due to an impurity trap.^{14b} Likewise, we attribute the emission at 453.9 nm to a trap in the low-energy tail of the inhomogeneous distribution of cation sites. The energy difference between this A trap and the level at the origin of line C of the $[\text{Rh}(\text{phpy})_2\text{bpy}]^+$ cation is 98 cm^{-1} .

In the mixed crystals, the luminescence of the dopant $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$, with its origin at 532.2 nm (18789 cm^{-1}), is well separated from that of the host material, as can be seen in Figure 2.^{16a} The spectrum of Figure 2 also shows that the intensity ratio of the host and the dopant emissions is about 1:5 at 5 K, although $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ is only 0.9% abundant in the crystal. Since optical measurements have shown similar oscillator strengths for the emissive transitions in both molecules,^{16b} the relatively strong $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ emission implies that the excitation is predominantly trapped at the $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ cation sites.

Following picosecond pulsed laser excitation of the crystal at 317 nm, the temporal behavior of the phosphorescence

Figure 3. Phosphorescence transients of the A-trap emission in a single crystal of $[\text{Rh}(\text{phpy})_2\text{bpy}]\text{PF}_6$ doped with 0.9% $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$, observed at a detection wavelength of 454 nm after pulsed picosecond laser excitation at 317.5 nm, for (a) $T = 130$ K, (b) $T = 190$ K, and (c) $T = 250$ K, respectively.

intensity of both A trap and dopant Ir^{3+} complex was studied. The experiments were performed in the temperature range $130 \text{ K} \leq T \leq 290 \text{ K}$. Figure 3 shows the decay of the A-trap luminescence of 454 nm, for $T = 130$, 190, and 250 K. As illustrated by Figure 3, when the temperature is increased, the initial intensity amplitude, I_0 , diminishes. From semilog plots of the decays, it is inferred that the decay behavior changes from multiexponential at the lower temperatures to predominantly monoexponential for $T > 230 \text{ K}$, although typically the decay remains on the order of 100 ns in the temperature range 130–250 K. For temperatures above 270 K, the signal-to-noise ratio of the A-trap phosphorescence has dropped to an extent that the decays could no longer reliably be used for further analysis.

At low temperatures (5 K), upon pulsed UV excitation, a rise time of about 80 ns for the A-trap luminescence has previously been observed.^{14b} In the present experiments, when detecting the luminescence intensity over a time range of 1 μs with a time resolution of 1 ns, no rise in the A-trap phosphorescence intensity could be observed. Apparently, above 130 K, the rate for energy trapping at the A site and/or the host-to-host energy-transfer rate is at least 1 order of magnitude faster.

Concurrent with the A-trap phosphorescence decay, the emission intensity of $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$, measured at 533 nm, rises to a maximum in about 250 ns; eventually, the phosphorescence rise is followed by the lifetime-limited decay to the ground state on a time scale of about 10 μs . For temperatures up to 230 K, the characteristic rise time remained practically constant and was on the order of 100 ns. Above 230 K, the rise time of the luminescence clearly decreases, as well as the emission intensity amplitude.

Discussion

As described above, the decay of the A-trap phosphorescence, as experimentally observed after the laser pulse, is accompanied by a growth of the $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ phosphorescence on the same time scale of about 100 ns. The observations are pertinent to energy transfer from the host A-trap molecules to the guest $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ molecules. The multiexponential functional decay behavior of the A-trap emission and also the change of the multiexponential function into a monoexponential one with increasing temperature (cf. Figure 3) exclude a simple unimo-

lecular direct transfer from a donor to an acceptor at a fixed distance, since the latter process would simply give rise to a monoexponential decay of the donor emission (characterized by a fixed energy-transfer rate constant) and, likewise, a monoexponential feeding of the acceptor population. From the multiexponential decay behavior, it thus follows that we cannot ignore the distance dependence of the transfer rate constant for energy transfer among the donor and acceptor molecules or, equivalently, the concentrations of these molecules.

In order to further discuss the temporal behavior of the observed transients, we first remark that the excitation at the donor A-trap site and the acceptor $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ site is trapped at one of the organic ligand molecules in the excited triplet state.^{14–17} It is likely that transfer from the donor to the acceptor sites is mediated *via* organic ligand molecular triplet states as well. It is for this reason that the energy-transfer process in the molecular crystals under investigation can be treated as in the case of phosphorescent disordered organic molecular solids.^{3–5} Inokuti and Hirayama⁸ were the first to analyze the time dependence of the donor population probability in the event of energy loss due to exchange interactions in a three-dimensional lattice, by statistical averaging over the distances R between the donor and acceptor molecules. A generalization to all dimensions was given by Blumen for exchange^{9a} and multipolar^{9b} interactions, yielding for the exchange mechanism the following expression for the donor luminescence intensity as a function of time,

$$I(t) = \exp\left[-aV_{\Delta}\frac{c_A}{(\gamma d)^{\Delta}}g_{\Delta}\left(\frac{t}{\tau}\right)\right]\exp\left(-\frac{t}{\tau_0}\right) \quad (1)$$

V_{Δ} is the volume of a unit sphere in a space of Δ dimensions, a is a constant that is ~ 1 , c_A is the acceptor concentration, and τ_0 is the intrinsic donor lifetime limited by all other processes except energy transfer. d equals the lattice spacing between neighboring complexes, and τ is the hopping time between nearest neighbors. The parameter γd is a measure of the range of interaction and is larger when the interaction is of shorter range.⁹ As is well-known,^{4,5,9} exchange interactions usually are short-range; i.e., the interaction parameter $\gamma d \gg 1$, a typical value for γd in many aromatic systems being 5.^{4,9c} The function g_{Δ} has the general form

$$g_i(z) \equiv z \int_0^{\infty} \exp(-zy) [-(\ln y)]^i dy \quad (2)$$

It is generally accepted that for triplet–triplet energy transfer, dipole–dipole interactions are not important and that energy migration is determined mainly by (super)exchange interactions.^{3–11} For energy transfer in the $[\text{Rh}(\text{thpy})_2\text{bpy}]^+$ -doped $[\text{Rh}(\text{phpy})_2\text{bpy}]\text{PF}_6$ crystal, the contribution of the dipole–dipole mechanism to the total transfer rate was estimated to be less than 1%.¹⁴ Therefore, we have performed best fit simulations for the experimentally detected A-trap decay signals using expression 1 for one-, two-, and three-dimensional energy transport, where γd , τ_0 , and τ are fit parameters. Satisfactory agreement between the simulated curves and the experimental results was obtained only with the expressions for two- and three-dimensional energy transfer, with $0.5 \leq \gamma d \leq 1.5$ assuming 2D-exchange interactions and $2 \leq \gamma d \leq 5$ for 3D-exchange interactions, respectively. Acceptable fitting of the experimental decay curves within the one-dimensional exchange framework appeared impossible. In Figure 4, illustrative computer-calculated results are presented. Within the 3D-exchange model, best fit results were obtained for $\gamma d = 2$. The simulations in the 2D-exchange interaction case were of almost

Figure 4. Best computer fits to the experimental A-trap luminescence decay curves in 0.9% $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ -doped single-crystal $[\text{Rh}(\text{phpy})_2\text{bpy}]\text{-PF}_6$, observed at 454 nm and $T = 130$ K, assuming (a) 3D-exchange ($\gamma d = 2$), (b) 2D-exchange ($\gamma d = 0.75$), and (c) 1D-exchange ($\gamma d = 0.25$) interactions. In a and b, the experimental data coincide exactly with the simulated curves and have been omitted for clarity.

equal quality for $\gamma d = 0.75$. However, the value of $\gamma d \geq 2$ in the 3D model seems more realistic for the system studied than the value of 0.75 in the 2D model, and therefore, we infer that the energy-transfer mechanism is 3D exchange at all times. Needless to say, the 3D-exchange mechanism is as expected, because the crystal structure of $[\text{Rh}(\text{phpy})_2\text{bpy}]\text{PF}_6$ is such that the packing of the complexes and ligand molecules is three-dimensional without any preferred orientation.

It should be added that also in the event of energy transfer based on superexchange couplings, an expression similar to that of eq 1 is obtained, with γd now being equivalent to $-\ln(\beta/\Delta E)$,^{4,9c} and that our simulations cannot differentiate between exchange and superexchange. Here, β is the exchange integral for exchange between nearest-neighbor molecules and ΔE is the energy difference of 98 cm^{-1} between host and donor phosphorescence origins. One anticipates for a concentration on the order of a few percent for the donor and acceptor sites that on the average, energy transport involves about 100 molecules. It may be, therefore, that superexchange interactions are of significance in our system. Assuming comparable exchange interactions for the host-to-host molecular energy transfer and donor-to-trap transfer and taking $\gamma d = 2$, as inferred from the best 3D-exchange fits, a value of $\beta = 13.5 \text{ cm}^{-1}$ is obtained for the nearest-neighbor energy-transfer matrix element. This value seems of the right order of magnitude, although slightly higher than previously found for organic solids like benzene and naphthalene ($1\text{--}2 \text{ cm}^{-1}$)^{4,9c} and 1,4-dibromonaphthalene (7.4 cm^{-1}).^{4,5} When making these comparisons, we have to keep in mind that we are comparing very different $3\pi\pi^*$ excitations. In the Rh^{3+} and Ir^{3+} complexes of the title compound, admixture of MLCT (metal-to-ligand charge transfer) states is known to be considerable^{16b,17c} (as may be inferred from the 3–4 orders of magnitude shorter lifetimes of these complexes as compared to the free ligand values). As a consequence, for the interligand energy transfer, the relevant energy-transfer matrix elements may be significantly enhanced.

An interesting feature of our experimental results is the change of the A-trap decay kinetics with temperature. Upon raising the temperature from 130 to 250 K, the decay signals could be well fitted by means of eq 1 maintaining $\Delta = 3$ and a value of 2 for γd ; the hopping time (τ) then had to be adapted

Figure 5. Temperature dependence of the characteristic hopping time, τ_{hop} , obtained from the best computer fits of the A-trap phosphorescence decay curves according to 3D-exchange interactions with $\gamma d = 2$.

and, thus, appeared temperature-dependent. Typically, the simulations yield that τ increases from approximately 5 ns, at 130 K, up to about 100 ns, at 250 K. Figure 5 summarizes the temperature dependence of τ as extracted from the computer fits for the A-trap luminescence decays. The slowing down of the energy transfer as the temperature is raised is incompatible with what one might intuitively expect, namely, a simple thermally activated energy-transfer process. The temperature dependence of τ suggests that at the higher temperatures, also the preexponential rate constant, k_0 , in $k_0 \exp(-\Delta E/kT)$ changes, possibly because of a change in the nature of the exchange interactions or, equivalently, because different molecular entities become involved in the energy-transfer process. A plausible picture explaining the phenomenon in a qualitative manner is the following.

The zero-phonon lines in the emission spectra of the $[\text{Rh}(\text{phpy})_2\text{bpy}]^+$ and $[\text{Ir}(\text{thpy})_2\text{bpy}]^+$ cations^{14–16} show appreciable inhomogeneous line broadening (FWHM is about 250 cm^{-1} at 250 K) comparable to that known for orientationally disordered organic molecular crystals.^{3–5} As has been discussed for the latter, at liquid helium temperatures, the steady-state emission is due to sites that contribute to the low-energy tail of the inhomogeneously broadened zero-phonon transition. In a pulsed-excitation experiment where the excitation frequency, ν_{exc} , is at a higher than cw emission frequency, the time dependence of the donor emission revealed a cascade down to the sites emitting at lower energies. In a similar way, at the lowest temperatures of our experiments, one expects for the donor luminescence that mainly the A-trap sites in the low-energy tail of the inhomogeneous distribution will contribute. As the temperature is increased, one might expect that the time-dependent donor emission entails a larger portion due to thermally populated higher-energy sites. It is remarked that these sites may consist of A traps as well as energetically accessible host complex cations. Assuming a random Gaussian distribution of the energetically different donor sites in the crystal, one notes that as the temperature is raised, the concentration of sites which can act as energy donors may increase. As mentioned above, at the same time the characteristic hopping time, τ , as deduced from the best fit curves, is found to increase as well, and it thus follows that apparently for larger donor concentrations, hopping is slower. Thus, energy transfer is hampered at the larger donor concentrations, possibly because now different molecular entities take part in the energy-transfer process.

A decrease in the trap-to-supertrap energy-transfer rate at increased trap concentrations has been reported elsewhere for naphthalene- h_8 -doped crystals of naphthalene- d_8 ¹⁰ and DCB-

doped crystals of DBB.¹¹ The slowing down of the transfer rate was attributed to the role of trap aggregates, showing strong interactions within and surrounded by dopant-induced host X traps, acting as energy funnels. Within the clusters, energy is rapidly transported, whereas for long-range energy transfer out of the funnels, thermal activation to the higher host sites in the funnel is required.^{10,11} Whereas the excitation will spend a relatively long time on the extended cluster (consisting of many donor sites), intercluster hopping occurs on a longer time scale. Similarly, one can visualize the emission data of this work as follows. At the higher temperatures, the contribution from clusters to the observed emission intensity is enhanced. Simulations based on expression 1 (which, strictly speaking, may then no longer be applicable) then give the qualitative result that the incoherent hopping time, τ , for hopping between clusters slows down at higher temperatures.

In summary, we have studied the energy migration in 0.9% [Ir(thpy)₂bpy]⁺-doped [Rh(phpy)₂bpy]PF₆ single crystals by performing transient phosphorescence experiments. A decrease in the host A-trap phosphorescence intensity was accompanied by a rise in the [Ir(thpy)₂bpy]⁺ emission intensity on the same time scale of 100 ns. The decay curves were found to be temperature-dependent, yielding an increase in the "nearest-neighbor" hopping time when the temperature is raised. We attributed this increase to the role of clusters of donor sites, the levels of which become thermally populated as the temperature is raised.

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