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Excited-State Properties and Energy Migration in [RhL$_2$(2,2'-bipyridine)]PF$_6$ (L = 2-Phenylpyridinate(1−) or 2-Thienylpyridinate(1−))

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Received May 8, 1991

The optical spectroscopic properties of the title compounds were investigated by absorption, luminescence, excitation, and Raman spectroscopy down to 1.5 K. The [Rh(thpy)$_2$(bpy)]$^+$ complex was introduced into the [Rh(phpy)$_2$(bpy)]PF$_6$ lattice as a radiative excitation trap, in order to study the migration of excitation in the host lattice. The low-temperature luminescence and excitation spectra of the dopant ion are extremely sharp and allow a detailed characterization of the first excited states. The two lowest-energy excited states are separated by 22 and 275 cm^{-1} in neat [Rh(phpy)$_2$(bpy)]PF$_6$ and neat [Rh(thpy)$_2$(bpy)]PF$_6$, respectively. They are essentially $^3\pi\pi^*$ excitations localized on the two crystallographically inequivalent phpy$^-$ and thpy$^-$ ligands, respectively. Nonradiative excitation transfer between neighboring complexes is dominant down to 1.5 K, with an estimated rate constant $k \geq 10^9$ s^{-1} for host-to-host transfer. The electric dipole–dipole mechanism is found to play a negligible role in these processes.

Introduction

The present study is devoted to the cyclometalated rhodium(III) complexes [Rh(phpy)$_2$(bpy)]$^+$ (phpy$^-$H$^+$ = 2-phenylpyridine, bpy = 2,2'-bipyridine) and [Rh(thpy)$_2$(bpy)]$^+$ (thpy$^-$H$^+$ = 2-(2-thienyl)pyridine), which will be abbreviated [PhpyBpy] and [ThpyBpy] in the following. We have started a program to systematically investigate such (4d)^6 and related (5d)^6 complexes by low-temperature high-resolution spectroscopy.[1-4] The primary interest is a characterization of the metastable lowest-energy excited states, which are responsible for the photocatalytic and photochemical activity of these complexes. Here we report the excited-state dynamics in the crystalline compound [PhpyBpy]PF$_6$ and the intrinsic spectroscopic properties of the complexes [PhpyBpy] and [ThpyBpy].

The question of localization of excitation in coordination compounds with metastable excited states is a very important one. In molecular complexes with organic ligands, as exemplified by Ru(bpy)$_3^{2+}$, it is important to know whether the excitation is localized on one ligand and on what time scale it should be considered localized or delocalized.[5-7] We find mixed complexes of Rh^{3+} with two or three different chelate ligands particularly suited for the study of such questions. In the crystalline state there is the additional possibility of excitation transfer between neighboring complexes and, as a result, energy migration through the lattice. There is a great deal of literature on the exciton dynamics in molecular organic crystals, on the one hand,[8] and on extended inorganic ionic lattices, on the other hand.[9] Coordination compounds of chelate complexes take an intermediate position between these two classes. Depending on the nature of the excitation, we might expect energy-transfer properties with more or less "organic" and "inorganic" character, respectively. Evidence of excitation migration and the subsequent trapping of the excitation has been found in some osmium-doped Ru(bpy)$_3^{2+}$ salts,[10] but the phenomenological behavior is quite different from that of the present study.

We recently reported the low-temperature absorption and luminescence spectra of nominally pure [PhpyBpy]PF$_6$.[1] Our failure in ref 1 to unambiguously assign the low-temperature luminescence as being intrinsic or as being due to a trap was part of the motivation for the present study. By introducing [ThpyBpy] complexes in small concentration, which substitute for [PhpyBpy] in the crystal and act as excitation traps, we can resolve this question and obtain estimates of the relevant energy-transfer rates. In addition, we obtain luminescence and excitation spectra of the [ThpyBpy] guest complexes with very sharp lines. In combination with the results of a recent crystal structure determination of [PhpyBpy]PF$_6$,[11] the new spectroscopic results provide a clear picture of the first excited states of the cyclometalated complexes [PhpyBpy] and [ThpyBpy].

Experimental Section

[PhpyBpy]PF$_6$ and [ThpyBpy]PF$_6$ were synthesized as described in ref 12. The salts were repeatedly recrystallized from dichloromethane until no change in the crystal-luminescence spectrum was detected. The identity of the compounds was checked with 400-MHz ^{1}H-NMR spectra and powder X-ray diffraction. Single crystals of [PhpyBpy]PF$_6$ and [ThpyBpy]PF$_6$ were grown from a dichloromethane solution by slow addition of ether (isothermal distillation). The hexagonal plates of [ThpyBpy]PF$_6$ with typical dimensions 2 × 2 × 0.4 mm showed no extinction directions. For the luminescence spectra of a glassy matrix, [PhpyBpy]PF$_6$ was dissolved in a 4/5 proprionitrile/butyronitrile mixture as in ref 12 (complex concentration 6.6×10^{-4} M). [ThpyBpy]PF$_6$ was doped in Plexiglas by evaporation of a 10% w/v solution of poly(methyl methacrylate) (PMMA) in dichloromethane (complex concentration ~ 10^{-3} M).

The samples were cooled either in a helium gas flow tube[13] (for temperatures down to 5 K) or in an Oxford MD4 bath cryostat (between 4.2 and 1.5 K).

Single-crystal and PMMA film absorption spectra of [PhpyBpy]PF$_6$ were taken from ref 1. A 1402 Spex double monochromator equipped with a double-beam attachment built in this laboratory was used for the absorption spectra of the [ThpyBpy]PF$_6$ crystals. Light of a 100-W halogen lamp was dispersed by two gratings (1200 grooves/mm) blazed at 500 nm and detected with an EMI 9781A PM tube. The excitation spectrum was recorded with the same apparatus, but the light was detected at a right angle through a cutoff filter (Schott OG570) by a cooled RCA 31034 end window PM and a photon-counting system (Spex DPC-2).

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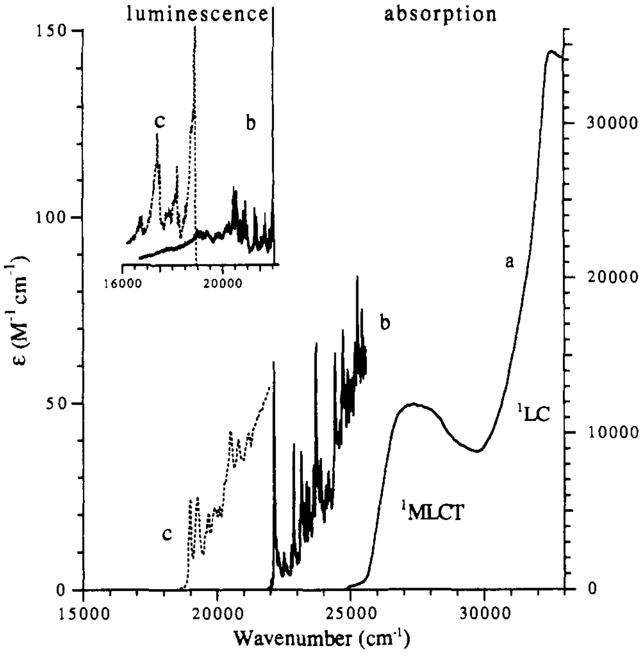

Figure 1. Single-crystal absorption (at 10 K) and luminescence (at 5 K) spectra of [PhpyBpy]PF_6 (b) and [ThpyBpy]PF_6 (c) and absorption spectrum (at 20 K) of [PhpyBpy] in a poly(methyl methacrylate) plastic (a). Use left axis for spectra b and c and right axis for spectrum a. Spectrum c is 5 times enlarged.

Luminescence was excited (a) with lines of an Ar^+ laser (Spectra Physics 2045) or (b) with the third harmonic of a pulsed Nd:YAG laser (QuantaRay DCR-3, 354.7 nm) with an average power of about 100 μW on the sample. Raman spectra were excited with a Kr^+ laser (Coherent CR-500K). Spectral purity of the lines was achieved with a Claassen filter. The detection system consisted of the 1402 Spex double monochromator, the RCA 31034 photomultiplier, and a photon-counting system (Stanford Research SR-400).

Luminescence and excitation spectra were corrected for apparatus response. The accuracy in the energy determination is estimated to be ±2 cm^{-1}. A Tektronix 4052A microcomputer was used for monochromator control and data acquisition.

Results

Figure 1 shows a survey of the low-temperature spectroscopic properties of [PhpyBpy]PF_6 (traces a and b) and [ThpyBpy]PF_6 (traces c). The metal-to-ligand charge-transfer (MLCT) band at about 27 000 cm^{-1} is the lowest-energy feature observable in the absorption spectrum of a Plexiglas foil at 20 K (trace a). High-resolution single-crystal spectroscopy of [PhpyBpy]PF_6 at 5 K reveals a highly structured absorption between 22 000 and 26 000 cm^{-1} and an equally well resolved luminescence between 22 000 and 16 000 cm^{-1} (traces b). This has been reported in ref 1. Replacing the cyclometalated ligand phpy⁻ by thpy⁻ leads to a red shift of the structured crystal absorption and emission spectra by about 3000 cm^{-1} (traces c). We notice that the absorption and emission lines are considerably broader in this salt than in [PhpyBpy]PF_6.

Figure 2 shows an enlarged picture of the origin region of [PhpyBpy]PF_6 in absorption and emission down to 1.5 K. The coincidence of the intense emission origin with the very weak absorption line A has been noted before.[1,2] Here we see that lowering the temperature from 4.2 to 1.5 K has no appreciable effect on the emission spectrum. In particular, the intensity ratio of the lines A/B appears to be temperature independent in emission below 4.2 K.

In Figure 3 we compare three different low-temperature luminescence spectra of [PhpyBpy] with the Raman spectrum of a polycrystalline sample at 10 K. The spectra have been shifted to coincide at the laser excitation energy (traces a–c) or luminescence maximum (trace d). Wavenumbers of the most prominent vibrational sidebands are listed in Table Ia. The luminescence line narrowing (LLN) technique used for spectra b and c has been described in refs 2–4. We notice a near coincidence of the vibrational energy patterns in traces a–c whereas pattern d is distinctly different. The intensity distribution in the Raman spectrum (trace a) is obviously quite different from that in the luminescence spectra. In spectrum d the laser excitation occurs at higher energy than line A in the absorption spectrum, and in spectrum c it occurs at lower energy. This strong dependence of the luminescence spectrum on the excitation wavelength will be a key to understanding the excited-state dynamics; see the section "Energy Transfer".

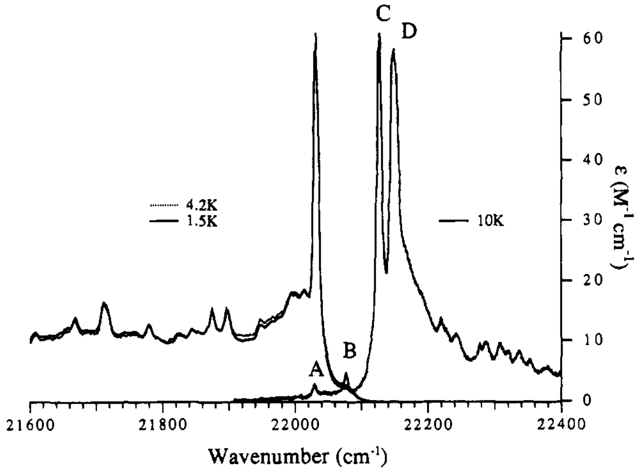

Figure 2. Region of electronic origins of [PhpyBpy]PF_6 as measured in low-temperature absorption and luminescence spectra. Absorption lines A–D are discussed in the section "Energy Transfer".

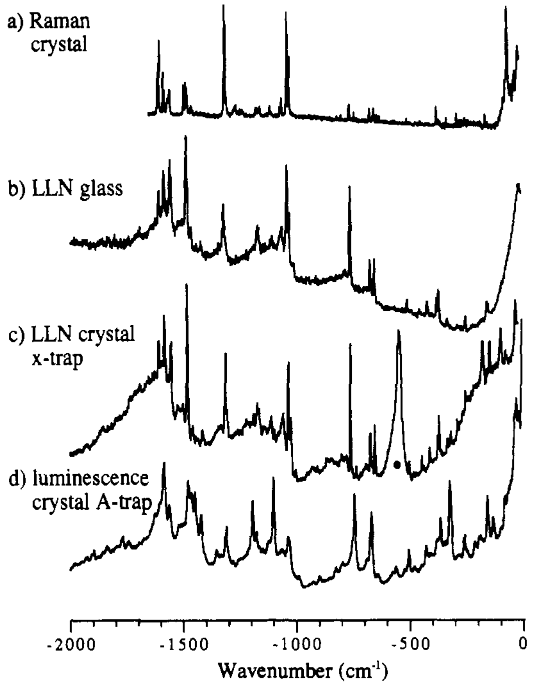

Figure 3. Vibrational sideband patterns of [PhpyBpy] in various environments at 5 K: (a) Raman spectrum of neat [PhpyBpy]PF_6 (λ_0 = 514.5 nm); (b) narrowed luminescence spectrum of [PhpyBpy] in a glass (λ_0 = 457.9 nm); (c) [PhpyBpy]PF_6 luminescence excited below absorption line A (λ_0 = 454.5 nm); (d) unselectively excited spectrum of [PhpyBpy]PF_6 (λ_0 = 363.8 nm). • in trace c marks the electronic origin of a trap, which is probably due to an Ir impurity.[25]

Figure 4 shows 5 K luminescence and excitation spectra of [PhpyBpy]PF_6 doped with 1% [ThpyBpy]. Excitation is at 363.8 nm, where [PhpyBpy] and [ThpyBpy] have relatively strong ($\epsilon \approx$ 7000 M^{-1} cm^{-1}) MLCT absorptions. The luminescence spectrum consists of two parts, I and II, separated by about 2900 cm^{-1} with about equal total intensity. Both parts are highly structured; but in part II the lines are exceedingly sharp (≤5 cm^{-1}), whereas

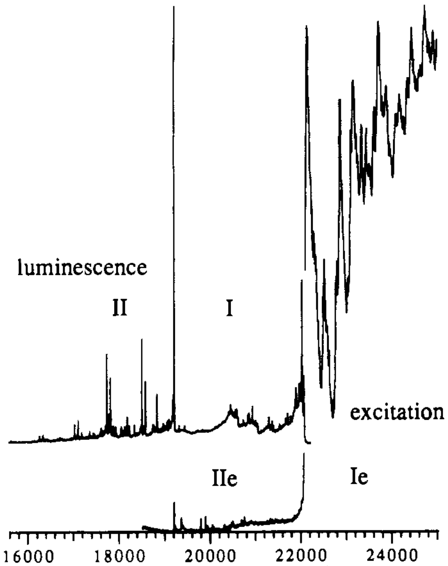

Figure 4. Luminescence (excited at 363.8 nm) and excitation (monitored below 17 500 cm^{-1}) spectra of 1%-[ThpyBpy]-doped [PhpyBpy]PF$_6$ at 5 K. Spectral regions I and II refer to transitions on [PhpyBpy] and [ThpyBpy], respectively.

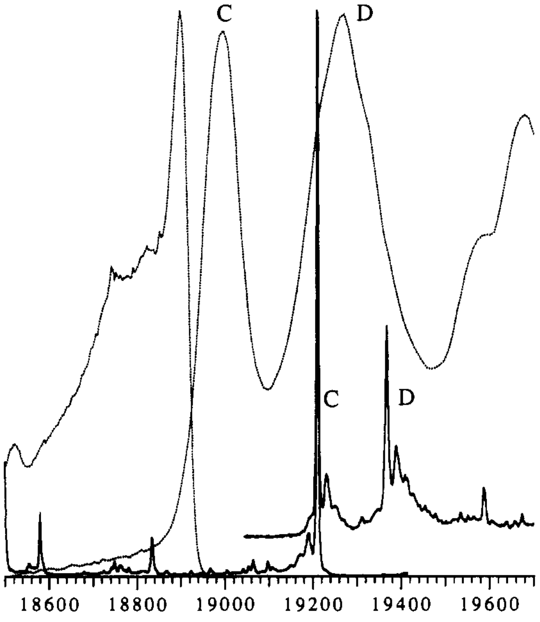

Figure 5. Absorption and luminescence spectra of neat [ThpyBpy]PF$_6$ (···) and excitation and luminescence spectra of 1%-[ThpyBpy]-doped [PhpyBpy]PF$_6$ (—), all at 5 K. Absorption lines C and D are discussed in the text.

in part I there is some underlying intensity with much less fine structure. The assignment of parts I and II to [PhpyBpy] and [ThpyBpy] luminescence is straightforward from a comparison with Figure 1. For the excitation spectrum, the [ThpyBpy] luminescence was monitored through a cutoff filter below 17 500 cm^{-1}. We observe two distinct spectral regions again, Ie and IIe, corresponding to [PhpyBpy] and [ThpyBpy] excitations, respectively. Their intensity ratio is roughly estimated as 100/1. The lines in region IIe are an order of magnitude narrower than those in region Ie.

Figure 5 shows the origin region II of Figure 4 in detail. Also included is the origin region of absorption and luminescence of pure [ThpyBpy]PF$_6$ at 5 K (dotted line). This figure clearly demonstrates the following important points: (i) The spectral lines of [ThpyBpy] doped into [PhpyBpy]PF$_6$ are at least an order of magnitude narrower than those of pure [ThpyBpy]PF$_6$; (ii) there is exact coincidence of the prominent [ThpyBpy] origin lines in the emission and excitation spectra of the doped crystal, whereas the maxima of the two origins have an energy difference of 95 cm^{-1} in the neat material. Within the first 100 cm^{-1} from the origin, the excitation spectrum is an exact mirror image of the luminescence spectrum for the doped system, but the same is not true for the undiluted sample. Both samples show a second origin of comparable intensity in their excitation or absorption spectra. The energy difference between the two electronic origins is 156 cm^{-1} for [ThpyBpy] doped [ThpyBpy]PF$_6$ and about 275 cm^{-1} for neat [ThpyBpy]PF$_6$. In analogy to [PhpyBpy] (Figure 2), we designate the two origins as C and D. The energies of corresponding vibrational sidebands on the common origin vary by up to ±8% in the excitation spectrum compared to the luminescence spectrum.

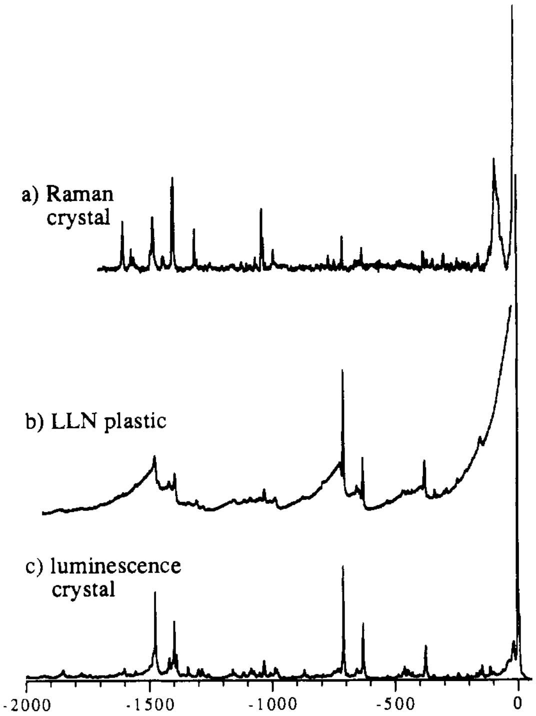

Figure 6. Vibrational sideband patterns of [ThpyBpy] in various environments at 5 K: (a) Raman spectrum of neat [ThpyBpy]PF$_6$ (λ_0 = 647.1 nm); (b) narrowed luminescence spectrum of [ThpyBpy] in a plastic (λ_0 = 530.9 nm); (c) luminescence of 1%-[ThpyBpy]-doped [PhpyBpy]PF$_6$ excited at λ_0 = 514.5 nm.

Figure 6 shows a comparison of low-temperature Raman and luminescence spectra of pure and doped [ThpyBpy]. The corresponding vibrational energies of the most prominent bands are listed in Table Ib. All three vibrational patterns are nearly coincident, despite the completely different physical surroundings of the [ThpyBpy] complexes in the three samples. We are obviously observing an intrinsic molecular property of [ThpyBpy].

Discussion

1. Intentional Traps. By introducing the chemically modified complexes [ThpyBpy] into [PhpyBpy]PF$_6$, we pursue two goals. First, we thus hope to gain some insight into the energy migration properties in the host lattice. Second, by diluting the guest complex in the mixed crystal, we should be able to determine its intrinsic properties. [ThpyBpy] should substitute without too much perturbation of the crystal lattice, because it has the same charge and a similar molecular structure. [PhpyBpy]PF$_6$ has been chosen as the host lattice because its crystal structure has recently been determined[11] and because its low-temperature absorption and emission spectra are unusually sharp.[1]

The structural properties at 100 K are summarized as follows: [PhpyBpy]PF$_6$ crystallizes in the orthorhombic space group *Pbca*. The unit cell contains eight equivalent Rh atoms. The two phpy$^-$ ligands of a complex are not related by a 2-fold rotation axis, which

Table I. Vibrational Sideband Energies (cm^{-1})[a]

(a) $[Rh(phpy)_2(bpy)]^+$ (Figure 3)

Raman trace a	LLN of glass trace b	LLN of crystal trace c
1609	1607	1607
1585	1584	1582
1556	1555	1554
1484	1484	1480
1314	1320	1313
1038	1038	1034
1029	1028	1022
761	760	759
673	672	672
653	653	651
509	509	502
378	380	376
370	372	369
252	253	253

(b) $[Rh(thpy)_2(bpy)]^+$ (Figure 6)

Raman trace a	LLN of plastic trace b	Luminescence of doped crystal trace c
1601	1607	1601
1557	1556	1556
1480	1477	1476
1401		1399
1396	1396	
1310	1307	
1301		1301
1030	1030	1033
986	986	988
710	709	711
630	630	630
379	377	376

[a] The estimated accuracy is ±2 cm^{-1}.

leads to crystallographically inequivalent ligands. The shortest Rh–Rh distance is 7.905 Å, and the shortest ligand–ligand separation (of ring–ring bond centers between neighboring complexes) is 4.995 Å.

[ThpyBpy] is an impurity trap with a depth of about 2900 cm^{-1}. By varying the excitation energy, we can either selectively excite it with a photon (Figure 6c) or excite it by way of energy transfer from the host lattice (Figure 4, band II, and Figure 5). Both spectra are identical, and the latter process is called host-sensitized luminescence. It thus appears that we are measuring the genuine luminescence spectrum of the [ThpyBpy] complex. Due to the sharpness of the lines (~5 cm^{-1}), we can do this with great accuracy. The inhomogeneous broadening is reduced by more than an order of magnitude compared to that of pure $[ThpyBpy]PF_6$; see Figure 5. Using the same principle of dilution in a host crystal, Yersin et al. have achieved similarly sharp fine structure in the luminescence spectrum of $Os(bpy)_3^{2+}$.[10]

The vibrational sideband structure of [ThpyBpy] in the $[PhpyBpy]PF_6$ crystal environment is thus very well defined, and we can compare it with the vibrational energies of [ThpyBpy] in other environments. The low-temperature Raman spectrum of neat $[ThpyBpy]PF_6$ (Figure 6a) shows several sharp lines between 300 and 1600 cm^{-1} due to intramolecular ligand vibrations which deviate in energy by no more than 6 cm^{-1} from the vibrational luminescence sideband energies of the doped crystal (Table Ib). In addition, the sharp features in the narrowed luminescence spectrum of [ThpyBpy] in a PMMA plastic at 5 K again show the same vibrational energy pattern. This coincidence of the vibrational energies of [ThpyBpy] in three completely different environments ($[PhpyBpy]PF_6$ and $[ThpyBpy]PF_6$ are not isostructural) is remarkable, although not really surprising. The mixing of internal and external molecular modes is extremely small due to their large energy difference.

We see evidence of external modes, so-called lattice modes or phonons in the low-energy wings accompanying the vibrational sidebands in the LLN spectrum (Figure 6b). Also, the electronic origins of [ThpyBpy] doped in $[PhpyBpy]PF_6$ are accompanied by phonon wings (Figure 5). The relative magnitude of the zero phonon line (I_{ZPL}) and the phonon wing (I_{PW}) is measured by the Debye–Waller factor[14]

Table II. Debye–Waller Factors α and Coupling Parameters S, As Defined in Ref 14 and Eqs 1 and 2 (Comparison with $^3\pi\pi^*$ Emitters and Charge-Transfer Emitters)

chromophore	α	S
naphthalene X-traps[a]	0.14–0.76	2.0–0.28
neat tetrachlorobenzene[b]	>0.5	<0.69
bpy in durene[c]	0.78	0.25
[ThpyBpy], line C[d]	0.46	0.78
[ThpyBpy], line D[d]	0.30	1.20
$Ru(bpy)_3(ClO_4)_2$[e]	0.0067	5
$Ru(bpy)_3(PF_6)_2$[e]	<0.0025	6–7

[a] References 15 and 26. [b] References 27 and 24. [c] Reference 18. [d] [ThpyBpy] doped in $[PhpyBpy]PF_6$; see Figure 5. [e] Reference 16.

$$\alpha = \frac{I_{ZPL}}{I_{ZPL} + I_{PW}} \tag{1}$$

Within the Condon approximation it is related to the coupling strength (S) of the chromophore to the lattice by

$$\alpha = \exp(-S) \tag{2}$$

We find a rather low value ($S = 0.78$) for the crystalline system, comparable to the values found for organic $^3\pi\pi^*$ emitters in crystalline environments (see Table II). This shows us that the guest complexes fit very well into the host lattice.[15] The coupling strength also depends on the size of the perturbation by heavy atoms.[15] For the complex salts $Ru(bpy)_3(PF_6)_2$ and $Ru(bpy)_3(ClO_4)_2$, much stronger coupling parameters were reported: $S = 5–7$.[16] Here the emitting states are considered to have charge-transfer character and therefore to contain appreciable metal character.

The exact coincidence of luminescence and excitation origins of [ThpyBpy]-doped $[PhpyBpy]PF_6$ shown in Figure 5 is another independent proof that both spectra originate from the same species. Due to the extreme sharpness of the vibrational sidebands compared to spectra of solutions or frozen glasses, we are able to determine the rather small differences of vibrational energies between the ground and excited states. The Huang–Rhys factors S_i are smaller than one for all the fundamental modes i. This information can be used to estimate the excited-state geometry, and we are presently studying this in greater detail.[17]

All the spectroscopic properties of [ThpyBpy] reported here, in particular those just described, are very typical of ligand-centered (LC) or $^3\pi\pi^*$ excited states. The sharpness of the vibrational sidebands and their energies as well as their intensity distribution are very similar in the luminescence spectra of free ligands such as bpy.[18,19] The observation of $^3\pi\pi^*$ excitations in absorption is only possible in crystals of metal complexes, because their intensity is enhanced by orders of magnitude with respect to the free ligand.

The two origins (denoted C and D) separated by 156 cm^{-1}, which we observe in the excitation spectrum of [ThpyBpy]-doped $[PhpyBpy]PF_6$, most likely correspond to excitations on two crystallographically inequivalent $thpy^-$ ligands. The recent crystal structure determination of $[PhpyBpy]PF_6$ has revealed that the two $phpy^-$ ligands are not equivalent, and thus the two $thpy^-$ ligands of the guest complex [ThpyBpy] will have a different surrounding. This leads to the observed difference of 156 cm^{-1}

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in electronic excitation energies. On the other hand, there are only minor differences ($\leq$9 cm^{-1}) in the vibrational energies of the C and D sideband structures. We have observed before that the vibrational energies are essentially independent of the molecular environment.

The relative intensities of band systems I and II in Figure 4 provide some insight into the efficiency of the processes involved in the energy migration. The [ThpyBpy] concentration is roughly 1%, so that laser excitation at 363.8 nm into the broad charge-transfer band will lead to a ratio of excited complexes [PhpyBpy]/[ThpyBpy] of about 100/1. The observed ratio of [PhpyBpy]/[ThpyBpy] luminescence, however, is about 1/1. The ratios of triplet absorption intensity (at 5 K) to luminescence lifetime of isolated complexes (at 77 K) are comparable for [PhpyBpy] and [ThpyBpy]. We conclude that they have comparable quantum efficiencies. From the observed intensity ratio of [PhpyBpy]/ThpyBpy] luminescence at 5 K we therefore conclude that about 50% of the initial [PhpyBpy] excitation nonradiatively migrates to the [ThpyBpy] traps.

2. Unintentional Traps. It is clear from the previous section that ET in [PhpyBpy]PF$_6$ is very efficient down to the lowest temperatures. Evidence for this was already provided in ref 1, but on the basis of some circumstantial evidence, it was concluded that lines A–D in Figure 2 are most likely intrinsic. In view of our results of the present study, which is directed to the problem of excitation transfer in pure coordination compounds, this earlier conclusion has to be questioned. And in the following we will show that lines A and B can clearly be identified as impurity traps. We can also demonstrate the importance of X-traps (slightly perturbed host complexes), another kind of unintentional trap, to the luminescence spectra of the neat materials [PhpyBpy]PF$_6$ and [ThpyBpy]PF$_6$.

Figure 5 demonstrates most clearly the effect of X-traps. Absorption and luminescence lines of the neat [ThpyBpy]PF$_6$ crystal are broader by an order of magnitude than those of [ThpyBpy]-doped [PhpyBpy]PF$_6$ as a result of inhomogeneities in the crystal. ET in [ThpyBpy]PF$_6$ is thus nonresonant, and at temperatures below 10 K the excitation will be on the complexes in the low-energy tail of the inhomogeneous distribution. Their concentration is so low that they serve as luminescent X-traps. Figure 5 shows that the maximum of the luminescence origin is coincident with the low-energy tail of the absorption profile, 95 cm^{-1} below the maximum of the absorption band.

Turning now to [PhpyBpy]PF$_6$, we can nicely see the effect of both impurity and X-traps. As shown in Figure 2, the weak absorption line A coincides with the origin of the luminescence below 5 K. The luminescence is very sharp, so that we can use it again as a fingerprint pattern to characterize the luminescent center. This is done in Figure 3 and Table Ia, and the result is very clear: the spectrum of the neat crystal is the only one with an abnormal sideband pattern. On the other hand, the Raman energies of the crystal coincide with the vibrational sideband energies of the [PhpyBpy] complex in a plastic matrix, very clear evidence that this is the genuine [PhpyBpy] pattern. We conclude that line A is an impurity trap, thus confirming our initial suspicion. Since the vibrational pattern is significantly different from the true [PhpyBpy] spectrum, it is most likely a complex with a defect ligand introduced through the starting material. Since line B retains some intensity in emission down to 1.5 K, it could be due to another impurity. However, it is also possible that lines A and B correspond to the two crystallographically inequivalent phpy$^-$ sites available to the impurity complex in this host. On the basis of the relative intensities of lines A and C and by assuming similar oscillator strengths, we estimate a concentration of trap A of about 2 mol %.

Perhaps the most interesting spectrum in Figure 3 is trace c. When we tune our laser to an energy below the A line, we can still excite some luminescence, and this luminescence shows the normal [PhpyBpy] vibrational pattern; see traces a and b and Table Ia. A very small fraction of [PhpyBpy] complexes, those in the lowest-energy tail of the inhomogeneous line C in Figure 2, have their first excited state below line A. They are X-traps which can be directly excited in this experiment. It is remarkable, but is in agreement with earlier conclusions, that their vibrational pattern is essentially unaffected by the fact that they are lying at the extreme tail of the inhomogeneous distribution. We have prepared several other salts of [PhpyBpy]. They all have significantly broader absorption and luminescence lines below 10 K than [PhpyBpy]PF$_6$. In the BPh$_4^-$ (tetraphenylborate) salt, the vibrational structure is sufficiently resolved to allow a comparison with the patterns in Figure 3: it corresponds to the genuine [PhpyBpy] pattern and not the trap pattern d. Impurity complexes of type A, which may also be present in [PhpyBpy]BPh$_4$ cannot act as excitation traps because their excited-state energy lies well within the inhomogeneous distribution of host complexes. An excitation on an A complex will therefore "boil out" into the "exciton band" and thus finally end up on an X-trap.

Many of the salts of [PhpyBpy] and [ThpyBpy] studied so far show two prominent origins, C and D, of comparable intensity in their absorption or excitation spectra. Their energy separation varies between 5 and 380 cm^{-1}. As for [ThpyBpy]-doped [PhpyBpy]PF$_6$, these two lines are assigned to excitations on two crystallographically inequivalent phpy$^-$ or thpy$^-$ ligands.[11] The range of C–D energy differences is about the same as the range of inhomogeneous bandwidths of lines C and D. This makes intuitive sense, since in both cases it is a measure of the energy variation induced by a variation of the crystal environment.

3. Energy Transfer. We obtain a rough estimate of the rate of transfer at 5 K between neighboring complexes in [PhpyBpy]PF$_6$ from the following observations. We are unable to observe any luminescence intensity at the position of line C in Figure 2, and we can give a lower limit for the luminescence intensity ratio A/C $\geq$ 2500 s^{-1}. Since the luminescence lifetime of an isolated [PhpyBpy] complex (at 77 K) is 150 μs, we conclude that the host-to-trap energy migration rate at 5 K is $k_{HT} \geq 10^7$ s^{-1}. This is in very good agreement with the measured risetime of the A luminescence upon pulsed UV excitation of 83 ± 8 ns at 5 K.

The macroscopic host-to-trap energy migration rate can be correlated with rate constants for microscopic transfer between neighboring complexes. One usually distinguishes the two limiting situations, in which (a) the trapping step (k_{ht}) is rate determining or (b) the host-to-host transfer step (k_{hh}) is limiting. For case b and an isotropic three-dimensional diffusion, we can write[20,21]

$$k_{HT} = x_T P k_{hh} \tag{3}$$

where k_{HT} is the experimentally observable host-to-trap transfer rate constant, x_T is the trap concentration, P depends on the lattice type and has a value of approximately 0.7 for a cubic lattice, and k_{hh} is the microscopic host-to-host transfer rate constant. If we are in limit b (i.e., the trapping step is very fast), we thus obtain at 5 K

$$k_{hh} \approx 10^9 \text{ s}^{-1} \tag{4a}$$

In limit a, k_{hh} would have to be larger:

$$k_{hh} > 10^9 \text{ s}^{-1} \tag{4b}$$

The contribution to this rate from a dipole–dipole mechanism can be estimated as follows. According to Fermi's Golden Rule, the rate constant for a resonant nonradiative donor (D) to acceptor (A) transfer step is given by[22]

$$k_{DA} = (2\pi/\hbar)\beta_{DA}{}^2\Omega_{DA} \tag{5}$$

where β_{DA} is the electronic interaction integral and Ω_{DA} the spectral overlap. From our absorption and luminescence spectra of [PhpyBpy]PF$_6$, we estimate

$$\Omega_{hh} \approx 10^{-4} \text{ cm} \tag{6}$$

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The contribution of an electric dipole–dipole mechanism can be expressed as[23]

$$k_{\mathrm{DA}}^{\mathrm{dd}} = \frac{1}{\epsilon^2}\left(\frac{3c}{8\pi^2}\right)\frac{e^4}{m^2c^4}\left(\frac{f_{\mathrm{D}}f_{\mathrm{A}}}{\tilde{\nu}_{\mathrm{DA}}{}^2R_{\mathrm{DA}}{}^6}\right)\Omega_{\mathrm{DA}} \qquad (7)$$

where f_{D} and f_{A} are the donor and acceptor oscillator strengths, respectively, R_{DA} is the donor–acceptor distance, and $\tilde{\nu}_{\mathrm{DA}}$ is the energy of the region of overlap. The remaining symbols in eq 7 have their usual meaning. In our situation, we obtain, from the absorption spectrum, $f_{\mathrm{D}} \approx 6 \times 10^{-6}$ and $f_{\mathrm{A}} \approx 2 \times 10^{-5}$. The shortest meaningful contact, which is the distance between ligand centers on neighboring complexes in the crystal, is 4.995 Å.[11] We obtain, in the dipole approximation, $k_{\mathrm{hh}} \approx 5 \times 10^{6}$ s^{-1}. The electric dipole–dipole mechanism thus makes a minor contribution to the total transfer rate. The dominant part originates from exchange or higher multipole interactions. In organic molecular crystals, rate constants for transfer between host molecules of the order of $k_{\mathrm{hh}} = 10^{11}$ s^{-1} have been reported, and also in these systems the contribution from a dipole–dipole mechanism was found to be negligible.[24]

Conclusions

High-resolution laser spectroscopy at cryogenic temperatures provides a very detailed picture of the complexes [Rh(phpy)$_2$(bpy)]$^+$ and [Rh(thpy)$_2$(bpy)]$^+$. In contrast to the case of conventional low-resolution absorption and luminescence spectroscopy of solutions and glassy matrices, we clearly identify two excited states separated by 22 and 156 cm^{-1} in [PhpyBpy]PF$_6$ and [ThpyBpy]-doped [PhpyBpy]PF$_6$, respectively. Their energy separation strongly depends on the environment for a given complex. In contrast, the vibrational energy pattern, which can be determined very accurately, is essentially independent of the environment. By doping [ThpyBpy] into [PhpyBpy]PF$_6$, we have achieved two major goals. Due to the sharpness of the luminescence and excitation spectra, we obtain an accurate picture of the ground- and excited-state properties of the [ThpyBpy] complex. The luminescent excitation traps in [PhpyBpy]PF$_6$ are identified, and they allow us to elucidate the excitation-transfer processes in the host lattice.

Acknowledgment. This work was financially supported by the Swiss National Science Foundation. We acknowledge a loan of RhCl$_3$ from Degussa.

Registry No. [Rh(phpy)$_2$(bpy)]PF$_6$, 108456-27-5; [Rh(thpy)$_2$(bpy)]PF$_6$, 127064-80-6.

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Electrochemical and Spectroscopic Properties of Dimeric Cofacial Porphyrins with Nonelectroactive Metal Centers. Delocalization Processes in the Porphyrin π-Cation-Radical Systems

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Received July 24, 1991

The proximity of two or more porphyrins has been shown to be crucial in numerous biological processes such as electron transfer or oxygen activation. We report the electrochemical and spectroscopic (UV–vis, EPR) behavior of two families of dimeric cofacial diporphyrins, either covalently linked by two amide bridges (FTF*n* family) or monolinked by a polyaromatic bridge ("Pacman" DPX family). The derivatives with nonelectroactive centers (H$_2$, Zn, Cu) are investigated; thus the redox systems are centered on the π-ring systems only. When the two rings are sufficiently far apart, the dimer nearly behaves as the juxtaposition of two monomers. A two-electron oxidation process formally gives rise to a π-cation diradical, and in one case a triplet-state spectrum can be observed. When the two rings are very close, strong π–π interactions generate mixed-valence behavior: the first oxidation process is split into two one-electron steps. The first oxidation product is a totally delocalized π-radical, while in the second the two delocalized electrons of the rings become spin-paired, giving rise to a kind of nonclassical π–π bond. Analysis of the results and rationalization with the literature demonstrate that from a redox standpoint these molecules have to be considered as a single redox entity. A qualitative molecular orbital diagram is proposed which accounts for the enhanced electronic properties of these dimers.

Introduction

Recent growing interest in the chemistry of polynuclear porphyrin and phthalocyanine derivatives, either natural or synthetic aggregates, sandwich complexes, or covalently linked oligomers, derives from their remarkable electron-transfer properties. Porphyrins have been shown to be interesting models of photosystems for energy conversion[2-11] as well as to display molecular conductivity.[11] Another area in which closely spaced porphyrinic systems are known to be involved is catalysis in natural systems

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