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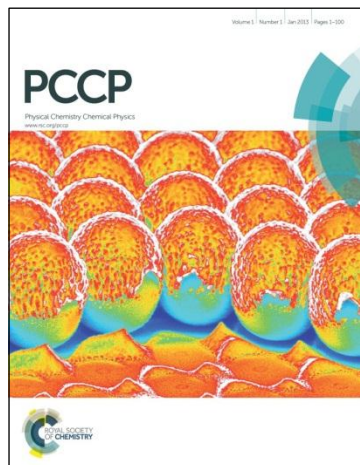
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Why vertically π -expanded imidazo[1,2-*a*]pyridines are weak fluorescence emitters: experimental and computational study

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Photophysics of π -expanded analogs of imidazo[1,2-*a*]pyridine, a well-known heterocyclic compound, have been experimentally and theoretically studied. Two regioisomeric systems differing only in arrangement of the benzene ring have shown different optical properties (electronic transition energies, fluorescence quantum yields and decay times). DFT calculations have been in agreement with experimental results. Low fluorescence quantum yields have been attributed to the $S_1 \rightarrow T_2$ intersystem crossing channel. Additional computations predict architectures which should possess higher fluorescence quantum yields.

Introduction

The combination of rapidly changing needs of society, combined with the advent of new synthetic methodologies¹ are responsible for the renaissance in the chemistry of π -expanded aromatic heterocycles.² Compounds of various architectures have emerged over the last two decades.³ Needless to say, efficient fluorescence,⁴ time-delayed fluorescence⁵ and other properties are highly sought, and they are usually discovered by a trial and error approach,⁶ although numerous attempts to predict optical properties are pursued.⁷ Unlike linear⁸ and ladder-type acenes,⁹ analogs of perylene ('vertically expanded heterocycles')¹⁰ are less explored. Consequently their optical properties are less well known and harder to predict.

π -Expanded relatives of imidazo[1,2-*a*]pyridine are of interest in the context of searches for new optical materials, because π -expansion may shift the emission range to lower energies.¹¹ However, the usefulness of these new systems depends on the efficiency of the system-specific radiative and non-radiative excitation energy dissipation pathways. In our previous paper¹² we studied imidazo[5,1,2-*de*]naphtho[1,8-*ab*]quinolizine (compound **1** in Fig. 1), - an example of vertically π -expanded imidazo[1,2-*a*]pyridine. We attributed the relatively low fluorescence quantum yield of this compound ($\Phi_f=4-5\%$) to efficient intersystem crossing from the lowest excited singlet state, S_1 , to the triplet manifold, manifested by the observation of phosphorescence emission. The possibility of efficient energy relaxation by this channel was confirmed by quantum chemistry calculations which showed that the energy of the excited triplet state T_2 is located at slightly lower energy than that of the S_1 state. Relative energies of the singlet and triplet states depend on the molecular structure. Therefore, in order to advance the understanding of the factors determining photophysics of the π -expanded analogs of imidazo[1,2-*a*]pyridine,

in the present contribution we focused on two other, not yet investigated, vertically π -expanded compounds, whose structures are also presented in Figure 1. Compounds **2** and **3**, whose synthesis was already described in ref. 13, are composed of the imidazo[1,2-*a*]pyridine moiety connected in two different fashions with a phenanthrene moiety.

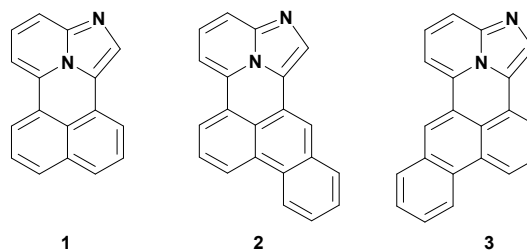


Figure 1 Structures of investigated compounds **2** and **3**, and reference compound, imidazo[5,1,2-*de*]naphtho[1,8-*ab*]quinolizine, indicated as **1**.

Results and discussion

Spectroscopic and kinetic results

Absorption and fluorescence spectra of compounds **2** and **3** dissolved in liquid *n*-hexane, are shown in Figure 2. They are made up of broad bands with weakly resolved vibrational structure. The maximum of the lowest energy absorption band, identified with the $S_0 \rightarrow S_1$ transition, is located at 19193 cm^{-1} for compound **2**, and at 19531 cm^{-1} for **3**. The fluorescence maxima, attributed to the $S_1 \rightarrow S_0$ transition, are at 18696 and 19061 cm^{-1} for **2** and **3**, respectively. Thus, the spectra of both compounds are located in a similar spectral range, although the onsets of the spectra of **3** are located at slightly higher energies than those of **2**. Interestingly, the onsets of the

spectra of the reference compound **1** (19050 cm^{-1} in absorption and 20400 cm^{-1} in fluorescence)¹² are close to those of compounds **2** and **3**. It can thus be concluded, that π -expansion of imidazo[1,2-*a*]pyridine by attaching a phenanthrene moiety, when compare with attaching a naphthalene moiety, does not contribute considerably to the energy separation between the ground and the lowest excited electronic singlet states.

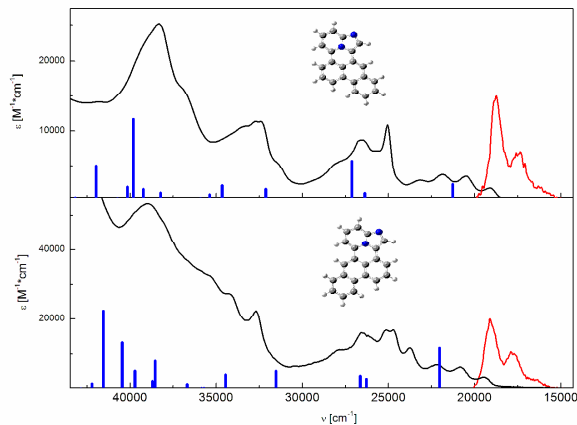


Figure 2 Absorption (black) and fluorescence (red) spectra of compounds **2** (top) and **3** (bottom) in liquid *n*-hexane at room temperature. Calculated energies of electronic transitions to the excited singlet states are presented in the form of vertical lines with heights proportional to the oscillator strengths.

Fluorescence quantum yields (Φ_f) and decay times (τ) obtained for both of the investigated compounds in *n*-hexane at room temperature are collected in Table 1. These data directly provide radiative (k_r) and non-radiative (k_{nr}) rate constants for depopulation of the S_1 state, calculated as $k_r = \Phi_f / \tau$ and $k_{nr} = (1 - \Phi_f) / \tau$.

It is interesting to notice that the radiative rate k_r is two times higher for compound **3** than for **2**. This is consistent with the absorption spectra presented in Fig. 2, which show maximum extinction values for the lowest energy transition band of $\sim 6000 \text{ M}^{-1}\text{cm}^{-1}$ and $\sim 3500 \text{ M}^{-1}\text{cm}^{-1}$ for compounds **3** and **2**, respectively.

The experimental data also shows that the non-radiative rate constant is roughly two orders of magnitude higher than the radiative rate constant. In general, two competing relaxation channels, internal conversion to the ground S_0 state and intersystem crossing to the triplet manifold, can contribute to the observed non-radiative depopulation. Internal conversion is ruled by the energy gap law,¹⁴ which states that its rate constant increases near exponentially with decreasing energy gap between electronic states involved in the transition. Slightly higher value of k_{nr} observed for **2** than for **3** is consistent with this rule and may suggest that an important channel of the S_1 state relaxation is via internal conversion. We cannot, however, exclude a significant contribution from the intersystem crossing. It is generally accepted that the $S_1 \rightarrow T_1$ crossing depends on the $S_1 - T_1$ energy gap, where T_1 state is near or below the S_1 .¹⁴ Precise location of the higher triplet states is experimentally difficult and usually based on theoretical calculations. Phosphorescence emission from the lowest energy triplet state T_1 provides fingerprint of intersystem crossing to triplet manifold, but this is seldom observed at room temperature. In order to search for this emission in the

investigated compounds we conducted optical experiments in low temperature *n*-alkane matrices, at 5 K.

Table 1 Fluorescence quantum yields (Φ_f), decay times (τ) and calculated radiative (k_r) and nonradiative (k_{nr}) rate constants.

Compd.	Φ_f	τ [ns]	k_r [s^{-1}]	k_{nr} [s^{-1}]
2	0.008	2.17	$(3.7 \pm 0.4) \cdot 10^6$	$(4.57 \pm 0.02) \cdot 10^8$
3	0.02	2.65	$(7.5 \pm 0.7) \cdot 10^6$	$(3.70 \pm 0.02) \cdot 10^8$

Fluorescence and phosphorescence spectra of compounds **2** and **3** in *n*-alkanes at low-temperature (5 K) are highly structured (Figure 3). The emission originates from several matrix sites, each site spectrum carrying information about the frequencies of the ground state vibrations. As in the case of room temperature spectra, the onset of the fluorescence spectrum of compound **2** is located at lower energy than that of compound **3**. Observation of phosphorescence indicates that intersystem crossing is operating, but we can not estimate how efficient this process is only from the intensity of the emission.

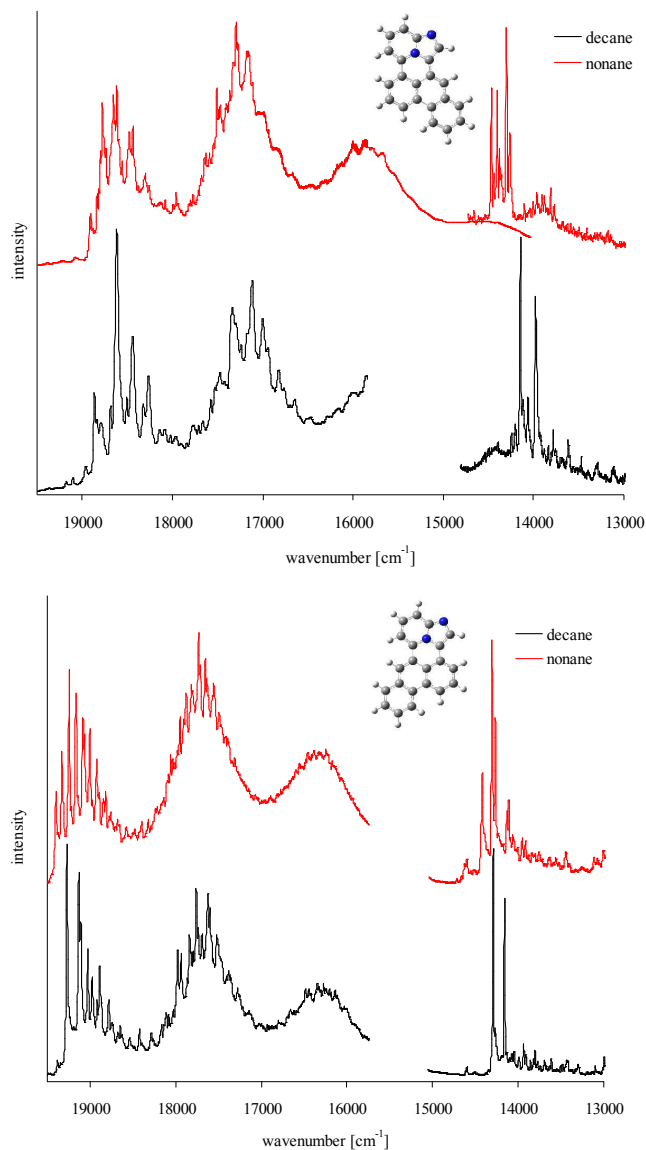
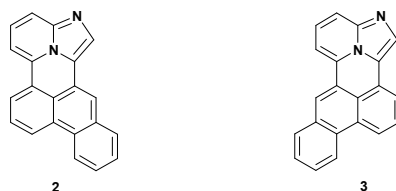


Figure 3 Fluorescence and phosphorescence spectra of compounds **2** and **3** in frozen matrices of *n*-nonane and *n*-decane at 5 K.

Quantum chemical calculations

Results of the calculations performed with the aid of DFT and TDDFT B3LYP/6-31G(d,p) methods, with the geometry optimization in the ground and lowest excited states, are summarized in Table 2. These data describe absorption ($S_0 \rightarrow S_1$) and fluorescence ($S_1 \rightarrow S_0$) of compounds **2** and **3** for molecular structures optimized in the S_0 and S_1 states, respectively. Stability of these states in both molecules is confirmed by positive values of all vibrational frequencies. Molecules **2** and **3** are planar in both electronic states, S_0 and S_1 . The S_1 states of both molecules are of $\pi\pi^*$ type. Lowest singlet states of $n\pi^*$ type for both molecules are located at much higher energies. The three lowest triplet states of both compounds, T_1 , T_2 and T_3 are of $\pi\pi^*$ type. More data (the transition energies for $S_0 \rightarrow S_i$, $i=1, \dots, 10$, energy diagrams, shapes of HOMO and LUMO orbitals, frequencies of vibration, directions of dipole moments and graphical presentation of some vibrations) are collected in ESI in Tables S1 - S4.

Table 2 Calculated and experimental data for the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_0$ transitions for compounds **2** and **3**. Frequencies (ν) and oscillator strengths (f) for the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_0$ transitions were calculated for the structures optimized in the S_0 and S_1 states, respectively. μ indicates dipole moments calculated in the S_0 and S_1 states.



	Calculation	Experiment, 5K	Calculation	Experiment, 5K
$\nu(S_0 \rightarrow S_1)$ [cm ⁻¹] (f)	21275 (0.116)		22036 (0.233)	
$\nu(S_1 \rightarrow S_0)$ [cm ⁻¹] (f)	16424 (0.071)		18253 (0.175)	
$\nu(0,0)$ [cm ⁻¹]	18282	18615 (decane), 18770 (nonane)	19505	19271 (decane), 19399 (nonane)
$\nu(T_1 \rightarrow S_0)$ [cm ⁻¹]	14515	14142 (decane), 14185 (nonane)	14149	14307 (decane), 14409 (nonane)
$\Delta(S_1, T_2)$ [cm ⁻¹]	2344		2300	
$\mu(S_0)$ [D]	3.23		3.14	
$\mu(S_1)$ [D]	3.80		2.89	

The calculated data reproduce the experimental data very well. Such conclusion pertains to the transition energies, where from the calculation the $\nu(0,0)$ band for compound **2** is lower than that for **3**, as well as kinetic parameters, where approximately two times higher oscillation strength is calculated for the S_0 - S_1 transition in compound **3** than in **2**, reproducing a similar ratio between the experimentally determined radiative rate constants k_r (Table 1) and extinction values (Fig. 2). The above agreement allows us to have confidence in the calculated energies of the higher triplet states. According to calculations that the T_3 state is located high above, whereas the T_2 below the singlet S_1 , with nearly the same energy separation $\Delta(S_1, T_2)$ in both compounds (see Table S1 in ESI). Thus, we may assume

that the intersystem crossing rate constant can be similar in both of the considered compounds.

Analysis of the vibrational structure of the spectra

An important aspect of this work was to understand the vibrational structure of the low temperature spectra.

Calculated fluorescence spectra for both compounds are shown in Figure 4 (detailed data of calculated frequencies and vibrations contributing to the Franck-Condon factors are presented in tables S3 and S4 of ESI). It can be easily seen that the vibrations of similar frequencies contribute to the spectra of both compounds, but a purely electronic (0,0) line is relatively stronger in the spectrum of compound **3**. The dominating "170" and "360" cm⁻¹ low-frequency modes, indicated in Figure 4 by arrows, as well as very active modes "1530" and "1540", have bending and bending-stretching character between the two moieties, as graphically presented in ESI.

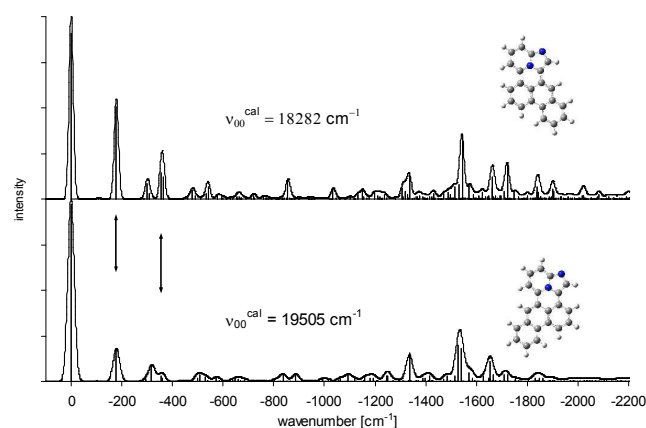


Figure 4 Calculated vibrational structure of fluorescence spectrum of both compounds. The 0 of energy corresponds to the (0,0) transition. The spectra are presented with $fwhm=10$ cm⁻¹.

On the basis of the spectra presented in Figure 4 we may reproduce the main vibrational features observed in the experimentally recorded fluorescence spectrum. Quasi linear spectra of organic molecules in *n*-alkane matrices are typically complex, dependent on the lengths of guest molecules and on available host cavities, and guest molecules occupy usually several matrix sites.¹⁵ Such a situation is also the case in the present system and in order to reproduce the fluorescence spectrum of compound **2** in *n*-decane we had to take into account two insertion sites, whereas in the case of compound **3** we had to consider at least four sites. The results of fits are shown in Figures 5 and 6.

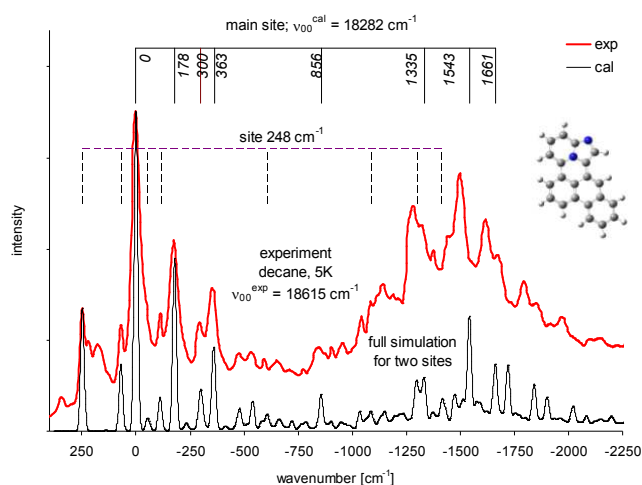


Figure 5 Experimental (top, red) and simulated (bottom, black) spectra of compound **2** in *n*-decane at 5 K. Simulated spectrum was obtained by adding the spectra originating from two matrix sites, main with the (0,0) line at 18282 cm^{-1} , and the second, shifted by 248 cm^{-1} to lower energy. Fwhm=10 cm^{-1} .

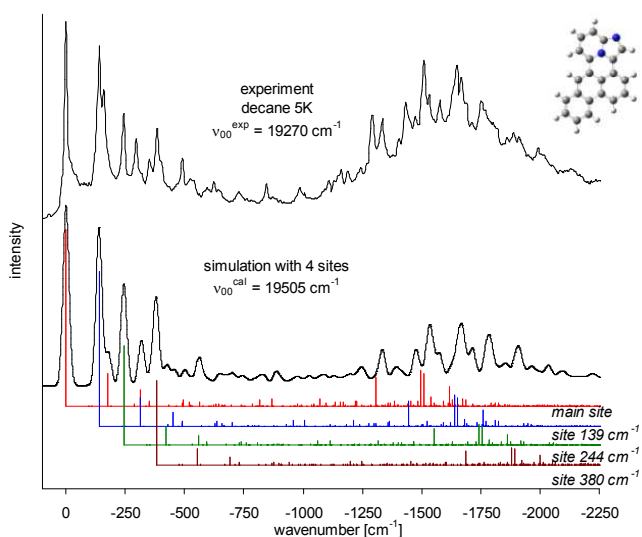


Figure 6 Experimental (top) and simulated (bottom) spectra of compound **3** in *n*-decane at 5 K. Simulated spectrum was obtained as composition of the emission originating from main matrix site with the (0,0) line at 19505 cm^{-1} , and from three other sites, shifted by 139, 244 and 380 cm^{-1} to lower energy. Fwhm=10 cm^{-1} .

Phosphorescence spectra of both compounds can be reproduced with the same set of vibrational lines as in the case of fluorescence. But for phosphorescence it was sufficient to consider that the emission originates from one or two sites, only (see ESI). Such an observation may indicate that intersystem crossing is a site selective process, but a more definitive conclusion would require more elaborate studies.

The spectra presented above of the two regioisomers show several similarities, but it is obvious that orientation of the imidazo[1,2-*a*]pyridine moiety with respect to the phenanthrene moiety is an important modifying factor. For example, the slightly smaller shortening of the bond lengths between the both moieties in compound **3** as compared with **2** lead to slightly smaller FC factors in the former. Direction of the ground state dipole moment in both isomers is given by the orientation of the imidazo[1,2-*a*]pyridine moiety (see Figure S)

and thus dipole moment is differently oriented with respect to the phenanthrene moiety. Small differences in the shapes of the HOMO and LUMO of both isomers are reflected in the oscillator strengths for the S_0 - S_1 transitions. All of these show that prediction of properties of π -expanded imidazo[1,2-*a*]pyridines is not a trivial problem, and needs careful investigation, as has previously been done for hydrocarbons.¹⁶

Suggestions for future studies

A characteristic feature of both of the investigated compounds, as well as of imidazo[5,1,2-*de*]naphtho[1,8-*ab*]quinolizine,¹² is very low fluorescence quantum yield. Nonradiative depopulation of the fluorescence emitting S_1 state proceeds either by internal conversion, $S_1 \rightarrow S_0$, and/or by intersystem crossing, $S_1 \rightarrow T_2 \rightarrow T_1$, channels. Both depopulation channels are sensitive to the energy separation between the involved excited states, and are dependent on the molecule structure. Very good agreement between the experimental and simulated data allowed us to go further, and by using quantum mechanical simulations to suggest the synthesis of new, not yet existing, π -expanded relatives of imidazo[1,2-*a*]pyridine, with the aim to find better fluorescence emitters. Five new molecular structures that are considered are shown in Fig. 7. The calculated spectroscopic properties of these compounds are collected in Table 3.

According to the data in Table 3, compounds **4**, **7**, and **8** have their T_2 state (or T_3 in the case of **7**) located less than 2500 cm^{-1} below the S_1 state. For these molecules we may expect, as already shown for **1**,¹² **2** and **3**, that the intersystem crossing channel may compete with internal conversion. Situation is different for molecules **5** and **6**, which have their triplet T_2 state located above the S_1 state, whereas T_1 is far below. Energy diagram of this type suggests inefficient intersystem crossing and lack of phosphorescence. By the same token, nonradiative relaxation may proceed in these two compounds predominantly via the internal conversion channel. These two molecules are thus our candidates for further studies. It is also interesting to notice that molecules **5** and **6** are nonplanar, which distinguishes them from the other molecules shown in Fig. 7. According to our calculations the angles between the planes of the imidazo[1,2-*a*]pyridine moiety and the anthracene moiety in **5** and the tetracene moiety in **6** are 17 and 18 degrees, respectively.

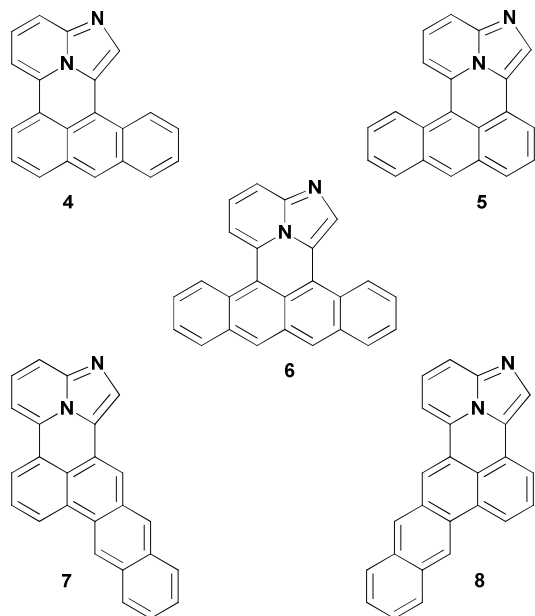


Figure 7 Structure of computationally investigated compounds 4 – 8.

Table 3 Computed spectroscopic properties of compounds 1-8.

C	S ₁ [cm ⁻¹]	f	T ₃ [cm ⁻¹]	T ₂ [cm ⁻¹]	T ₁ [cm ⁻¹]	Δ (S ₁ -T ₃)	Δ (S ₁ -T ₂)	Δ (S ₁ -T ₁)
1	21800	0.140	26175	19759	13780	-4375	2041	8020
2	21275	0.116	23455	18932	14615	-2180	2343	6660
3	22036	0.233	22994	19736	14149	-958	2299	7887
4	19026	0.201	24071	16718	9793	-5045	2307	9233
5	17885	0.166	21565	18765	9407	-3680	-880	8478
6	14892	0.151	20264	15355	5491	-5372	-463	9400
7	20432	0.068	20428	16298	13726	3	4134	6705
8	20708	0.292	19566	18406	12642	1142	2302	8066

Conclusions

Absorption, fluorescence and phosphorescence spectra of two vertically π -expanded relatives of imidazo[1,2-*a*]pyridine were studied at room temperature and in a low temperature matrix, at 5 K. A characteristic feature was low fluorescence quantum yield (0.8% and 2%), which is due to efficient nonradiative relaxation of the excitation energy, by internal conversion, S₁→S₀, and/or by intersystem crossing, S₁→T₂→T₁, channels. On the basis of our experimental data we were unable to decide which of these processes is dominant. The latter process, manifested by the phosphorescence emission, is operating because in both compounds the T₂ state, according to quantum chemistry calculations, is located some 2300 cm⁻¹ below the S₁ state.

Very good agreement between experimental and calculated data allowed us to propose studies of two new π -expanded relatives of imidazo[1,2-*a*]pyridine, which by blocking efficient intersystem crossing may appear to be better emitters of fluorescence.

Experimental

Compounds 2 and 3 were prepared as previously described.¹³ Absorption and fluorescence spectra of 2 and 3 in liquid solutions of *n*-hexane and *n*-heptane (spectroscopic grade) were measured at room temperature with the aid of a PerkinElmer UV/VIS Spectrometer Lambda 35, and a Perkin-Elmer 512 Fluorescence Spectrometer, respectively. Fluorescence quantum yield (Φ_f) was determined by using perylene in cyclohexane as a standard ($\Phi_f=0.96$).¹⁷ The error inherent with the Φ_f estimation does not exceeds 10%.

Fluorescence and phosphorescence spectra of 2 and 3 in *n*-nonane and *n*-decane matrix at 5 K were monitored and separated with the aid of a home-built Parker type phosphorimeter¹⁸ equipped with a McPherson 207 monochromator (300 G/mm) and an Andor DU420A-BR-DD CCD camera, electronically cooled to -90 degree Celsius. Excitation sources were cw diode lasers emitting either 405 or 445 nm light (~50 mW).

Fluorescence kinetics studies were performed with the aid of the "time correlated" single photon counting technique (in the inverted time mode). Excitation pulses were provided by the second harmonics of a mode-locked Coherent Mira-HP picosecond laser pumped by a Verdi 18 laser. Original repetition rate of a Mira laser was reduced with the aid of APE Pulse selector to 2 MHz. Fluorescence photons were dispersed with a McPherson 207 monochromator and detected with HMP-100-50 hybrid detector and SPC-150 module inserted into a PC, both from Becker&Hickl GmbH. Fluorescence decays were long, as compared with the time-width of the excitation pulses (~200 ps), and therefore the decay curves (delayed by 1 ns with respect to the excitation) were fitted to single exponential dependences without using a deconvolution procedure (see Fig. S1 of ESI). Estimated precision of the decay time determination was 10 ps.

All calculations within this work were made with the aid of the Gaussian 09 package.¹⁹ Optimization of the molecular geometry in the electronic ground (S₀) and in the lowest excited (S₁) states were done with the DFT and TD DFT B3LYP/6-31G(d,p) methods. The spectra of molecules in solutions were calculated within the framework of the PCM model, with the use of the default options of this model implemented in the Gaussian package. Vibrational structure of the electronic spectra was calculated with a procedure included into Gaussian 09, which uses the Franck-Condon factors and the Duchinsky matrix.²⁰

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Notes and references

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† Electronic Supplementary Information (ESI) available: details of DFT calculations, fluorescence decay curves, simulated phosphorescence spectrum and graphical presentation of main vibrations. See DOI:

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