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Photophysical studies on a series of new ethane-bridged dimeric bipyridine ligands

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Abstract

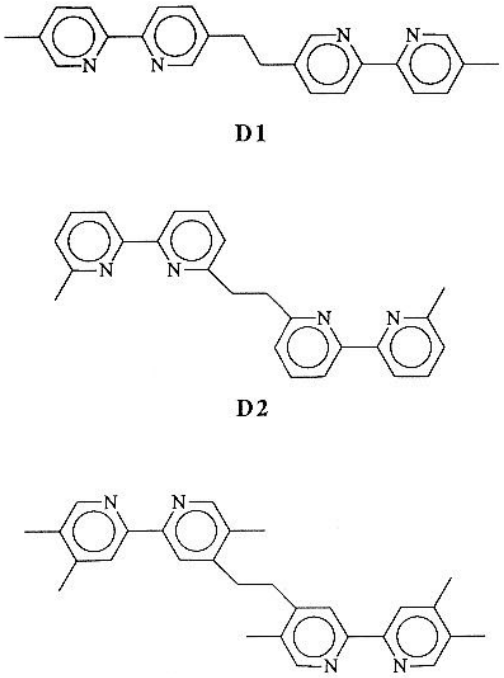
The photophysical properties of three 1,2-bis(2,2′-bipyridinyl)ethane ligands and their corresponding monomeric units have been studied in detail. The fluorescence quantum yields (about 3×10^{-3}), and the fluorescence lifetimes (about 50 ps) differ from those of the parent molecule 2,2′-bipyridine. The increased radiative constants are explained with the aid of quantum-mechanical semiempirical calculations.

1. Introduction

The polypyridinic compounds derived from the basic molecule 2,2′-bipyridine (bpy) are widely used as ligands for transition-metal complexes, which are interesting for their luminescence [1–3] and redox properties [3–5]. A new series of these ligands, based on two bipyridinic moieties bonded through single bonds (1,2-bis(2,2′-bipyridinyl)ethane), has been recently synthesized through oxidative coupling of the corresponding monomeric methylene carbanions [6]. The interest of such a series of ligands stands in their ability to give bimetallic complexes [7] that have the possibility of catalysing multielectron redox processes [8–10]. Some preliminary result on the spectral and emission properties of these ligands has already been published [6].

In this paper we present a detailed study on the photophysics of these organic compounds by extending the approach previously applied to the parent molecule bpy [11]. This approach, based on lifetime measurements in the picosecond scale, fluorescence quantum yields and semiempirical calculations, succeeded in giving a consistent picture of the main mechanism of deactivation of the low-lying electronic states of bpy, a molecule for a long time claimed to be non-fluorescent.

The compounds studied are bis-methylated and tetramethylated bipyridines (5,5′-dimethyl-2,2′-bipyridine (M1), 6,6′-dimethyl-2,2′-bipyridine (M2) and 4,4′,5,5′-tetramethyl-2,2′-bipyridine (M3)) in *cis* conformation and their corresponding dimeric compounds (1,2-bis(5′-methyl-2,2′-bipyridin-5-yl)ethane (D1), 1,2-bis(6′-methyl-2,2′-



D1

D2

D3

Fig. 1. Formulae for compounds D1, D2 and D3.

bipyridin-6-yl)ethane (D2) and 1,2-bis(4′,5′,5-trimethyl-2,2′-bipyridin-4-yl)ethane (D3)). Figure 1 shows the formulae of the latter compounds.

2. Experimental details

The dimeric 1,2-bis(2,2′-bipyridinyl)ethane ligands were prepared from the corresponding monomeric subunits by the published procedure [6]. Solvents for spectroscopic experiments were of spectroquality grade. When necessary, samples were degassed by bubbling nitrogen or argon.

Absorption spectra were recorded with a Perkin-Elmer Lambda-6 spectrophotometer. Figure 2 shows a typical absorption and emission spectra of a dimeric species (D2). For emission measurements, the sample concentration was in every case less than 2×10^{-5} M, in order to avoid aggregation problems. The (uncorrected) emission spectra were obtained with a Perkin–Elmer 650-40 spectrofluorometer equipped with a Hamamatsu R928 tube.

Emission quantum yields were measured at room temperature (20 °C) with the optically dilute method [12] calibrating the spectrofluorometer with a standard lamp. Quinine sulphate in 1 N aqueous H_2SO_4 was used as a quantum yield standard, assuming a value of 0.55 [13].

The fluorescence decay emission of all compounds has been measured with the time-correlated single-photon-counting technique operating in inverse configuration. Using this set-up [11] the ramp of the time-to-amplitude converter is initiated by the

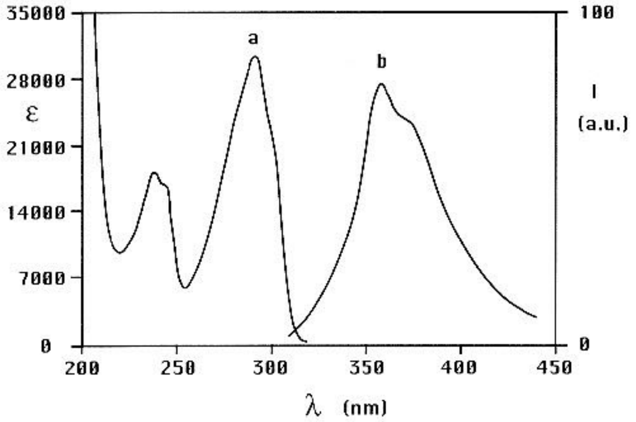


Fig. 2. (a) Absorption and (b) emission spectra of ligand D2 in cyclohexane solution at room temperature: a.u., arbitrary units.

fluorescence photon and stopped by a fast photodiode signal triggered by the exciting laser pulses or directly by the microwave mode-locker driver signal. A train of pulses of about 5 ps full width at half-maximum (FWHM) at 80 MHz repetition rate from a synchronously pumped dye laser were doubled in energy by a potassium dihydrogen phosphate SHG (second harmonic generation) crystal and used to excite the sample solution, typically about 10^{-5} M in cyclohexane. The laser wavelengths used were 590 nm from Rh 6G dye and 608 nm from Rh 110 dye. The laser intensity was about 150 mW, 10% of which was converted in the exciting UV radiation.

The fluorescence emission, after spectral discrimination in a 0.25 m double monochromator was detected with a MCP photomultiplier from Hamamatsu model 1564U/01. A large-band 1.2 GHz amplifier was used in a first stage of pre-amplification. More amplification was applied before entering the constant fraction discriminator. The START signal of the time-to-amplitude conversion was taken from fluorescence photons whereas the STOP signal to the conversion came directly from the mode-locker r.f. driver. The converted, statistically distributed amplitude signals were accumulated in the memory of a multichannel analyser up to about four decades of signal. The electronic jitter plus the unavoidable optic path distortion due to the gathering optic and the double-monochromator acceptance angle determined an instrumental function of 140 ps FWHM. This would allow a resolution of about 15 ps after deconvolution.

To avoid the production of photochemical species which can occur in a static sample illumination the solutions were circulated with the help of a pump. Fluorescence was collected at different wavelengths, chosen according to the emission spectra of the compounds. The instrumental function was collected recording the light scattered by the solution at the excitation wavelength. The parameters characterizing the fluorescence emissions, namely decay time, amplitude, background and number of exponentials, were obtained for each decay curve by fitting the convolved true decay and instrumental shape function to the experimental decay. A non-linear least-squares method was used as suggested in ref. 14.

Although all the curves obtained may be fairly well fitted with only one exponential decay law, more than one exponential was necessary for a good fit. However, the slowest decays (normally in the nanosecond range, with an amplitude less than 1%)

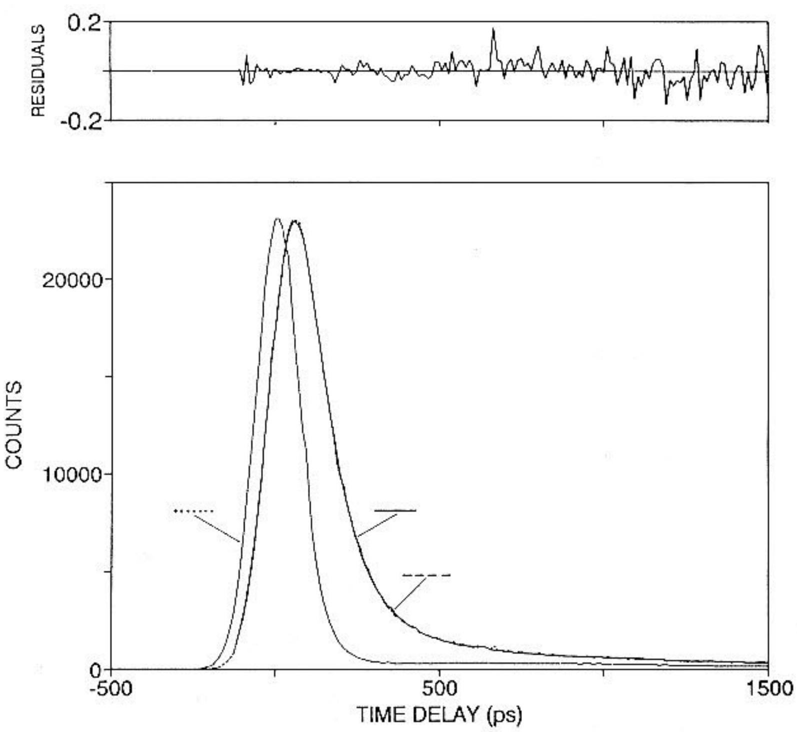


Fig. 3. Plot of the fluorescence decay with best fit and weighted residuals of the ligand M2 in cyclohexane solution; ·····, instrumental function; – – –, experimental; ——, best fit, $\chi^2 = 1.15$.

TABLE 1

Emission quantum yields, fluorescence lifetimes, radiative and non-radiative constants for the examined ligands

Compound	$\phi_F \times 10^3$ [a]	τ[a] (ps)	$k_r \times 10^{-7}$ (s^{-1})	$k_{nr} \times 10^{-10}$ (s^{-1})
M1	3.2	50	6.4	2.0
D1	4.3	60	7.2	1.7
M2	2.8	65	4.3	1.5
D2	4.2	60	7.0	1.7
M3	3.2	58	5.5	1.7
D3	3.5	22	6.3	4.5
bpy[b]	0.6	160	0.4	0.6

[a] In deaerated cyclohexane solution.
[b] In 3-methylpentane [11].

may be attributed to the presence of conformers, to impurities of the sample or to processes such as the emission of photoproducts not completely removed from the emitting volume by sample circulation. By including the full decay curve in the data to be fitted, a precise evaluation of the longest lifetimes was possible. These turned out to be independent of the emission and the excitation wavelengths. The earliest portion of the decay curves was always predominant so that the longest tail, although considered in the fitting procedure, was not given a physical meaning with respect to the decay process of the species considered. A typical decay with the best fit is presented in Fig. 3. The lifetimes of the predominant decays obtained by the convolution-fitting procedure are given in Table 1.

3. Calculations

In order to understand better the photophysics of the compounds under examination, a series of molecular orbital calculations was carried out, using the CNDO/S program [15], with Ohno–Klopman [16, 17] parametrization for the repulsion integrals and the configuration interaction including singly and doubly excited configurations in the space of the 80 configurations previously tested. The geometry of the molecule in the ground state was partially optimized using the program Alchemy [18]. It turns out that none of the M and D compounds is planar in the more stable configuration and that rotation around the hydrocarbon bond connecting the two bipyridinic subunits of the dimers leads to at least two conformers (rotamers) with equivalent energy. These geometrical features have important consequences in differentiating the photophysics of these compounds with respect to the parent planar bpy, and also in the possibility of multiple emissions.

A pictorial representation of the optimized geometries of the D compounds as obtained from the Alchemy program is displayed in Fig. 4. The calculated energies and oscillator strengths of the low-lying singlets are reported in Table 2.

4. Results and discussion

The absorption spectra for all the examined compounds are quite similar and feature two distinct bands centred at around 240 and 290 nm. The relative intensity of the lower-energy band is generally greater by a factor 1.5. From the results of the semiempirical calculations reported in Table 2 together with the main spectral features of these compounds, it turns out that these absorbing systems can be identified with two states carrying an appropriate oscillator strength in the region 4.15–4.60 eV. The calculated oscillator strength is particularly large for the lowest state of the dimeric species. The emission spectrum (see Fig. 2(b) for a typical example) presents a broad unstructured band centred at about 355 nm and very similar to that of bpy [11]. On the contrary, this apparent spectral similarity is in contrast with the dynamical properties of the emitting state, as reported in Table 1. Indeed, these compounds show larger fluorescence quantum yields (about 3×10^{-3} *vs.* 5×10^{-4}) and generally shorter lifetimes (50–60 ps). Combining the lifetime and quantum yield values, one can obtain the radiative constants k_r that are also reported in Table 1. The k_r values for our monomeric and dimeric ligands result one order of magnitude larger than the k_r of bpy, reflecting a much more allowed character of the emitting state. This feature is confirmed by the calculated oscillator strength of the lowest singlet, as reported in Table 2. By analysing the composition of the lowest excited singlet state, one can see that it derives from strong mixing of n–π^* and π–π^* configurations, because of the largely non-planar conformation of the equilibrium geometries. Moreover, methyl substitution also plays an important role in mixing these states, as revealed by comparison of the oscillator strengths with that of bpy.

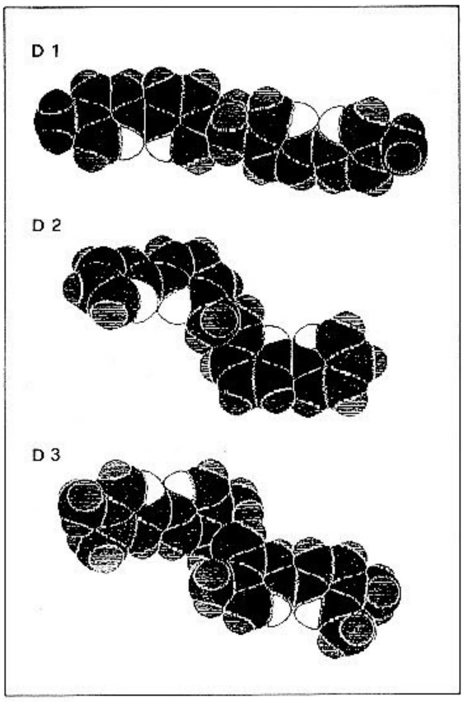


Fig. 4. Graphical representation of the studied dimers, from the program Alchemy.

TABLE 2

Absorption and emission spectra, calculated energies and oscillator strengths for the ligands under study[a]

Compound	λ_{abs} (ϵ) (nm)	λ_{abs} (ϵ) (nm)	λ_{em} (nm)	S_1 (eV)	f	S_2 (eV)	f
M1	244 (14900)	288 (19300)	352	4.15	0.123	4.16	0.385
D1	252 (35400)	291 (51200)	353	4.45	1.659	4.69	0.263
M2	238 (8440)	291 (13800)	357	4.20	0.008	4.22	0.494
D2	239 (18000)	292 (30400)	359	4.55	1.233	4.75	0.634
M3	254 (11500)	286 (14500)	354	4.20	0.224	4.22	0.214
D3	254 ([b])	287 ([b])	352	4.60	0.877	4.72	0.438
bpy[c]	240	285	350	4.13[d]	0.0006[d]	4.23[d]	0.034[d]

[a] Spectral data in cyclohexane solution, unless otherwise noted.
[b] Solubility too low to allow ϵ determination.
[c] In 3-methylpentane [11].
[d] Results obtained for *cis* configuration.

The experimental k_r values increase slightly on going from the monomers to the dimers, whereas the oscillator strengths f calculated for the lowest singlet show a much larger increment. However, it should be noted that the two lowest singlets of the M compounds are calculated so close in energy that a concentration of intensity in the lowest state can be expected within the error of the semiempirical method of calculation.

From the relationship $k_{nr} \approx 1/\tau_F - k_r \approx 1/\tau_F$, one can obtain the non-radiative constants reported in the last column of Table 1. These show a general increment of a factor of about 3 passing from the parent bpy molecule to the dimeric species. Taking into account the value of $k_{isc} = 7 \times 10^9$ s^{-1} calculated for bpy [11], and the addition of the spin–orbit couplings due to the nitrogen atoms [19], one gets $k_{nr} \approx 2.8 \times 10^{10}$ s^{-1}, in good agreement with the experimental values in Table 1. This confirms that also for the examined compounds the main non-radiative decay is due to a triplet mechanism, in line with the findings on bpy [20] and contrary to the findings on the isolated molecule pyridine [21]. On the contrary, similar large values of k_{nr} obtained for the monomers indicate a large contribution of the methyl groups to the intersystem crossing process, with a possible different role of the substituent position.

Finally, one can observe that the great flexibility of these molecules, with the possibility of reaching several energy minima along the potential surfaces relative to rotation of the subunits around the hydrocarbon bridges, could lead to multiple exponential decays. However, the presence of multiple emissions is limited to a few per cent only for D3, and in the absence of more detailed information on the role played by the bridge on the dynamic and kinetic parameters of these compounds, we cannot comment further on the presence of conformers for the compounds under examination.

5. Conclusions

In this paper we have reported a study on the photophysical properties of a series of methylated bipyridines and their dimeric counterparts. The results show a fairly homogeneous set of data as far as fluorescence lifetimes and emission quantum yields are concerned, but large differences when these data are compared with the parent molecule bpy. These differences, discussed in the light of the results of semiempirical calculations, can be explained on the basis of structural changes including non-planarity and substituent effects. The main non-radiative deactivation channel of the lowest singlet has been identified as the intersystem crossing to a nearby triplet state.

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