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Photophysics and evidence of excimer formation, linear bipyridines in solution and solid films

Shih-Sheng Sun, Alistair J. Lees*

Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13902-6016, USA

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Abstract

The photophysical properties of 1,4-bis(4′-pyridylethynyl)-2,5-di(*n*-hexyloxy)benzene and 1,4-bis(4′-pyridylethynyl)benzene in both solution as well as in solid films were investigated. Both compounds exhibit concentration-dependent fluorescence in solution. The fluorescent bands red shift in solution at high concentration and in solid films and the emission is ascribed to the formation of excimers.

Keywords: Fluorescence; Photophysics; Excimer; Bipyridine; Solid films

1. Introduction

Conjugated organic polymers have been widely studied for their applications in optoelectronic technologies [1]. Attaching electron-withdrawing or -donating groups on a carbon framework changes the redox and optical properties of the molecules [2]. Pendant groups with different degrees of length and size may be used to increase the solubility [3]. However, it is sometimes difficult to predict and, thus, pre-design such polymeric compounds because of the coexistence of crystalline and amorphous regions in the structure and unavoidable distribution of chain lengths [4]. To overcome this problem, well-defined oligomer structures have been successfully used to study the structure–properties relationships [5–7].

During the course of our work on luminescent supramolecular complexes, we have recently prepared an unusual molecular triangular species with the formula, $[Br(CO)_3Re(\mu\text{-}\mathbf{1})]_3$ (**1**: 1,4-bis(4′-pyridylethynyl)-2,5-di(*n*-hexyloxy) benzene), by self-assembly of $BrRe(CO)_5$ and **1** in benzene solution [8]. Unlike typical rhenium diimine carbonyl complexes which exhibit luminescence originating from the lowest triplet metal-to-ligand charge transfer (^{3}MLCT) excited states [9], the luminescence of this compound is apparently from a ligand-localized π–π^* excited state, as evidenced by its short lifetime ($\tau = 0.36$ ns), structured emission band and relatively high emission energy position ($\lambda_{em} = 499$ nm and $\lambda_{em} = 477$ nm) [8]. However, in order to fully comprehend the interactions between the π–π^* and MLCT excited states, it is necessary to have a firm understanding of the photophysical properties of the bridging ligand itself. Here, we report the results of a photophysical study of **1** and its analogue 1,4-bis(4′-pyridylethynyl)benzene (**2**) with evidence for molecular excimer formation of both **1** and **2** in solution as well as in solid films. The structures of **1**, **2** and their aromatic analogues (**3** and **4**) are shown in Scheme 1.

2. Results

Table 1 summarizes the photophysical data obtained for **1** and **2** in 1,2-dichloroethane (DCE) and 2-methyltetrahydrofuran (MeTHF) solution, respectively. Three absorption bands are observed at 377 nm, 317 nm, and 307 nm for **1** and two absorption bands at 335 nm and 317 nm for **2**. These structured bands are assigned as π–π^* absorption bands. The band at 377 nm of compound **1** is substantially red-shifted compared to the corresponding band at 335 nm for compound **2**, presumably due to the electron donating effect of the hexyloxy groups. A similar finding has also been reported for the absorption band that is red-shifted when 1,4-bis(4′-phenylethynyl)-2,5-di(*n*-hexyloxy)benzene (**3**) [10] is compared to 1,4-bis(4′-phenylethynyl)benzene (**4**) [11].

Excitation of **1** at 360 nm in dilute DCE solution at 293 K afforded a strong luminescence centered at 420 nm and a shoulder at 438 nm with an overall emission quantum yield (Φ_{em}) of 0.59 and a single emission lifetime (τ) of 2.5 ns

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* Corresponding author. Tel.: +1-607-777-2362; fax: +1-607-777-4478.
E-mail address: alees@binghamton.edu (A.J. Lees).

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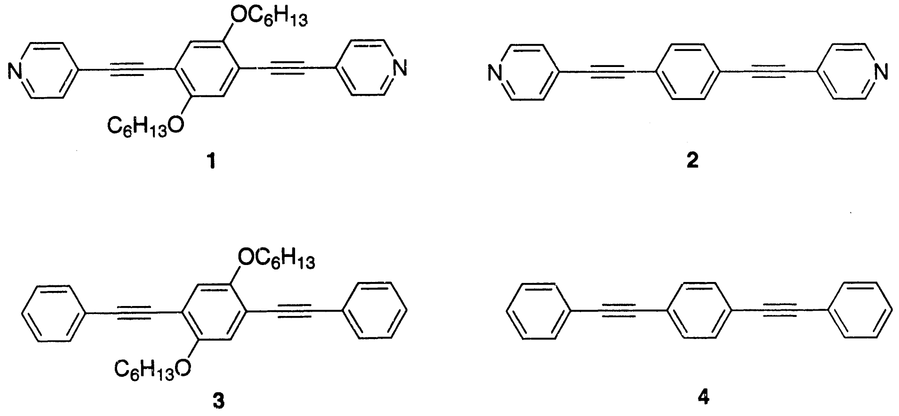

Scheme 1.

Table 1
Obtained photophysical data for **1** and **2** in dilute solution and thin films[a]

Compound	λ_{max} (nm)		τ (ns)	Φ_{em}
	Absorption ($\varepsilon \times 10^{-3}$)	Emission		
1[b]	308 (14.8), 318 (14.0), 377 (13.6)	438, 420	2.5	0.59
1[c]	308 (20.6), 318 (17.8), 376 (17.1)	444	2.9, 0.40	0.49
1[d]	309, 396, 420 (sh)	518		0.026
2[e]	317 (76.2), 335 (51.1)	390, 371, 360, 344	0.32	0.37
2[d]	315, 362 (sh)	440, 420, 400, 390		0.019

[a] $\lambda_{ex} = 350$ nm, sh: shoulder.
[b] The data were collected in 10^{-6} M DCE solution.
[c] The data were collected in 10^{-6} M DMF solution.
[d] The data were collected from solid films.
[e] The data were collected in 10^{-6} M MeTHF solution.

irrespective of the monitoring wavelength throughout the emission band. The electronic absorption and luminescence spectra of **1** in dilute DCE solution are shown in Fig. 1. An excitation spectrum was obtained while monitoring the emission at its maximum and this is found to be superimposable on the absorption spectrum and independent of the emission wavelength. However, the luminescence spectra from **1** showed strong concentration-dependent effects with

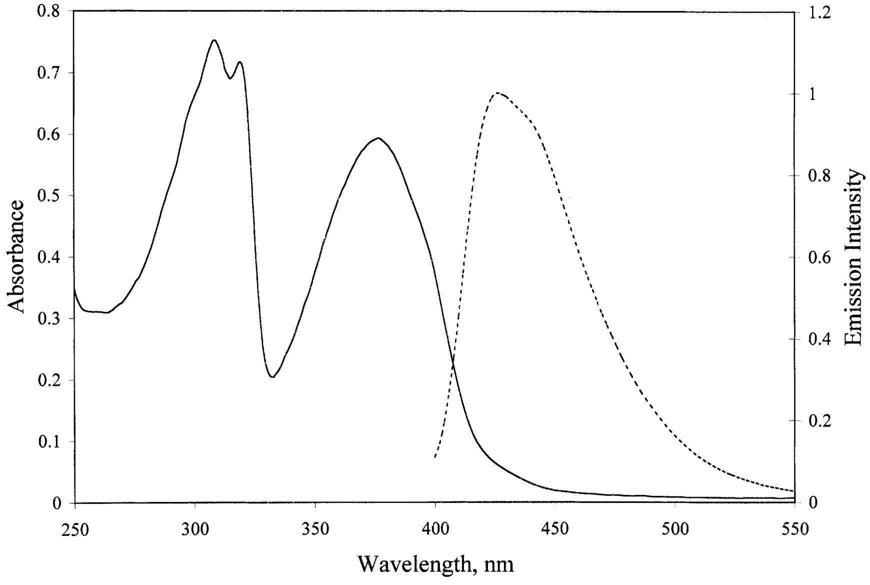

Fig. 1. Electronic absorption (solid line) and emission (dashed line) spectra of **1** in DCE.

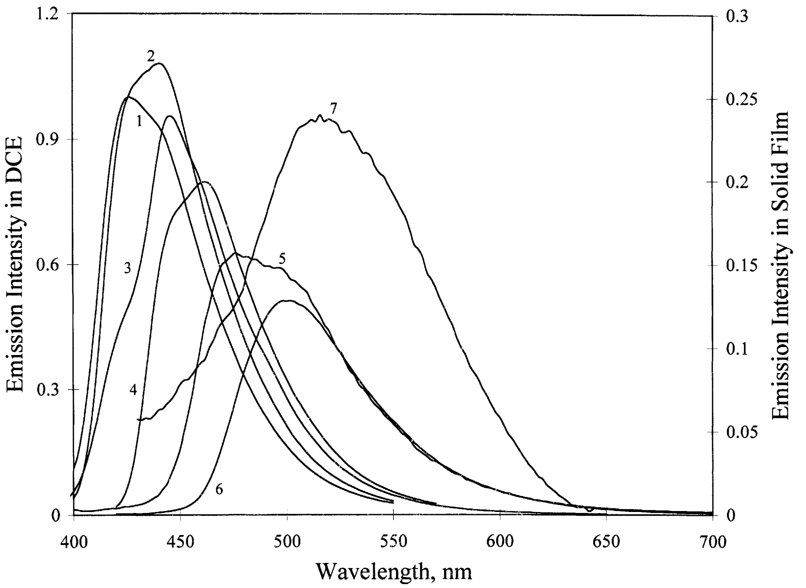

Fig. 2. Concentration-dependent luminescence spectra in DCE and film luminescence spectrum of **1**: curve 1, 4.64×10^{-6} M; curve 2, 9.93×10^{-5} M; curve 3, 9.88×10^{-4} M; curve 4, 3.23×10^{-3} M; curve 5, 5.50×10^{-3} M; curve 6, 1.02×10^{-2} M; curve 7, solid film.

the bands being red-shifted with increasing concentration. Concentration-dependent luminescence spectra and the solid film luminescence spectrum of **1** are shown in Fig. 2. It is noticeable that the component of the emission band which is at longest wavelength increases substantially in intensity at higher solution concentration. In the solid film, this emission is red-shifted even further and its maximum now appears at 518 nm. Significantly, the emission bands from both the concentrated solution and the thin films are broad and structureless.

Fig. 3 shows the luminescence spectra of **1** from a mixture of DCE and DMF. It can be noted that the long wavelength emission component increases with an increasing amount of DMF present in the solution. Importantly, the excited state decay in DMF solution indicated biexponential decay, which was fitted to lifetimes of 2.9 ns and 0.40 s. A similar biexponential decay with lifetimes of 2.8 and 0.60 ns was also observed in 10^{-2} M DCE solution. The luminescence spectrum of **2** in dilute MeTHF features an intense band at 344 nm and several structured bands at 360, 371, and 390 nm with an overall emission quantum yield of 0.37 and an emission lifetime of 0.32 ns. The concentration-dependent luminescence was also observed for **2** in MeTHF solution (see Fig. 4) and the changes of the relative intensities were

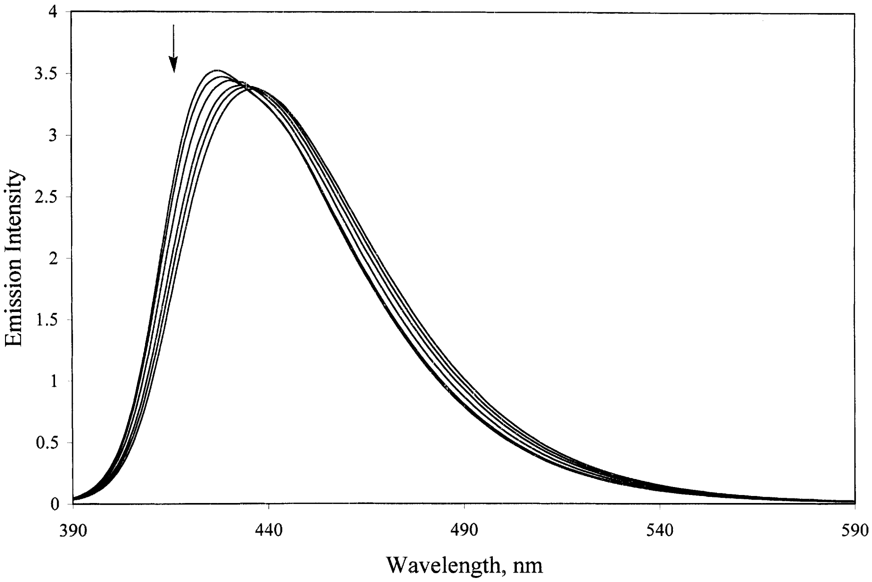

Fig. 3. Fluorescence spectra of **1** in a mixture of DCE and DMF. The percent of DMF in solution is 0, 9.1, 28.6, 54.5, 75, and 100% (from top to bottom).

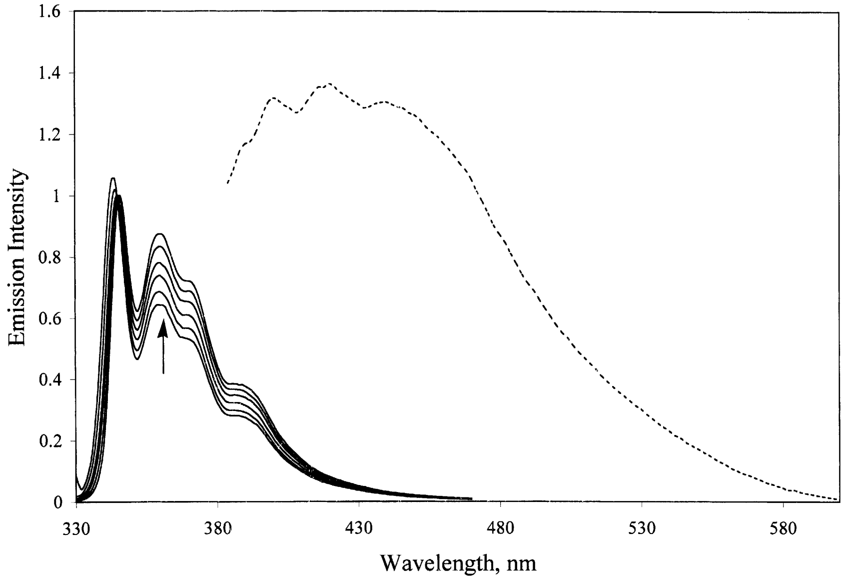

Fig. 4. Concentration-dependent luminescence spectra in MeTHF (solid line) and film luminescence spectrum (dashed line) of **2**. The concentrations from bottom to top are: 1.35×10^{-6} M, 7.84×10^{-6} M, 1.63×10^{-5} M, 2.15×10^{-5} M, 2.90×10^{-5} M, and 3.49×10^{-5} M. The solution emission spectra have been normalized at 317 nm.

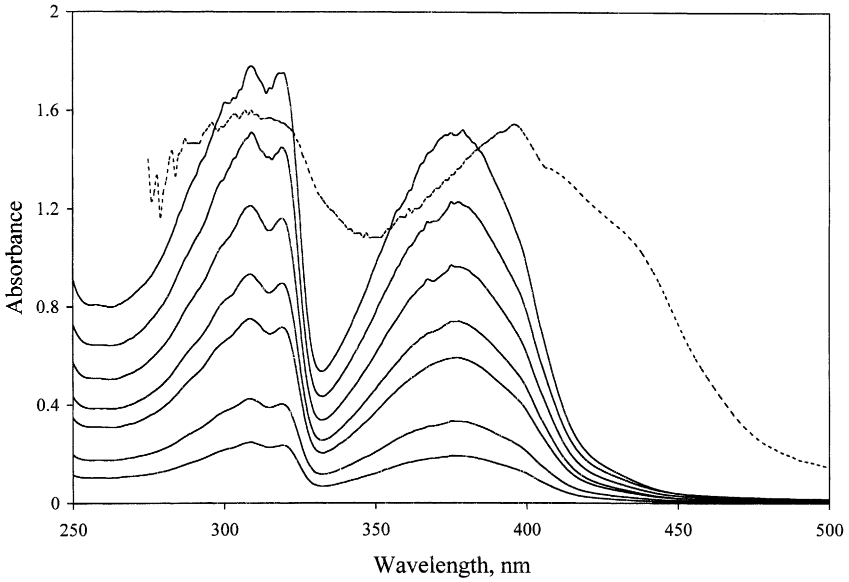

Fig. 5. Absorption spectra of **1** with different concentration in DCE solution (solid line) and in solid film (dashed line). The concentrations from bottom to top are: 1.67×10^{-5} M, 2.86×10^{-5} M, 5.07×10^{-5} M, 6.30×10^{-5} M, 8.17×10^{-5} M, 1.01×10^{-4} M, and 1.20×10^{-4} M.

even more significant than **1**. The luminescence decay for **2** in MeTHF (10^{-2} M) also exhibited a biexponential decay with lifetimes 0.4 and 0.07 ns. In all cases, no corresponding concentration-dependent changes were observed in the absorption spectra but the absorption spectrum did shift to lower energy in the solid film (see Fig. 5). A similar red shift was also observed in the absorption and emission spectra of **2** in solid films compared to those in solution. In both **1** and **2**, the luminescence quantum yields are lowered either with increasing concentration or going to the solid films.

3. Discussion

Aromatic compounds are well known to form excited state dimeric species [12]. The first reported example for aromatic excimer formation was the concentration-dependent fluorescence of pyrene in solution [13,14]. Our results for both **1** and **2**, where there are concentration-dependent fluorescence and concentration-independent absorption spectra, strongly indicate the formation of excimers instead of ground state van der Waals dimers [15]. The absorption and emission spectra from solid films for both **1** and **2** are significantly shifted to lower energy. Moreover, the excited state decays in concentrated DCE for **1** and in concentrated MeTHF for **2** exhibit biexponential decay while only single exponential decays are observed in diluted solution for both **1** and **2**. This observation indicates that a new species is formed in high concentration solution. We suggest that the red shift of emission bands for **1** and **2** in both concentrated solutions and thin films are due to a new excimer emission.

In addition, the luminescence quantum yields for both **1** and **2** decrease with increasing concentration. The luminescence quantum yields in dilute DMF solution and solid films are both lower than those in dilute DCE solution. These results suggest that the decreasing emission quantum yields of solid films of **1** and **2** are caused by self-quenching because of more efficient energy transfer between the stacked molecules. In a more polar solvent like DMF, the π–π stacking effect is more prominent and, indeed, a stronger excimer emission was observed even in a diluted solution. The biexponential emission decay in DMF also indicates that two distinct species exist in the excited state. The observation of excimer emission is quite common in many conjugated polymeric systems [10,11,16,17] or polycyclic aromatic compounds [13,15,18], but there are much fewer reports for simple monomeric conjugated aromatic species. This excimer formation is apparently brought about by an effective π–π stacking effect and it is noted that structurally similar compounds **3** [10] and **4** [11] have also been postulated to form excimers in highly concentrated solutions.

4. Conclusion

We have demonstrated here that the monomeric conjugated aromatic compounds, **1** and **2** exhibit strong concentration-dependent fluorescence in room-temperature solution. The red-edge band(s) are assigned to the excimer emission and, in each case, effective aromatic stacking is understood to be responsible for the formation of the excimer in the excited states.

5. Experimental

All photophysical measurements were done at room temperature. UV–VIS spectra were obtained using a HP 8450A diode array spectrophotometer interfaced to an IBM computer. Emission, excitation spectra, and lifetime were recorded in deoxygenated solvent solution at 293 K with an SLM 48000S lifetime fluorescence spectrophotometer equipped with a red-sensitive photomultiplier tube. Luminescence quantum yields were taken as the average of three separate determinations and were reproducible to within 10%. The errors for fitted lifetimes are estimated to be within 10%. Thin films were prepared by first dissolving the sample in DCE or CH_2Cl_2. These solutions were then filtered to remove any undissolved particles present and then spin cast on clean borosilicate glass slides. The "wet" film was subsequently dried under vacuum overnight before acquiring the luminescence measurements. Film luminescence measurements were obtained by placing the sample film at a 22.5° angle to the incident beam. Fluorescence quantum yields in solution and in solid film were calculated relative to perylene ($\Phi_{\mathrm{em}} = 0.89$ in EtOH) [19] and 9,10-diphenylanthracene in poly(methyl methacrylate) (1 mM, $\Phi_{\mathrm{em}} = 0.83$), [20], respectively. Compounds **1** [8] and **2** [21] were prepared according to the published procedures.

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