Journal of Photochemistry, 37 (1987) 59 - 67

PHOTOPHYSICAL PROPERTIES OF 1,4,5,8-TETRAAZAPHENANTHRENE

SANG CHUL SHIM†, SEUNG KI PARK, EUN JU SHIN and HO KWON KANG

Department of Chemistry, Korea Advanced Institute of Science and Technology,
P.O. Box 150, Chongyangni, Seoul 131 (Korea)

(Received February 17, 1986; in revised form June 4, 1986)

Summary

1,4,5,8-Tetraazaphenanthrene (TAP) has close-lying n,π^* and π,π^* singlet states and therefore shows very weak fluorescence ($\Phi_f = 0.001$); laser flash photolysis indicated that it undergoes efficient intersystem crossing ($\Phi_{isc} = 0.95$). The intensity of fluorescence of TAP increases on addition of sodium acetate because N–Na cation coordination elevates the lowest excited $^1(n,\pi^*)$ state to a higher energy. Because of mixing between the lowest excited $^1(n,\pi^*)$ state and $^1(\pi,\pi^*)$, TAP shows the heavy-atom effect, which is generally not observed in the pure $^1(n,\pi^*)$ state. Since the phosphorescence lifetime is relatively long (about 0.5 - 0.8 s) and the phosphorescence is negatively polarized, the lowest triplet state has the π,π^* configuration. The photoreactivity of TAP is compared with the photophysical parameters of azaphenanthrenes.

1. Introduction

Many photophysical and photochemical studies on heterocyclic compounds have served to emphasize the important role of the n,π^* state: for example, vibronic interaction between n,π^* and π,π^* states and spin–orbit coupling [1 - 3]. It is now strongly suspected that the vibronic perturbation of the lowest energy π,π^* (or n,π^*) singlet state by the close-lying n,π^* (or π,π^*) state leads to an efficient $S_1 \rightsquigarrow S_0$ internal conversion for nitrogen heterocyclic and aromatic carbonyl compounds in the condensed phase [4].

The effects of nitrogen positional isomerism and the internal heavy atom on the photophysical behavior of some mono-azaphenanthrenes (APhs) have been reported [5, 6]. The general features of the absorption and emission spectra of phenanthrene are maintained on introduction of the heteroatom, indicating the common π,π^* nature of the emitting singlet (S_1) and triplet (T_1) states.

---

† Author to whom correspondence should be addressed.

0047-2670/87/$3.50

1,4,5,8-Tetraazaphenanthrene (TAP), an azaphenanthrene analogue, is an attractive candidate for spectroscopic and photochemical studies since the compound has both n,π^* and π,π^* states, in contrast to phenanthrene, and the photophysical properties of TAP were therefore investigated.

2. Experimental details

2.1. *Materials*

TAP [7] was prepared by the photocyclization reaction of *trans*-1,2-bispyrazylethylene [8]. 9,10-Diphenylanthracene (Aldrich) was purified by successive recrystallization from ethanol. The solvents for spectroscopic study were of spectroquality.

2.2. *Spectroscopic measurements*

UV spectra were recorded on a Cary 17 spectrophotometer. Emission spectra were measured on an Aminco–Bowman spectrophotometer with an Aminco *XY* recorder at room temperature and at 77 K with modification of the cell compartment. A cylindrical chopper whose maximum rotating frequency was 10 000 rev min^{-1} with two windows opposite to each other was used to isolate phosphorescence from other emissions. The phosphorescence lifetime was measured with this instrument, using a mechanical shutter to cut off the excitation light, in conjunction with a Tektronix 5115 storage oscilloscope. The polarized excitation and emission spectra were obtained with a Glan–Prism polarizer and the polarized spectra were corrected by the Azumi–McGlynn formulation [9]. In the measurements of polarized spectra, short-wavelength cut-off filters [10] were employed on the exciting and emitting paths to avoid interference from scattered light. The fluorescence quantum yields at room temperature were determined relative to 9,10-diphenylanthracene ($\Phi_f(298\text{ K}) = 1.0$ in cyclohexane) by using the following relationship:

$$\Phi_f^s = \Phi_f^r \frac{I_s A_r n_s^2}{I_r A_s n_r^2}$$

where Φ_f^r represents the fluorescence quantum yield of the reference. I_s, I_r and A_s, A_r are the areas integrated under the fluorescence spectra and the absorbance at the exciting wavelength of the sample and the reference respectively, and n_r, n_s are the refractive indices of the solvents for the reference and the sample. In the quantum yield determinations, the absorbance at the excitation wavelength was kept as low as possible, usually below 0.3, in order to minimize errors due to the front surface imprisonment and inner-filter effects. The Aminco–Bowman instrument was also employed to measure low temperature (77 K) fluorescence quantum yields relative to 9,10-diphenylanthracene ($\Phi_f(77\text{ K}) = 1.0$ in ethanol). Fluorescence quantum yields at 77 K were also calculated by the same method as that used for room temperature results, assuming that the relative values of the optical densities and refractive indices of all the solutions at 77 K were the same as at room temperature [11]. The phosphorescence quantum yield at 77 K was determined relative to 2,5-dibiphenyloxazole ($\Phi_f(77\ \mathrm{K}) = 0.95$). The ratios of phosphorescence to fluorescence quantum yields were estimated by the following correlation:

$$\frac{\Phi_p}{\Phi_f} = \frac{\text{area of phosphorescence}}{\text{area of fluorescence}}$$

2.3. *Laser flash photolysis*

The nanosecond laser flash photolysis apparatus has been described elsewhere [12]. The laser flash photolysis experiments were carried out by using XeF (351 nm) and KrF (248 nm) excimer lasers (Lambda Physik EMG 101E) as the excitation light sources. Transient species were monitored with a pulsed XeF lamp. The concentrations ((1.0×10^{-5}) - (5.9×10^{-5}) M) of TAP were adjusted such that a suitable amount of the laser light was absorbed.

3. Results and discussion

The absorption and fluorescence spectra of TAP, which has both n,π^* and π,π^* excited states, are very different from those of phenanthrene, which only has a π,π^* state, indicating that the photophysical and photochemical properties of TAP are different from those of phenanthrene (Fig. 1). The shape and maxima of the absorption and fluorescence spectra of TAP are insensitive to a change of solvent. The absorption maximum at 280 nm is due to the π,π^* band of the conjugated system of TAP and the band due to the lowest excited state is probably in the tail of the spectrum shown around 300 - 350 nm. In nitrogen heterocyclic compounds with close-lying π,π^* and n,π^* singlet states, the $^1(n,\pi^*)$ state is generally undetectable spectroscopically, and vibronic interaction between the n,π^* and π,π^* states leads to efficient $S_1 \rightsquigarrow S_0$ internal conversion or to $S_1 \rightsquigarrow T_1$ intersystem crossing and the fluorescence quantum yield is generally low [13, 14]. In the case of TAP, the $^1(n,\pi^*)$ state has about the same energy as the $^1(\pi,\pi^*)$ state, and consequently extensive mixing between these two states results in the $^1(n,\pi^*)$ band being obscured. In the second derivative UV spectrum of TAP (Fig. 1), the absorption band of the spectroscopically hidden $^1(n,\pi^*)$ state appears at 292 nm and $^1(\pi,\pi^*)$ bands appear at 281 and 231 nm in methanol (but this spectrum does not show any maximum in the range 300 - 350 nm).

TAP shows very weak fluorescence ($\Phi_f = 0.001$) and laser flash photolysis in methanol indicated efficient intersystem crossing from the excited singlet state to the triplet state ($\Phi_{isc} = 0.95$). The fluorescence maximum is shifted slightly to the blue on increasing the solvent polarity.

The salt effect on the fluorescence intensity of TAP is shown in Table 1. The intensity of fluorescence of TAP increases on addition of an alkaline

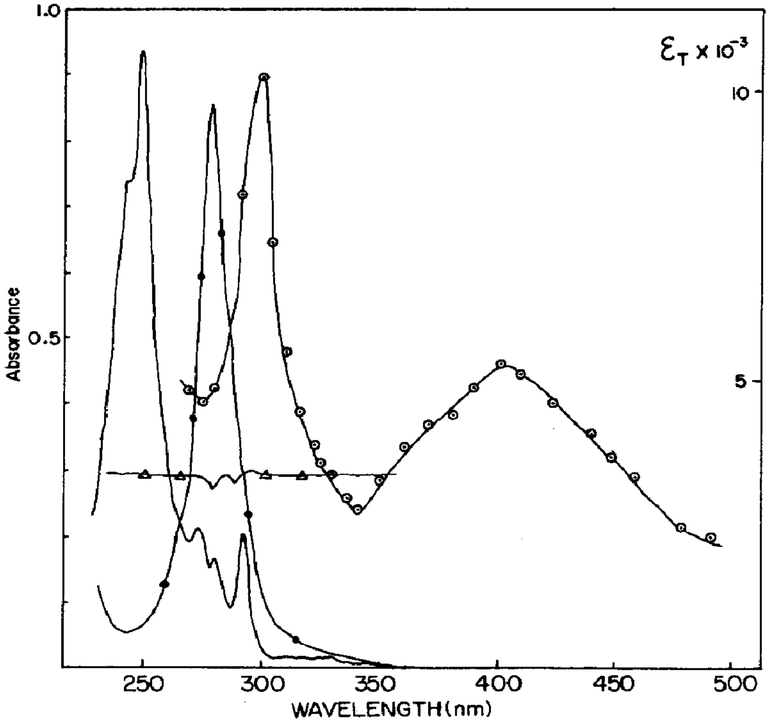

Fig. 1. Second derivative (-△-) UV spectra and triplet–triplet absorption spectrum (—⊙—) of TAP in methanol. UV spectra of TAP (—●—) and phenanthrene (———) in ethanol.

TABLE 1

Salt effect on the fluorescence intensity of TAP in ethanol at λ_{ex} = 330 nm

[NaOAc] (M)	I_f/I_f° [a]
0	1.0
0.0001	1.20
0.0005	1.26
0.001	1.32
0.005	1.34

[a] I_f° is the fluorescence intensity in the absence of NaOAc.

salt, sodium acetate (NaOAc), as shown in Fig. 2, probably owing to complexation between the nitrogen of TAP with Na^+ ion. Addition of 18-crown-6 ether [15], which specifically traps alkaline metal monocations, thus inhibiting TAP–Na^+ complexation, diminishes the NaOAc enhancement of fluorescence. This kind of enhanced fluorescence has been explained in terms of a blue shift of the lowest excited $^1(n,\pi^*)$ state as a result of the formation of nitrogen–cation coordination complexes; this would contribute to a change in the relative position of the fluorescing π,π^* and non-fluorescing n,π^* energy levels. Fluorescence activation by hydroxyl solvents is quite general for heterocyclic and aromatic carbonyl compounds [16], and has been interpreted as

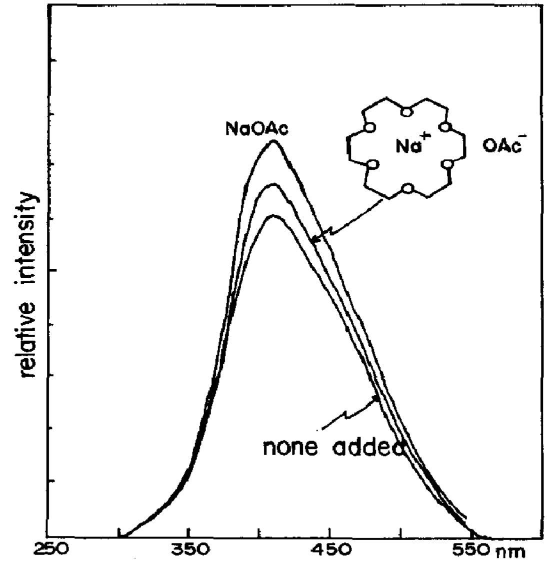

Fig. 2. Effect of crown ether (18-crown-6, 0.0005 M) on the NaOAc-enhanced fluorescence of TAP in ethanol at λ_{ex} = 330 nm. [NaOAc] = 0.0005 M.

arising from the change in the lowest excited singlet state from the n,π^* type in non-polar solvents to the π,π^* type in hydroxyl solvents [17, 18]. In the case of TAP, the absorbance at 280 nm is slightly increased in the presence of alkali metal salts and a shoulder at 324 nm is slightly red shifted in going from ethanol (shoulder at 324 nm) to ethanol plus 0.001 M NaOAc solutions (shoulder at 326 nm). However, no other changes in spectral shape or maxima are observed in the absorption and fluorescence spectra on addition of alkali metal salts.

Table 2 shows the heavy-atom effect on the fluorescence intensity of TAP. In general, no heavy-atom effect is observed for the pure $^1(n,\pi^*)$ state. Because of the extensive mixing between the lowest excited $^1(n,\pi^*)$ and $^1(\pi,\pi^*)$ states, the $^1(n,\pi^*)$ state of TAP has some $^1(\pi,\pi^*)$ character and the fluorescence intensity of TAP is decreased as the concentration of ethyl iodide increases.

TABLE 2

Heavy-atom effect on the fluorescence intensity of TAP at λ_{ex} = 330 nm

[Ethyl iodide] (M)	I_f/I_f° [a]
0	1.0
0.001	0.93
0.005	0.89
0.01	0.78
0.05	0.65
0.1	0.48

[a] I_f° is the fluorescence intensity in the absence of ethyl iodide in chloroform.

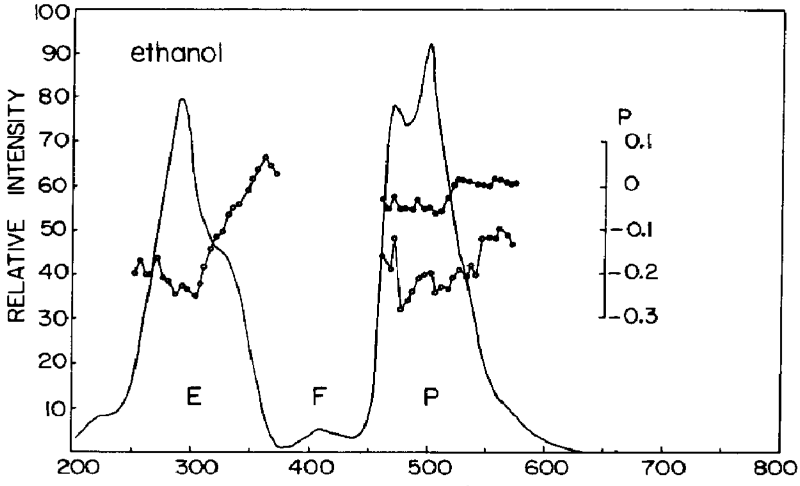

Fig. 3. Spectra of TAP in ethanol at 77 K. E, excitation spectrum and polarized phosphorescence excitation with respect to λ_{em} = 500 nm (—○—); F, fluorescence spectrum with respect to λ_{ex} = 280 nm; P, phosphorescence spectrum and polarization with respect to λ_{ex} = 280 nm (—○—) and λ_{ex} = 330 nm (—●—).

The polarized phosphorescence spectrum of TAP in ethanol at 77 K is shown in Fig. 3. TAP shows very strong phosphorescence, with maxima at 470 and 500 nm in ethanol at 77 K; at this temperature the fluorescence is very weak in comparison with the phosphorescence. The phosphorescence shows a broad band at about 460 - 600 nm and is negatively polarized with respect to $\pi \rightarrow \pi^*$ excitation, indicating that phosphorescence originates from the lowest π,π^* triplet state. The phosphorescence polarization with respect to 280 nm excitation is more negative than that for λ_{ex} = 330 nm, and this is consistent with the polarized phosphorescence excitation spectrum. In dry isopentane, the phosphorescence polarization with respect to λ_{ex} = 280 nm is less negative than in ethanol.

Table 3 shows the solvent effect on the fluorescence and phosphorescence of TAP at 77 K. The closeness of the fluorescence and phosphorescence maxima suggests that the energy levels of the lowest excited singlet

TABLE 3

Fluorescence quantum yields Φ_f, fluorescence maxima λ_{max}^f, phosphorescence maxima λ_{max}^p, phosphorescence quantum yields Φ_p and phosphorescence lifetimes τ_p of TAP at 77 K with λ_{ex} = 280 nm

Solvent	ϵ(20 °C)[a]	Φ_f	λ_{max}^f (nm)	λ_{max}^p (nm)	Φ_p (77 K)	Φ_p/Φ_f	τ_p (s)
Isopentane	1.84	0.001	420	475, 495	—	3.0	0.45
Ethyl ether	4.34	0.003	416	475, 500	—	9.4	0.69
Ethanol	24.30	0.005	410	470, 500	0.26	50.1	0.78

[a] Solvent bulk dielectric constant.

and triplet states are closely situated. The phosphorescence maxima are not significantly influenced by the solvent. The fluorescence quantum yield at 77 K increases as the solvent polarity increases. As the solvent polarity decreases, the phosphorescence lifetime at 77 K decreases and is still relatively long in isopentane. When an n,π^* triplet state is the lowest triplet state of a molecule, the phosphorescence is short lived (typically 10^{-3} s). In contrast, when the emission occurs from a π,π^* triplet state, the phosphorescence lifetime is in general considerably longer [19]. Therefore, the lowest triplet state of TAP can be assigned to the $^3(\pi,\pi^*)$ state. The phosphorescence lifetime may be expected to show a strong solvent dependence because there is a significant difference between the luminescence of TAP in hydrocarbon solvents and in hydroxy solvents. The mean phosphorescence lifetimes of nitrogen heterocyclic compounds possessing lowest triplet states of π,π^* character are, in general, considerably shorter in hydrocarbon glasses than in alcoholic glasses [1]. The decrease in the mean phosphorescence lifetime of TAP in hydrocarbon glasses is accompanied by a diminution of the out-of-plane-polarized phosphorescence intensity, as evidenced by the decreased degree of negative polarization of the emission obtained on excitation of the in-plane-polarized π,π^* absorption bands of TAP. Since the n,π^* triplet-to-ground state transition is expected to be short lived and in-plane polarized owing to vibronic coupling with allowed π,π^* transitions [20, 21], and the energy gap between the emitting π,π^* triplet and higher lying n,π^* triplet states is expected to be smaller in hydrocarbon solvents than in hydroxyl solvents, the decrease in lifetime and intensity of out-of-plane-polarized phosphorescence in hydrocarbon matrices can be taken as an evidence for the occurrence of vibronic interaction between the n,π^* and π,π^* triplet states.

The nanosecond time-resolved transient absorption spectrum was obtained in methanol at room temperature (shown in Fig. 1). In order to determine the molar absorption coefficient ϵ_T for triplet–triplet absorption, 1,2-benzanthracene (which has a molar absorption coefficient of 2.0×10^4 M^{-1} cm^{-1} at 455 nm) was used as a reference compound. The plot of ϵ_T *vs.* wavelength from the equation

$$\Delta\epsilon_{obs}(t = 0) = \Phi_{isc}{}^{TAP}(\epsilon_T{}^{TAP} - \epsilon_g)$$

shows the triplet–triplet absorption spectra. $\Delta\epsilon_{obs}$ is the difference absorption coefficient at each wavelength and ϵ_g is the absorption coefficient of ground state TAP. The intersystem crossing quantum yield $\Phi_{isc} \approx 0.95$ was obtained.

Comparison of the results for APhs and the parent hydrocarbon, phenanthrene, with those for TAP shows that there are some significant differences (Table 4). In APhs, the general features of the absorption and emission spectra of phenanthrene are maintained on introduction of the heteroatom, indicating the common π,π^* nature of the emitting singlet (S_1) and triplet (T_1) states [5]. But the absorption and fluorescence spectra of TAP are very different from those of phenanthrene, indicating that the n,π^* state could

TABLE 4

Photophysical parameters of mono-azaphenanthrenes[a] and TAP[b]

Compound	Φ_f (20 °C)	Φ_{isc}	Φ_f(77 K)	$\tau_f^{77\,K}$ (ns)	Φ_p(77 K)	$\tau_p^{77\,K}$ (s)
TAP	0.001	0.95	0.005	—	0.26	0.78
Phenanthrene	0.11	0.82	0.14[c]	70	0.11[c]	3.90[d]
1-APh	—	—	0.22	8	0.10	3.20
2-APh	—	—	0.48	22	0.04	3.12
3-APh	—	—	0.16	20	0.10	2.65
4-APh	—	—	0.22	8.5	0.07	2.13
9-APh	—	—	0.29	18.5	0.05	1.18

[a] From ref. 6.
[b] This work.
[c] From ref. 23.
[d] From ref. 24.

have an important effect on the photophysical properties of TAP. The position of the nitrogen has a significant effect on the luminescence properties of APhs [6]. 5,6-Benzisoquinoline (2-APh) has the highest Φ_f and 7,8-benzisoquinoline (3-APh) has the lowest Φ_f. 5,6-Benzoquinoline (1-APh) and 7,8-benzoquinoline (4-APh) have similar values of τ_f and Φ_f. Phenanthridine (9-APh) has the lowest phosphorescence lifetime τ_p among the APhs. TAP, having four nitrogen atoms in the 1,4,5,8-positions, shows fluorescence weaker than any APh and has a high intersystem crossing quantum yield. The phosphorescence quantum yield of TAP is higher than those of phenanthrene and APhs but the lifetime is shorter. The short phosphorescence lifetime of TAP is due to extensive vibronic interaction between the n,π^* and π,π^* triplet states. In comparison with APhs, significant differences are observed because the n,π^* states probably play a more important role in the photophysical behavior of TAP compared with that of APhs.

From these results, it is concluded that the photoreactivity of TAP is different from that of APhs and phenanthrene. It was found that direct irradiation of TAP populates the triplet state very efficiently; this is supported by the results for the photocycloaddition reaction of TAP with olefins which proceeds through the triplet excited state, in contrast to phenanthrene [22]. TAP did not react with olefins such as dimethyl fumarate which yield photoproduct with phenanthrene via a singlet exciplex, but TAP did react with halogenated olefins such as *trans*-1,2-dichloroethylene to yield the photocycloadduct stereoselectively via a triplet excited state.

Acknowledgments

This investigation was supported by the Korea Advanced Institute of Science and Technology. The authors thank Dr. N. Nakashima of the Institute for Molecular Science, Japan, and Professor Kyu Ho Chae for performing laser flash photolysis experiments.

References

1 E. C. Lim and J. M. H. Yu, *J. Chem. Phys.*, *45* (1966) 4742; *47* (1967) 3270.
2 R. Li and E. C. Lim, *J. Chem. Phys.*, *57* (1972) 605.
3 S. Babiak and A. C. Testa, *J. Phys. Chem.*, *80* (1976) 1882.
4 E. C. Lim, in E. C. Lim (ed), *Excited States*, Vol. 3, Academic Press, New York, 1977, p. 305.
5 G. Favaro, F. Masetti and U. Mazzucato, *Spectrochim. Acta, Part A*, *27* (1971) 915.
6 F. Masetti, U. Mazzucato and J. B. Birks, *Chem. Phys.*, *9* (1975) 301.
7 S. C. Shim and S. K. Lee, *Synthesis*, *2* (1980) 116.
8 S. C. Shim, D. S. Lee, J. S. Chae and P. S. Song, *J. Korean Chem. Soc.*, *20* (1976) 398.
9 T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, *37* (1962) 2413.
10 C. A. Parker, in C. A. Parker (ed.), *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968, Chapter 3.
11 C. A. Parker and C. G. Harchard, *Analyst*, *87* (1962) 664.
12 N. Nakashima and K. Yoshihara, *J. Chem. Phys.*, *77* (1982) 6040.
13 E. C. Lim, Vibronic interactions and luminescence in aromatic molecules with nonbonding electrons, in E. C. Lim (ed.), *Excited States*, Vol. 3, Academic Press, New York, 1977, p. 305.
14 W. A. Wassam, Jr., and E. C. Lim, *J. Chem. Phys.*, *68* (1978) 433; *69* (1978) 2175.
15 P. S. Song, Q. Chae, M. Fujita and H. Baba, *J. Am. Chem. Soc.*, *98* (1976) 819.
16 K. Brederek, Th. Forster and H. G. Oesterlin, in H. P. Kallmann and G. M. Spruch (eds.), *Luminescence of Organic and Inorganic Materials*, Wiley, New York, 1962, p. 161.
17 M. A. El-Sayed and M. Kasha, *Spectrochim. Acta*, *15* (1960) 758.
18 J. R. Platt, in A. Hollaender (ed.), *Radiation Biology*, Vol. 3, McGraw-Hill, New York, 1956, p. 71.
19 D. R. Kearns and W. A. Case, *J. Am. Chem. Soc.*, *88* (1966) 5087.
20 E. Clementi and M. Kasha, *J. Mol. Spectrosc.*, *2* (1958) 297.
21 J. Sidman, *J. Mol. Spectrosc.*, *2* (1958) 333.
22 S. C. Shim and S. K. Park, *Chem. Lett.*, (1986) 23.
23 C. A. Parker and C. G. Hatchard, *Analyst*, *87* (1962) 664.
24 F. Masetti, U. Mazzucato and G. Galiazzo, *J. Lumin.*, *4* (1971) 8.