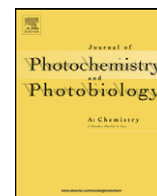




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# Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: [www.elsevier.com/locate/jphotochem](http://www.elsevier.com/locate/jphotochem)

## Spectroscopic characteristics of a novel highly fluorescent *p*-phenylenediamine: Tetracyano-*p*-phenylenediamine

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### ARTICLE INFO

#### Article history:

Received 25 March 2008

Received in revised form 13 May 2008

Accepted 19 May 2008

Available online 27 May 2008

#### Keywords:

Molecular fluorescence

High quantum yield

Long lifetime

LSER

Solvent basicity

### ABSTRACT

We present here some of the physicochemical properties of tetracyano-*p*-phenylenediamine (TCPPD). This is the second highly fluorescent *p*-phenylenediamine (PPD) presented in the literature. The molecule emits with a very long lifetime (20 ns) and an oxygen insensitive high quantum yield (up to 0.9) for this class of molecules. Its emission peak is located in the range of 540–630 nm depending on the solvent. Both, absorption and fluorescence solvatochromism are mainly controlled by the solvent basicity parameter,  $\beta$ , which makes this molecule unique. Despite the electrochemical characteristics of other members of the PPD family, TCPPD can be reversibly reduced ( $-0.72$  V vs SCE) but not oxidized. These properties make TCPPD a very interesting candidate for several applications in fluorescence sensing, or as building block for *n*-type conducting polymers for solar cells, organic transistors or OLED devices.

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### 1. Introduction

The search for new pigments for dyeing and in photography has a long tradition [1]. *p*-Phenylenediamines (PPDs) have been used as pigments in photography ever since due to their low oxidation potentials and the colorful properties of their products, such as Wurster's blue [2]. For the same reason, they have been subject of a huge number of basic research works, but none of them showed noteworthy fluorescence till recently [3]. This new feature started our interest to investigate more compounds of this class as fluorescence sensors, or fluorescent solvatochromic probes. Moreover, the wide range of reactions accomplished by PPDs make any new member of its family immediately interesting. For example, they are known to polymerize producing *p*-type (hole transporter) long chains [4], with possible applications in OLEDs, solar cells, molecular transistors, etc.

In a previous paper we presented the electronic spectroscopic characteristics of the first example of a highly fluo-

rescent *p*-phenylenediamine, 2,5-dicyano-*N,N,N',N'*-tetramethyl-*p*-phenylenediamine (DCTMPPD) [3]. It was shown that in liquid solution it displays emission fluorescence with a maximum ranging from about 450 nm in cyclohexane to 550 nm in water (neutral pH) with a quantum yield as high as around 0.5 and a fluorescence lifetime of 20 ns. Applying a LSER (linear solvent energy relationship [5]) analysis to the fluorescence solvatochromism resulted in a pronounced sensitivity towards the solvent polarity and acidity but none with respect to the solvent basicity. As other PPDs, DCTMPPD was found to be reversibly oxidizable and decomposed under reductant reaction conditions.

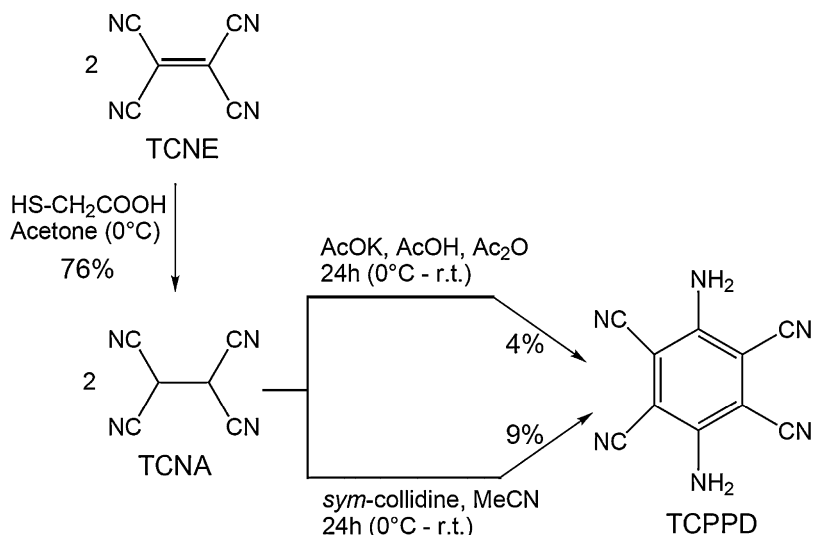
Conceptually, tetracyano-*p*-phenylenediamine (TCPPD) results from the insertion of two more cyano groups and the removal of the methyl groups, which has dramatic consequences on its properties. Due to its symmetry the molecule is not expected to have a pronounced permanent dipole moment, neither in the ground, nor in the excited state. Small variations in the permanent dipole moment, however, could be due to an asymmetric bending of the amino groups with respect to the aromatic plane. Thus, it is to be expected that the solvatochromism in this case should be governed either by higher order multipolar moments, dispersion forces, or specific interactions [6].

Additionally, it is no longer clear whether from the electrochemical point of view TCPPD should be regarded as a PPD or rather as part of the group of cyanobenzenes (that show emission in the UV, with high fluorescence quantum yields) [7].

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**Scheme 1.** Synthesis of TCPDP.

Besides the specific interest of the aforementioned questions that concern the comparative properties of the fluorescing PPDs, TCPDP presents a new and interesting case of the interplay of electron donor and acceptor groups in aromatic molecules. This molecule is also connected to *p*-aminobenzonitrile and other related dually fluorescing species. However, it is not the aim of this work to discuss the mechanistic origin of the dual fluorescence, but in line with previous comparative studies performed by Zachariasse et al. [8], DCTMPPD did not present such phenomenon, most likely due to the energy of the excited states, and hence to the mixture between the polar and non-polar ones. In TCPDP the introduction of two more cyano groups does not change the situation in this respect.

This paper is organized as follows: in the experimental section a brief description of the synthetic route together with the characterization of the product will be given. The rest of the paper will be devoted to the photophysics of the molecule in solution with an emphasis on its solvatochromic behavior. Finally, the properties of the molecule will be summarized and compared to the other related compounds.

## 2. Experimental

### 2.1. Solvents and reactants

All solvents, of p.a. grade, were dried over molecular sieve and distilled except for water which was distilled twice. The samples for electrochemical and photophysical measurements were deaerated by saturating them with argon gas.

### 2.2. Synthesis

In the synthesis published by Webster et al. [9], TCPDP was obtained from two molecules 1,1,2,2-tetracyanoethane – most likely by a double Thorpe–Ziegler condensation. The reaction scheme seems meaningful considering that Gardner and Kochi [10] reported similar ring-closure-reactions leading to 4-alkyltetracyanophenylamines. In the opinion of Webster et al. the very low yield (4%) could be ascribed to TCPDP's high nucleophilicity. However, we could not increase the yield appreciably (9%) by using the non-nucleophilic *sym*-collidine as a base (see Scheme 1). We believe, that the complex reaction mechanism, which consists

of two condensation steps (one of it intermolecular), two eliminations and a reduction, is responsible for the low yield of the desired final product. Thus, a completely different synthesis starting with the very cheap *p*-phenylenediamine which is transformed into the *N*-sulfinyldiamine by thionyl chloride followed by an aromatic substitution reaction using dicyan is a very promising alternative and is the subject of present studies. Analogue reactions have shown the possibility of substituting all four ring hydrogens in *p*-phenylenediamine by chlorine [11] and bromine. TCPDP is a red microcrystalline substance that is stable under air and light. The sample was recrystallized twice from acetonitrile for analysis. Its structure was proven by infrared and mass spectroscopy and the EPR spectrum of its radical anion.

### 2.3. IR spectrum

The infrared spectrum was recorded on a *Perkin Elmer IR spectrometer 325* in a potassium bromide disc, and consists of a few narrow lines as expected for a highly symmetrical species analogous to that of *p*-phenylenediamine (see Table 1).

### 2.4. Mass spectrum

The base peak in the mass spectrum (recorded on a double focusing magnetic sector instrument type *Kratos* with direct probe inlet and electron impact ionization) is the molecule peak at 208 *m/z* and other fragments are due to the loss of HCN each showing the expected isotopic pattern (209 (9), 181 (20), 182 (2), 154 (23), 127 (16)).

**Table 1**  
IR spectrum data of TCPDP in KBr

$\tilde{\nu}(\text{cm}^{-1})$	Intensity and shape	Related normal mode
3420	Medium	$\nu(\text{NH})$
3350	Medium	$\nu(\text{NH})$
3250	Medium	Mixture of NH bands
2220	Strong, sharp	$\nu(\text{CN})$ in nitriles
1650	Very strong	$\nu(\text{CC})$ and in-plane $\delta(\text{NH}_2)$
1470	Very strong	CC in benzene
1280	Very strong	CN in amines
860	Weak, broad	Out-of-plane $\delta(\text{NH}_2)$

**Table 2**  
EPR simulated spectrum of TCPPD radical anion

Constant	Spin	Quantity	Value (G)	$\sigma$ (G)
$a_{\text{CN}}^{\text{N}}$	1	4	1.182	0.0001
$a_{\text{NH}_2}^{\text{H}}$	1/2	4	0.389	0.0003
$a_{\text{NH}_2}^{\text{N}}$	1	2	0.280	0.0002

Values refer to the obtained hyperfine coupling constants for each nucleus and the standard deviations are given. The used linewidth was 64 mG.

### 2.5. EPR-spectrum of the radical anion

The cw-EPR spectrum was acquired using a Bruker ElexSys E-500 spectrometer and a home-built electrochemical flow-through cell located directly below the EPR cavity. Electrochemical reduction leads to the corresponding radical anion. No signal was obtained under oxidative conditions. The obtained spectrum in 20 mM TBABF<sub>4</sub>/acetonitrile solution was simulated (correlation coefficient  $R=0.98$ ) with a dataset of four equivalent nitrogens (in the cyano groups), four equivalent hydrogens and two nitrogens (in the amino groups) leading to the results collected in Table 2.

### 2.6. Electrochemistry

Detection of the half-wave potentials of TCPPD was carried out at 25 °C in acetonitrile with 0.1 mol/L tetrabutylammonium perchlorate serving as supporting electrolyte. Materials for the electrodes were gold and platinum for the working and counter electrode, respectively. The reference electrode was a Flexref electrode by World Precision Instruments and the potentials were corrected using ferrocene as internal reference.

### 2.7. Photophysical studies

Absorption spectra were recorded on a Shimadzu UV-3101PC UV-VIS-NIR spectrophotometer (bandpass 1 nm). Corrected fluorescence and excitation spectra were recorded with a Jobin–Yvon Spex FluoroMax-2 spectrofluorimeter (scan range from 250 to

900 nm, bandpass 2 nm). The fluorescence quantum yield was determined using rhodamin 6G in ethanol and fluorescein in basic ethanol as quantum references [12]. The error in the results is within the 10% range common for relative quantum yield measurements. The following equation [13,14], the validity of which was recently approved by Kotelevskiy [15], was applied:

$$\Phi_S = \Phi_R \frac{I_S (1 - 10^{-OD_R})}{I_R (1 - 10^{-OD_S})} \left( \frac{n_S}{n_R} \right)^2 \quad (1)$$

where  $I$  is the emission intensity calculated from the integrated corrected spectrum, OD represents the optical density at the excitation wavelength and  $n_X$  the refractive index at 25 °C of the corresponding solvent. The subscripts S and R refer to the sample and to the reference, respectively. The optical density at and beyond the excitation wavelength did not exceed 0.10. All spectra have been represented in the Transition Dipole Moment (TDM) representation for their analysis [16].

Lifetime measurements were performed on a home-built modulation spectrofluorometer and a single photon counting apparatus, both described elsewhere [3,17]. A total of 1 million counts (in 4096 channels) was recorded in every individual experiment to secure a good signal to noise ratio, even at long times.

All photophysical data are collected in Table 3.

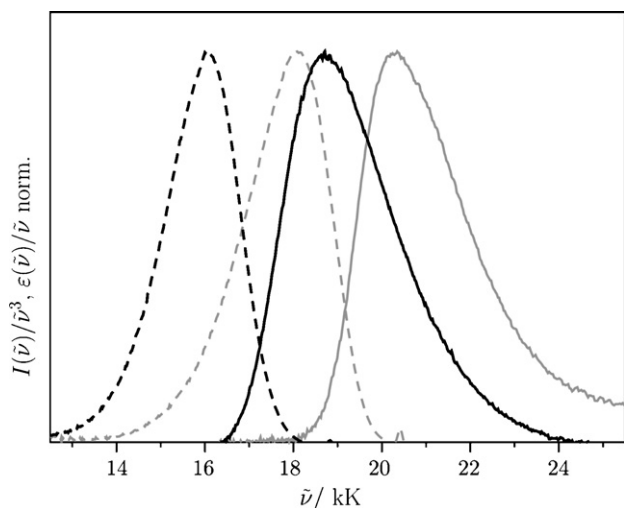
## 3. Results and Discussion

### 3.1. General remarks on the photophysics

The color of TCPPD solutions changes from pale green (1,2-dichlorobenzene) to red (dimethylsulfoxide). Two representative pairs of absorption and fluorescence spectra are shown in Fig. 1. The electronic absorption spectrum consists of two well separated bands, about 100 nm from each other. The object of the solvatochromism analysis here performed is the  $S_0$ – $S_1$  transition at longer wavelengths. Hence, in first approximation, we can exclude a major effect of other electronic transitions on the absorption band to the first excited singlet state. The absorption band maximum shifts from 490 nm in 1,2-dichlorobenzene to 530 nm in

**Table 3**  
Solvent properties and photophysical properties of TCPPD

	Solvent	$\alpha$	$\beta$	$\pi^*$	$\tilde{\nu}_{\text{abs}}(\text{kK})$	$\tilde{\nu}_{\text{em}}(\text{kK})$	$\tau(\text{ns})$	$\phi$	$k_f(\text{ns}^{-1})$	$k_{\text{nr}}(\text{ns}^{-1})$
1	1,2-Dichlorobenzene	0.00	0.03	0.77	20.36	18.38	17.9	0.77	0.043	0.013
2	Bromobenzene	0.00	0.06	0.77	20.30	18.16	16.8	0.47	0.028	0.032
3	Chlorobenzene	0.00	0.07	0.68	20.34	18.29	18.8	0.75	0.040	0.013
4	Benzene	0.00	0.10	0.55	20.30	18.10	20.0	0.73	0.036	0.014
5	Chloroform	0.20	0.10	0.69	20.22	17.64	18.7	0.79	0.042	0.011
6	1,2-Dichloroethane	0.00	0.10	0.73	20.29	18.12	20.2	0.82	0.041	0.009
7	Dichloromethane	0.13	0.10	0.82	20.32	18.30	18.4	0.74	0.040	0.014
8	Toluene	0.00	0.11	0.49	20.32	18.03	21.1	0.72	0.034	0.013
9	<i>p</i> -Xylene	0.00	0.12	0.45	20.27	18.05	22.9	0.87	0.038	0.006
10	Ethylbenzene	0.00	0.12	0.53	20.31	18.08	20.6	0.75	0.036	0.012
11	Isopropylbenzene	0.00	0.18	0.41	19.96	17.20	20.3	0.69	0.034	0.015
12	1,4-Dioxane	0.00	0.37	0.49	19.59	17.21	20.8	0.83	0.040	0.008
13	Benzonitrile	0.00	0.37	0.88	19.71	17.19	18.0	0.74	0.041	0.014
14	Acetonitrile	0.19	0.40	0.66	19.95	17.22	22.1	0.75	0.034	0.011
15	Propylenecarbonate	0.00	0.40	0.83	19.84	17.13	19.7	0.77	0.039	0.012
16	Butylether	0.00	0.46	0.18	19.87	17.62	21.1	0.74	0.035	0.012
17	Propylether	0.00	0.46	0.27	19.82	17.49	21.4	0.70	0.033	0.014
18	Ethylether	0.00	0.47	0.24	19.68	17.40	23.1	0.89	0.039	0.005
19	Water	1.17	0.47	1.09	19.92	16.44	13.2	0.33	0.025	0.051
20	Acetone	0.08	0.48	0.62	19.68	17.12	22.2	0.74	0.033	0.012
21	Tetrahydrofurane	0.00	0.55	0.55	19.39	17.04	21.4	0.73	0.034	0.013
22	Methanol	0.98	0.66	0.60	19.51	16.64	19.2	0.65	0.034	0.018
23	Dimethylformamide	0.00	0.69	0.88	18.99	16.38	19.3	0.61	0.032	0.020
24	Ethanol	0.86	0.75	0.54	19.54	16.64	19.5	0.58	0.030	0.022
25	Dimethylsulfoxide	0.00	0.76	1.00	18.71	16.09	17.4	0.46	0.026	0.031
26	Hexamethylphosphoramide	0.00	1.00	0.87	18.62	15.97	16.4	0.36	0.022	0.039



**Fig. 1.** Normalized absorption (solid lines) and emission (broken lines) spectra of TCPPD in dichlorobenzene (gray) and DMSO (black) in TDM coordinates.

dimethylsulfoxide (20.4 and 18.7 kK,<sup>2</sup> respectively, in the TDM representation), and its shape – a slightly blue distorted gaussian of some 3 kK width – does change appreciably on changing the solvent. The decadic molar extinction coefficient in the maximum of about 8000 M<sup>-1</sup> cm<sup>-1</sup> does not change with the solvent. The Strickler–Berg (SB) equation [18] leads to a radiative lifetime of 30 ns in acetonitrile.

$$\frac{1}{\tau_r} = k_r = 8\pi 10^5 \ln(10) \frac{c n_D^2}{N_L} \frac{\int F(\nu) d\nu}{\int \nu^{-3} F(\nu) d\nu} \int \nu^{-1} \epsilon(\nu) d\nu \quad (2)$$

In this version of the SB equation apparently no mirror symmetry between absorption and fluorescence is used, although it is deeply rooted in the principles from which it is derived.  $\tau_r$  and  $k_r$  stand for the radiative lifetime and rate constant respectively,  $c$  is the speed of light in vacuum,  $n_D$  is the refractive index of the solvent at 589 nm – the D line of sodium, but a more exact equation should take into account the change in the refractive index with the absorption and emission wavelength, which would not lead to a major correction in our case but has to be seriously considered when approaching the ultraviolet –  $N_L$  is the Loschmidt number,  $F(\nu)$  is the fluorescence spectrum and  $\epsilon(\nu)$  the absorption spectrum (the contribution of the absorption to higher states has been subtracted by appropriate decomposition of the bands).

The excitation spectra are invariant with the emission wavelength and are congruent with the absorption spectra in all solvents studied. This means that the entire observed absorption band leads to the emissive state in ultimate instance.

The emission is also a single distorted gaussian. Its width increases from 1.9 to 2.2 kK upon increasing the energy of the emission. This ranges from 540 to 620 nm on going from 1,2-dichlorobenzene to dimethylsulfoxide (18.3 and 15.9 kK, respectively, in the TDM representation). The Stokes shift ranges from 2 to 3 kK in the TDM representation.

The emission quantum yield goes from 0.33 in water to 0.89 in *p*-xylene, and the fluorescence lifetime in the same solvents, from 13.2 to 22.9 ns. These values do not depend on the excitation wavelength in any solvent, and all the fluorescence decays are perfectly monoexponential. It is important to note, that despite the long lifetimes obtained, no sensitivity to the oxygen content of the

**Table 4**

LSER coefficients for the multilinear fits to the absorption and fluorescence

	Absorption			Fluorescence		
	Value (kK)	$\sigma$ (kK)	t-Student	Value (kK)	$\sigma$ (kK)	t-Student
Correlation with all parameters						
<i>a</i>	0.45	0.08	5.56	-0.1	0.16	-1.13
<i>b</i>	-1.87	0.09	-19.25	-2.3	0.19	-11.89
<i>s</i>	-0.31	0.11	-2.79	-0.5	0.22	-2.53
XYZ <sub>0</sub>	20.66	0.07	265.92	18.6	0.15	118.97
<i>R</i>		0.973			0.946	
Correlation only with $\beta$						
<i>b</i>	-1.8	0.13	-	-2.5	0.21	-
XYZ <sub>0</sub>	20.47	0.06	-	18.28	0.09	-
<i>R</i>		0.939			0.917	

solution of neither the quantum yield nor the lifetime has been noticed.

### 3.2. Solvatochromism

Both, absorption and fluorescence emission maxima shift with the solvent, have been analyzed by means of several approximations. There is no clear correlation with the empirical  $E_T(30)$  scale [19]. Neither with Lippert's model nor any similar theory, which accounts only for non-specific solute–solvent interactions [20–23]. Only the use of the Kamlet–Taft LSER approach [5] leads to a convincing rationalization of the data. A multiple linear regression has been successfully performed for both the absorption and the emission, using:

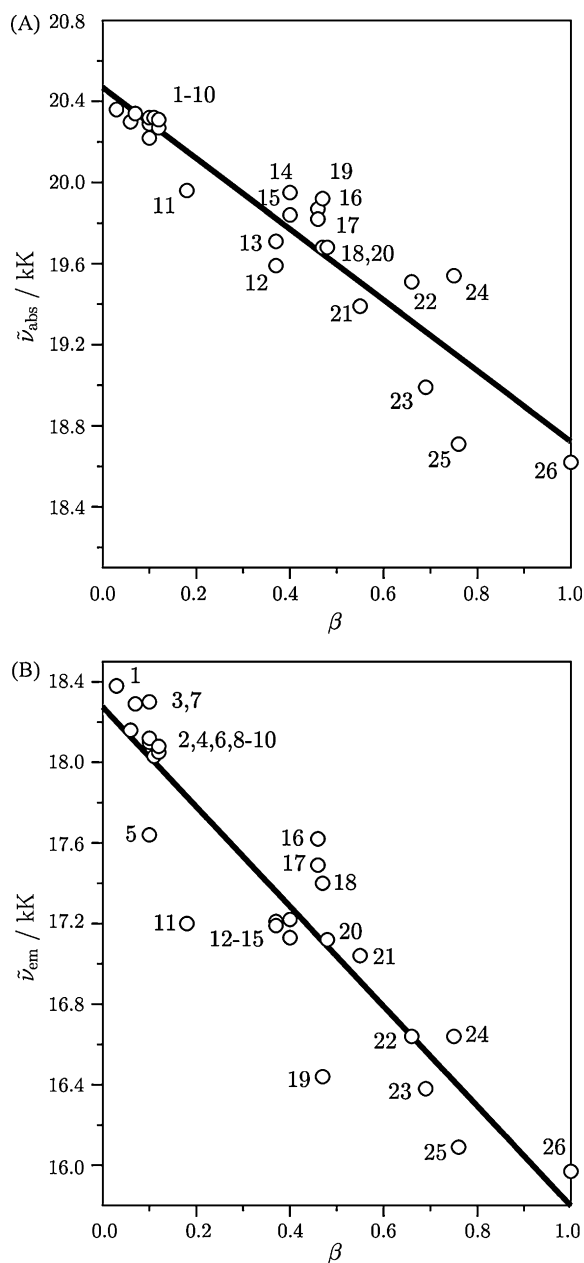
$$\tilde{\nu}_x = \tilde{\nu}_x^0 + s\pi^* + a\alpha + b\beta, \quad (3)$$

where  $\tilde{\nu}_x$  denotes the maximum of the corrected absorption or fluorescence spectrum in a given solvent [3], and  $\tilde{\nu}_x^0$  in the gas phase. The  $\alpha$ -scale is an index of solvent acidity (hydrogen bond donor ability) and the  $\beta$ -scale is an index of solvent basicity (hydrogen bond acceptor ability) and  $\pi^*$  is a measure of the polarity/polarizability of the solvent. While  $\pi^*$ ,  $\alpha$  and  $\beta$  denote the solvent properties for each of the above mentioned contributions for solute–solvent interactions, the coefficients *s*, *a* and *b* describe the corresponding susceptibilities of the solute. Therefore the advantage of the Kamlet–Taft treatment is obviously to sort out the quantitative role of properties such as hydrogen bonding. The fit data are collected in Table 4. Interestingly, from these three parameters the basicity of the solvent is capable of quantitatively explaining the solvatochromism for both cases, absorption and emission, despite a minor contribution of the acidity (which completely vanishes when excluding strong hydrogen donors, i.e. the alcohols and water from the analysis). The change of the absorption and emission maxima with  $\beta$  is shown in Fig. 2. This means, that the specific interaction between the amino hydrogens and the accepting groups of the solvents is responsible for the displacement of the bands. The emission is more sensitive to it than the absorption, revealing an additional stabilization of the excited state due to such interactions with respect to the ground state. These findings are coherent with the chemical intuition: the TCPPD molecule does not possess a permanent dipole moment due to its symmetry; thence the polarity scales and the continuum non-specific models will fail to explain the results, even more in the presence of specific interactions. The same holds for less important higher order interactions (induced dipoles and quadrupolar solvation may become relevant for the *N,N,N,N'*-tetramethyl derivative of TCPPD).

### 3.3. Quantum yield and fluorescence lifetime

As already mentioned, the influence of the solvent on the fluorescence quantum yield and lifetime is considerable, as it is to be

<sup>2</sup> kK stands for kiloKaysler, 1000 cm<sup>-1</sup>.



**Fig. 2.** Absorption (A) and fluorescence (B) maxima dependence with  $\beta$ . The solid lines are the best fits using only the hydrogen bond accepting ability of the solvents shown in Table 4. The numbers correspond to the solvents listed in Table 3.

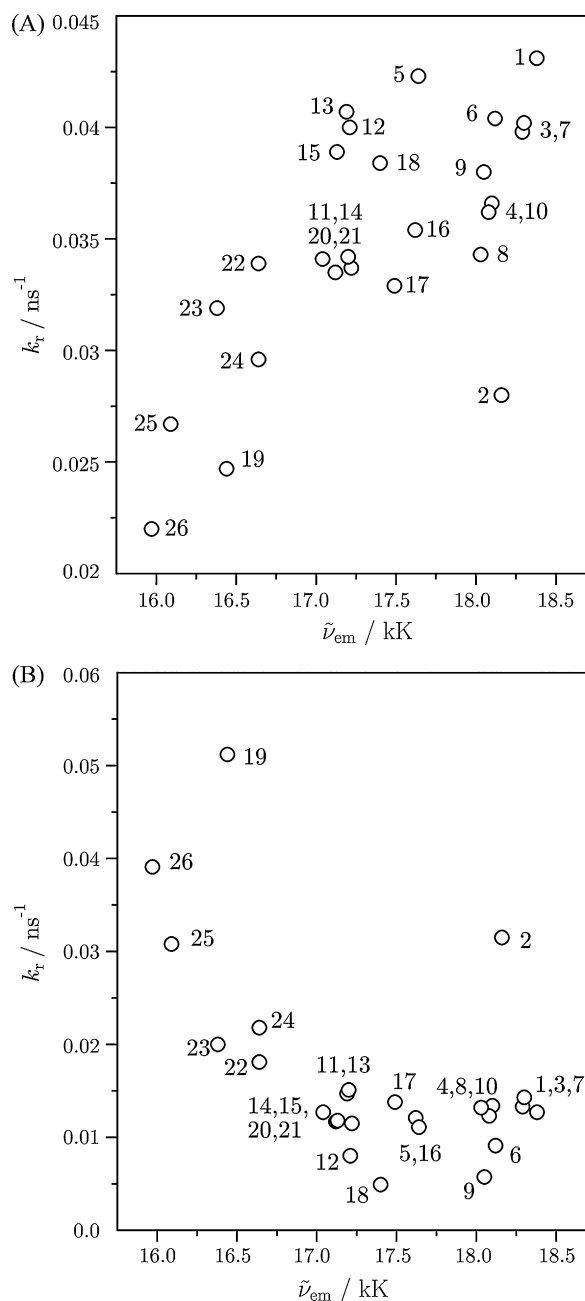
expected. It is not appropriate to correlate these magnitudes with the solvent basicity. On the contrary, the experimentally obtained radiative ( $k_r$ ) and non-radiative ( $k_{nr}$ ) decay rate constants,

$$k_r = \frac{\phi}{\tau} \quad (4)$$

$$k_{nr} = \frac{(1-\phi)}{\tau}$$

obtained from the relationship to the experimental quantum yield and lifetime of fluorescence, can be well understood on the following basis as functions of the transition energy.

Instead of searching for a correlation with  $\beta$ , we have plotted the change of these rate constants against the energy of the corresponding transition, the emission. This is in fact equivalent to a correlation with  $\beta$ , but holds the advantage of using models and theories that correlate energy and transition probabilities, although



**Fig. 3.** Radiative (A) and non-radiative (B) excited state decay rate constants as a function of the fluorescence maximum of TCPDP in the solvents listed in Table 3.

the data scattering prevents a detailed quantitative analysis. Fig. 3 depicts the change of both constants with the emission energy.

The simplest comparison can be done in terms of the SB result already mentioned above [18]. The radiative decay lifetime of 30 ns obtained in this way, coincides very well with the experimental value in acetonitrile. The good performance of the SB equation is relatively surprising taking into account that the mirror symmetry between absorption and emission spectra is not completely fulfilled in this case [13]. A tentative explanation is that the Franck–Condon excited state is contaminated by a non-emissive higher lying excited state. Thus, the absorption spectra are broader than the emission spectra by 1 kK. The well known underestimation of the radiative lifetime by the SB model would then compensate this leading to the observed agreement. The effect of higher lying excited states on the upper vibronic levels has been used to explain

excitation wavelength dependencies of the initial anisotropy value, even in rather rigid molecules such as perylene [24].

Another possible explanation is that due to the displacement of the excited state, the higher vibronic levels of the Franck–Condon ground state will show a smaller coupling to the ground vibronic relaxed excited state, with respect to the symmetric absorption transition. This is in accordance not only with the broader absorption but also with the narrowing of the emission spectra upon increasing interaction with the solvent at large  $\beta$  values. In this context, the SB model is supposed to give a good result, and the lack of symmetry due to the described effect does not influence the lifetime because it does not change the electronic transition dipole moment of emission. It must be reminded that the derivation of the SB equation considers absolutely identical transition dipole moments for the absorption and emission, which may not be the case if the hypothesis of the former paragraph is correct. More precisely, in the case of the radiative rate constant a close to linear increase with the transition energy can be observed, coherently with the SB equation. Although the theoretical dependence is cubic, in such a short energy diapason, the departure from a straight line is negligible compared with the data dispersion.

The non-radiative rate constant shows an exponential decay trend with the transition energy. This can be understood in terms of Jortner's model for the multiphonon induced internal conversion [25–27].

$$k_{\text{nr}} = \frac{2\pi V^2}{\hbar} \left( \frac{1}{2\pi\hbar\omega_M\Delta E} \right)^{1/2} \exp(-S) \exp\left(\frac{-\gamma\Delta E}{\hbar\omega_M}\right)$$

$$\gamma \sim \ln\left(\frac{2\Delta E}{\hbar\omega_M\Delta_M^2}\right) - 1 \quad (5)$$

$$S = \frac{1}{2} \sum_j \Delta_j^2$$

In the former equation, the non-radiative rate constant  $k_{\text{nr}}$  is related to the coupling between the electronic states through the matrix element  $V$ , the difference in energy between both  $\Delta E$  (the fluorescence transition energy in our case), the average frequency of the phonon coupled to the non-radiative transition  $\omega_M$ , the phonon–electron coupling or Huang–Rhys factor,  $S$  ( $S < 1$  in this weak coupling case), and the displacement  $\Delta$ , average,  $\Delta_M$ , or of each vibrational mode considered,  $\Delta_j$  (which is considered to be small). So, basically, the equation explains how the vibrational coupling to the electronic levels induces the non-radiative transition.

Following Meyer [26], a linear decrease of the logarithm of  $k_{\text{nr}}$  with the transition energy is expected, with a slope inversely proportional to the main vibrational quantum mode that couples the upper to the lower state. Although scattered due to the changing nature of the solvent, an approximate value of  $400\text{ cm}^{-1}$  can thereby be obtained for TCPPD. This frequency is in the range of the amino wagging and twisting modes [28]. It is also the range for the hydrogen bond stretching mode [29]. In any case, it is clear that the most relevant deactivation mode is connected to those molecule moieties that interact specifically with the solvent via hydrogen bonds. Following the latter idea, it can be well understood that different kinds of hydrogen bonding solvent molecules will lead to different frequencies, yielding the observed dispersion. Moreover, as the displacement may not be constant – as suggested by the differences in spectral widths between the absorption and emission bands and their solvent dependence – the data will be further dispersed.

Therewith the reason for the lack of correlation between the quantum yield and the lifetime with the  $\beta$  parameter of the solvent becomes clear: while the radiative rate constant increases with the energy of the transition, the non-radiative rate constant decreases,

leading to yields and lifetimes, which are uncorrelated with the emission energy. There are several additional considerations that should be made regarding some solvents: it is observed that in bromobenzene the non-radiative decay is larger than expected. This could be related to a solvent induced inter-system crossing, when in the former discussion the entire  $S_1$  non-radiative relaxation has been ascribed to internal conversion. The assumption of a very small inter-system crossing yield in general (except in bromobenzene) is supported by the insensitivity of the fluorescence to the solution oxygen content. The deviation of water in Fig. 3B could be explained by the presence of other prototropic species in either the ground or the excited state, but attempts to determine the corresponding  $pK_a$  values were unsuccessful due to the very small changes observed in the spectra. The former discussion on the non-radiative decay rate constant is purely qualitative because of the diversity of factors that contribute to the data dispersion.

### 3.4. Comparison with related species

PPD and 1,2,4,6-tetracyanobenzene (TCNB) absorb light about 300 nm, in the excitation from  $S_0$  to  $S_1$ , while TCPPD, that can be seen as a mixture of both, has the same transition about 450 nm in low polar/low  $\beta$  solvents. Taking the HOMOs and LUMOs of the former two molecules, the corresponding molecular orbitals of the TCPPD could be constructed. The energy differences between the resulting HOMO and LUMO lie at lower energies, in agreement with the experimental absorption band, and the second excitation and third excitations around the PPD and TCNB first one. In other words, the stabilization introduced by the conjunction of the electron withdrawing and the electron withdrawing groups of the excited state and the destabilization of the ground state, leads to the observed shift with respect to PPD and TCNB.

In a previous work we reported on the photophysics of the first highly fluorescent PPD: DCTMPPD. TCPPD spectra are red shifted with respect to DCTMPPD both in absorption (5 kK) and in emission (1.5–2 kK). This means that in TCPPD the Stokes shift is smaller, most likely due to the major change in dipole moment suffered by DCTMPPD after excitation. The solvatochromism DCTMPPD was found to be sensitive to  $\alpha$  and, mostly,  $\pi^*$ , and could be well explained by models based on the Onsager reaction field treatment, while the TCPPD solvatochromism is solely governed by the solvent basicity parameter,  $\beta$ . The fluorescence quantum yields are similar, although in some solvents TCPPD shows higher values, close to 0.9. Also the lifetimes do not differ much, but in the present case they are insensitive to oxygen.

There are other solvatochromic dyes, like aminobenzodifurones [30], which show comparable sensitivity to the basicity parameter as the one presented here. In these other cases the sensitivity is, however, restricted to the absorption transition and additionally superimposed by an appreciable dependence on  $\pi^*$  and  $\alpha$ .

With respect to dually fluorescing parent compounds, like *p*-dimethylaminobenzonitrile (*p*-DMABN) [31], the lack of a second emission band can be explained in the same terms as already applied to 3,5-dicyanoaminobenzene (3,5-DCAB) [8], or even DCTMPPD: the stabilization of the locally excited state due to the presence of the four electron withdrawing groups and the symmetry of TCPPD preclude any adiabatic reaction yielding a charge transfer state. This is well supported by the almost complete insensitivity of its photophysics to the solvent polarity.

Upon oxidation *p*-phenylenediamine derivatives give stable radical cations (e.g. Wuerster's blue from TMPPD [32]) which in a second oxidation step react to give quinonediimines. For TCPPD no such oxidation step was found, but its first reduction is fully reversible with a potential of  $-0.71\text{ V}$  vs SCE in acetonitrile, followed

by a second irreversible step. This is not unexpected since the electron withdrawing effect of the cyano groups surely disfavors the formation of an electron lacking species whereas it stabilizes the anion. The electrochemistry of the dicyano compound DCTMPPD, on the other hand, is still governed by the amino groups, i.e. its behavior resembles the one of TMPPD, while that of TCPPD is similar to that of TCNB, which in fact has a very similar reduction potential [33]. It is worth noting that the TCPPD potential renders it a very good electron acceptor, better than dicyanoanthracene ( $-0.89\text{ V}$ ) but worse than tetracyanoanthracene ( $-0.46\text{ V}$ ) [34].

#### 4. Conclusions

TCPPD is a good oxidant and highly fluorescent. Its absorption and emission are almost exclusively governed by the basicity of the solvent and this solvent property leads to colors in solution from pale green to brilliant orange to red. Its fluorescence quantum yield reaches values close to 0.9, and the excited state decays with a  $S_1$  state lifetime of about 20 ns. Both these properties are insensitive to the oxygen content of the solution. These properties make TCPPD unique in several senses: first, to our knowledge, it is the first reported purely organic molecule with a lifetime of 20 ns emitting beyond 600 nm [12]; secondly, it is one of the very few examples, if not the sole one, of a molecule whose solvatochromism is almost exclusively governed by the Kamlet–Taft  $\beta$  parameter of the solvent; Finally, it is the first example of a PPD showing a reversible reduction but not oxidation. These properties make it very appropriate for several applications, like plastic solar cells or as a fluorescence probe for microscopy, and an interesting fluorophore for basic research in electron transfer and solvation related fields.

#### Acknowledgements

This work has been made possible by the financial support of the EU-Erasmus programme and the TU-Graz. The help of Prof. Bernardo Herold and Prof. João Telo at IST/TU-Lisbon in the syntheses is gratefully acknowledged. We would like to thank also Prof. Robert Saf at ICTOS/TU-Graz, Dr. Claudia Muresano, Prof. Karl Gatterer, Dr. Boryana Mladenova and Daniel Kattnig at PTC/TU-Graz for their assistance in the characterization of TCPPD.

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