

# A comparative study of the photophysical properties of perylenediimides in liquid phase, PVC and sol-gel host matrices

Canan Karapire<sup>a</sup>, Celil Timur<sup>b</sup>, Sıddık İçli<sup>c,\*</sup>

<sup>a</sup>Department of Chemistry, Faculty of Science, Ege University, Bornova, 35100 Izmir, Turkey

<sup>b</sup>DYO Paint Factory, Izmir, Turkey

<sup>c</sup>Solar Energy Institute, Ege University, Bornova, 35100 Izmir, Turkey

Received 1 June 2002; received in revised form 28 August 2002; accepted 10 October 2002

## Abstract

The photophysical and photochemical properties of three different perylenediimide derivatives, *N,N'*-di-dodecylperylene-3,4,9,10-bis(dicarboximide), *N,N'*-di-(1-dehydroabietyl)perylene-3,4,9,10-bis(dicarboximide) and *N,N'*-di-(4-carboxy phenyl)perylene-3,4,9,10-bis(dicarboximide) (*N*-DODEPER, ABIPER and PECA, respectively), were determined in immobilized phases (PVC films, both plasticized and non-plasticized, and sol-gel matrix) using steady state fluorescence spectroscopy and compared with the data in solution phase. It was found that the plasticizers support the interaction of the dyes with the quencher and bis-(2-ethylhexyl)phthalate (DOP) itself acts as a quencher for the perylenediimide derivatives with aromatic substituents. The sol-gel matrix imparted serious changes to the properties of the perylenediimides.

© 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Perylenediimides; Fluorescence spectroscopy; Sol-gel matrix; PVC films; Immobilization; Plasticizer

## 1. Introduction

In recent years immobilisation of organic dye molecules within polymer and sol-gel matrices has gained interest due not only to the application areas that immobilisation provides and their easy pathways of preparation, but also because of the need to understand the ground and excited state properties of single molecules [1,2]. Liquid polymer

[highly plasticized poly(vinyl chloride)] films are commonly used to prepare fluorescent optical fiber sensors [3–6]. A sol-gel glassy matrix is very attractive because of its low preparation temperature and high chemical and mechanical stabilities [2,7–9]. In the sol-gel process, transparent oxide glasses are prepared by hydrolysis and condensation of tetra alkylorthosilicates and, in one sol-gel preparation technique, molecules can become entrapped in the growing covalent silica network.

Perylenediimides (PDI) and the basic 3,4,9,10-perylenetetracarboxylic dianhydride compounds represent one of the most widely studied classes of

\* Corresponding author. Tel.: +90-232-388-4000; fax: +90-232-388-8264.

E-mail address: [icli@bornova.ege.edu.tr](mailto:icli@bornova.ege.edu.tr) (Sıddık İçli).

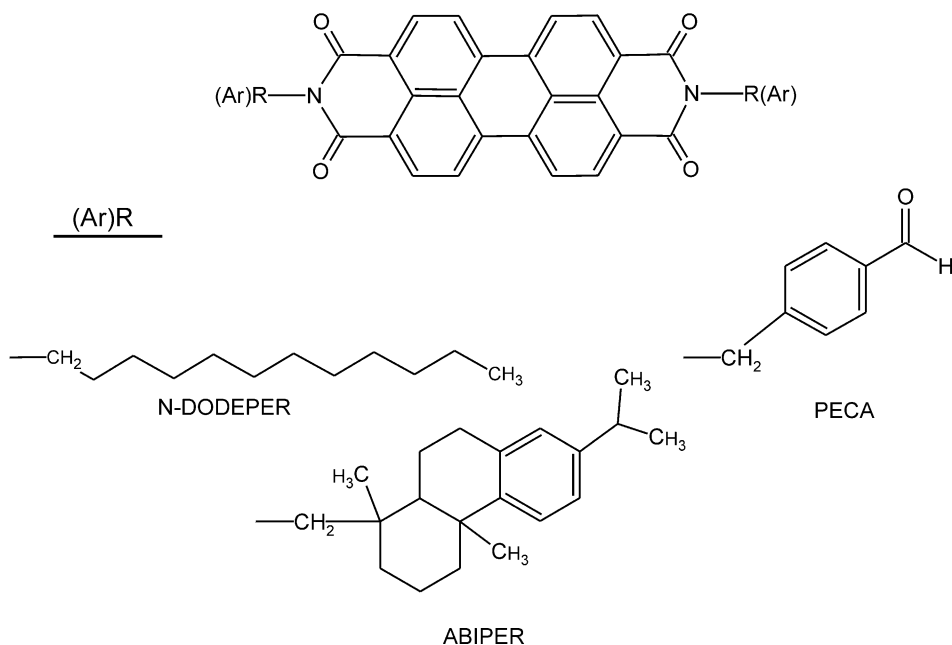
organic semiconductors and enjoy possible application in electroluminescent displays, electrophotography and as n-type photovoltaic materials for solar energy conversion [10–13]. Because of their high fluorescence quantum yields in the 500–650 nm region and their high photo- and thermal- stabilities, they have begun to be investigated as new convenient fluorescence quantum yield standards [14–16]. Perylene derivatives are also useful as laser dyes, photosensitisers and in energy and electron-transfer reactions [17–19]. The literature provides numerous data on the energy and electron transfer reactions of perylene diimide derivatives in solution, but there are only a limited number of reported studies concerning their photophysical and photochemical behaviour in immobilised phases [20–22]. The energy and/or electron transfer processes between a perylene derivative in an immobilised phase and the quencher in solution phase have not been reported. The aim of this paper was to determine the photophysical properties of three PDI derivatives [*N,N'*-di-dodecylperylene-3,4,9,10-bis(dicarboximide), *N,N'*-di-(1-dehydroabietyl) perylene-3,4,9,10-bis(dicarboximide) and *N,N'*-di-(4-carboxy phenyl)perylene-3,4,9,10-bis(dicarboximide),

*N*-DODEPER, ABIPER and PECA, respectively] in immobilised phases (PVC and sol-gel matrices) using steady state fluorescence experiments.

## 2. Experimental

### 2.1. Materials

*N*-DODEPER, ABIPER and PECA were synthesised and purified as described previously [19,23,24]. High Mv PVC and the plasticizers bis-(2-ethylhexyl)phthalate (DOP) and bis-(2-ethylhexyl)adipate (DAO) used in PVC film preparation were obtained from Fluka. The organic solvents used (chloroform, tetrahydrofuran) were all of spectrophotometric grade and were used as supplied. The polyester support (Mylar type) was provided by Du Pont. The sol-gel precursor tetraethyl orthosilicate (tetraethoxysilane, TEOS), the surfactant additive Triton X-100 (polyethylene glycol *t*-octylphenyl ether) and analytical grade concentrated hydrochloric acid were obtained from Merck. Acid solutions were prepared using high quality pure water obtained from a reverse osmosis ELGA apparatus. Absolute ethanol used



throughout the studies was used as received. The cobalt salt ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) used in quenching experiments was purchased from Merck.

## 2.2. Polymer film preparation

Polymer films were prepared from a mixture of 120 mg of PVC, 240 mg of plasticizer (DOP or DOA), and 1.5 ml  $\sim 10^{-6}$  M perylene dye in THF (dry). The concentration of the dyes in mixture was in the range of  $10^{-3}$ – $10^{-4}$  M. The resulting polymer solutions were spread onto a 125  $\mu\text{m}$  polyester support (Mylar type) having a width of 120 mm, using a manual spreading device (from Heidelberg, Germany). PVC films were kept in a THF containing dessicator to avoid damage from the air. Each PVC film was placed diagonally into the sample cuvette, improve the reproducibility of the measurements. Using a Leitz Ortopcan Polarise Microscope, connected to a PC, the PVC film thicknesses were measured with reference to that of Mylar type polyester support; PVC film thicknesses were found to be in the range of 5–10  $\mu\text{m}$ .

## 2.3. Sol-gel matrix and film preparation process

Perylenediimide doped silica gel glasses were derived from a starting composition of 4 moles high quality acidic water ( $\text{pH}=2$ , adjustment is done by HCl) and 1 mol of TEOS. These constituents were sonicated for 40 min in closed vials. It is well known phenomena that ultrasonically prepared polysiloxanes have high  $M_v$  [25]. 1.5 ml dopant was then added in the concentration range of  $10^{-5}$ – $10^{-6}$  M in THF. The resulting dopant concentration in sol was  $10^{-3}$ – $10^{-4}$  M. The addition of a few drops of Triton X-100, to improve the homogeneity of the silica sol-gel and to give a crack-free monolith, was also performed. The doped sol was stirred for at least half an hour or until the dye was completely dissolved before coating a glass slide (11 $\times$ 40 $\times$ 1 mm) which had been activated by treatment with concentrated  $\text{HNO}_3$  for 24 h, washed with distilled water and then ethanol. Immersing the doped gel glass that was pale pink and transparent, in ethanol gave no detectable removal of dye.

Coating was performed by dip coating and the coated glass slides were kept in a dessicator for several days at room temperature. After evaporation of the solvent, the coated glass slides were fixed diagonally in a quartz sample cuvette as for the PVC films. The thicknesses of the coatings were approximately 2  $\mu\text{m}$ . In the preparation of the sol, no alcohol addition (EtOH in our case) was made because alcohol has been stated as an unnecessary additive in the silicon alkoxide sol-gel process [7].

## 2.4. Spectroscopic measurements

The absorption spectra of the polymer films and sol-gel glass slides were measured using a Jasco V-530 UV–vis spectrophotometer and the fluorescence emission spectra was recorded on PTI-QM1 fluorescence spectrophotometer. Fluorescence quantum yields of *N*-DODEPER, ABIPER and PECA were measured with reference to the absorption and fluorescence emission spectra of *N*-DODEPER in the corresponding matrix (PVC or sol-gel) and all excitations were carried out at the wavelength that is abbreviated as  $\lambda_2$  in Table 1. The calculated relative fluorescence quantum yields were the values corrected for the index of refraction differences generated from matrix (indexes of refraction were taken as 1.40, 1.52 and 1.44 for THF, PVC and sol-gel respectively). The equation used in calculation of fluorescence quantum yield is given in (1), where  $\phi_f$ , is the quantum yield,  $A$ , is the absorption intensity,  $S$ , is the integrated emission band area and  $n$ , is the solvent reflective index,  $u$  and  $s$  refer the unknown and standard respectively.

$$\phi_{fu} = \phi_{fs} \times \frac{S_u}{S_s} \times \frac{A_s}{A_u} \times \frac{n_u^2}{n_s^2} \quad (1)$$

Absorption and fluorescence emission spectra were measured in quartz UV cells, which were filled with water. The quenching of the fluorescence emission of the dyes in both THF solution and the immobilized phases were monitored using a PTI-QM1 spectrophotometer.

Table 1

UV-vis spectroscopic data ( $\lambda/\text{nm}$ ) and  $\varepsilon/\text{l mol}^{-1} \text{cm}^{-1}$ ) of ABIPER, *N*-DODEPER and PECA in solution and immobilized phases

Ar(R)	Solvent	Plasticiser	$\lambda_1$	$\varepsilon_1$	$\lambda_2$	$\varepsilon_2$	$\lambda_3$	$\varepsilon_3$
ABIPER	CHCl <sub>3</sub> [23]	–	526	93 200	490	58 950	458	25 800
	THF	–	520	76 242	486	47 225	454	18 150
	PVC	–	526	61 700	490	61 400	458	50 700
	PVC	DOP	526	98 900	490	78 600	460	43 000
	PVC	DOA	524	90 400	488	79 500	458	54 300
	Sol-gel	–	544	10 2500	496	153 000	474	14 3000
<i>N</i> -DODEPER	CHCl <sub>3</sub> [24]	–	526	76 200	490	47 400	460	17 400
	THF	–	520	70 548	486	48 966	454	19 200
	PVC	–	526	62 800	490	61 400	460	52 800
	PVC	DOP	526	88 100	490	80 700	458	44 300
	PVC	DOA	524	86 200	488	81 100	458	48 100
	Sol-gel	–	544	101 500	496	14 4500	472	137 000
PECA	H <sub>2</sub> O [19]	–	466	18 800	–	–	–	–
	THF	–	520	11 500	484	7760	454	3450
	PVC	–	528	6100	490	6400	452	6390
	PVC	DOP	528	26 300	492	26 800	452	27 300
	PVC	DOA	526	22 700	488	23 600	452	19 400
	Sol-gel	–	546	102 000	492	148 000	474	140 000

For fluorescence emission studies, excitations were done at  $\lambda_2$ .

### 2.5. Fluorescence quenching measurements

Fluorescence quenching of ABIPER, *N*-DODEPER and PECA in both the immobilized and solution phases were studied at increasing concentration of the cobalt ions, CoCl<sub>2</sub>·6H<sub>2</sub>O. The solutions of CoCl<sub>2</sub>·6H<sub>2</sub>O in water were added to the THF solutions of the dyes in increasing amounts. In the immobilized phases, the films and coated glass slides were placed directly into the Co<sup>2+</sup> solutions at different concentrations. As in THF solutions the Stern–Volmer plots deviated from linearity for Co<sup>2+</sup> concentrations of  $(8.4\text{--}13.4) \times 10^{-5}$  M, calculations of the slopes were made by taking the Co<sup>2+</sup> concentrations corresponding to the linear part of the plot. 10 to 100 fold concentrated solutions of Co<sup>2+</sup> were needed to be used in order to detect a quenching effect on the emission spectra for the three perylenediimides in the immobilized phases. The Stern–Volmer plots lost their linearity at [Co<sup>2+</sup>] higher than  $6 \times 10^{-4}$  M for the non-plasticized films and films that were plasticized with DOA,  $6 \times 10^{-3}$  M for the films that were plasticized with DOP and  $4 \times 10^{-3}$  M for the dye in sol-gel matrices.

## 3. Results and discussion

### 3.1. Ground state absorption and fluorescence in different host matrices

Absorption and fluorescence data of all three perylenediimide derivatives in different host matrices are summarised in Tables 1 and 2; Solution phase results, in CHCl<sub>3</sub> and H<sub>2</sub>O, were taken from literature, are included for comparison. As in solution, the absorption and fluorescence spectra of ABIPER, *N*-DODEPER and PECA in the PVC film matrix show consistent mirror-image behaviour. Compared to the  $\lambda_{\text{max}}$  in THF solution, in all of the three different PVC film matrices (ABIPER, *N*-DODEPER and PECA), red shifts corresponding to a maximum of 8 nm were observed. However, there were no significant differences between CHCl<sub>3</sub> solutions and PVC film matrices. As perylenediimides are rigid molecules, immobilisation of them into a polymer phase is not expected to cause any difference in their vibrational rotational motions and, consequently, a minimal effect on the  $\lambda_{\text{max}}$  was expected. The molar extinction coefficients decreased for all of the three perylenediimide

Table 2

Fluorescence quantum yields  $\phi_f$ , radiative life times  $\tau_0$ /ns, fluorescence life times  $\tau_f$ /ns, fluorescence rate constants  $k_f \times 10^8 \text{ s}^{-1}$ , quenching rate constants  $k_q \times 10^{10}$ , maximum emission wavelength  $\lambda_{\text{em.max}}$ (nm) and Stokes shift  $\Delta\lambda$ /nm

Ar(R)	Solvent	Plasticizer	$\phi_f$	$\tau_0^a$	$\tau_f^b$	$k_f^c$	$k_q$	$\lambda_{\text{em.max}}$	$\Delta\lambda$
ABIPER	CHCl <sub>3</sub> [23]	–	1	8.4	8.4	1.2	–	536	46
	THF	–	0.93	6.3	5.85	1.7	40.3	530	44
	PVC	–	0.98	4.9	4.8	2.0	5.7	535	45
	PVC	DOP	0.44	11.2	5.1	1.4	3.2	535	45
	PVC	DOA	0.93	7.3	6.8	0.8	3.3	533	45
	Sol-gel	–	0.76	3	2.3	4.4	5.0	599	103
N-DODEPER	CHCl <sub>3</sub> [24]	–	1	10.4	10.4	0.9	–	533	43
	THF	–	0.93	8.5	7.9	1.2	30.2	530	44
	PVC	–	0.96	5.9	5.6	1.7	1.1	533	43
	PVC	DOP	0.92	6.0	5.5	1.8	4.9	533	43
	PVC	DOA	0.95	5.3	5.0	1.9	4.0	531	43
	Sol-gel	–	0.70	2.2	1.5	6.5	7.4	597	101
PECA	H <sub>2</sub> O [19]	–	1	–	–	–	230	–	–
	THF	–	0.92	17.2	15.8	0.6	19.8	531	47
	PVC	–	0.91	5.9	5.3	0.2	0.93	538	46
	PVC	DOP	0.62	13.5	8.4	1.2	2.0	535	43
	PVC	DOA	0.89	14.8	13.2	0.8	2.7	532	44
	Sol-gel	–	0.72	3.4	2.4	4.1	4.3	598	106

<sup>a</sup>  $\tau_0 = 3.5 \times 10^8 / \nu_{\text{max}}^2 \cdot \epsilon_{\text{max}} \cdot \Delta\nu_{1/2}$  where  $\nu_{\text{max}}$  is the wavenumber in  $\text{cm}^{-1}$ ,  $\epsilon_{\text{max}}$  the molar absorptivity coefficient at the selected absorption wavelength and  $\Delta\nu_{1/2}$  the half-width of the selected absorption in wavenumber units of  $\text{cm}^{-1}$  [26].

<sup>b</sup>  $\tau_f = \tau_0 \cdot \phi_f$

<sup>c</sup>  $k_f = 1/\tau_f$

derivatives under investigation in PVC film in which no plasticizer was used. If ratio of PVC and plasticizer used (33 and 66% by mass, respectively) in the preparation of polymer solutions is considered, one may conclude that the plasticizer is the component representing the solvent system. It is assumed that the improved strength of intensity of absorption in the plasticized films was caused by the improved solubility of the dye in the polymer solution upon addition of the plasticizer.

With the exception of the film that was plasticized with DOP, the relative quantum yield values were around unity. A lower fluorescence intensity for ABIPER and PECA, corresponding to higher absorption was seen, when the absorption and fluorescence spectra of the films that were plasticized with DOP were compared to the film plasticized with DOA (Fig. 1). The relative quantum yield values of ABIPER and PECA in DOP plasticized PVC films were 0.44 and 0.62, respectively. This decrease may be related to the interactions of

conjugated substituents with the aromatic ring of DOP. In order to prove this suggestion, the composition of the polymer solution was changed to 50% PVC and 49% DOP. For those films the  $\phi_f$  values increased to 0.82 and 0.80, respectively. The fluorescence quantum yield of N-DODEPER (0.92) which can be considered as around unity, in DOP plasticized film supports this suggestion. As a result it can be proposed that DOP acts as a quencher for the emission of ABIPER and PECA. The radiative life times  $\tau_0$  and fluorescence life times  $\tau_f$  were calculated to be in the range of 5–17 and 5–15 ns, respectively.

The photophysical properties of ABIPER, N-DODEPER and PECA in sol-gel thin films were found to be distinctly different (Tables 1 and 2). Stokes shifts are seen to be twofold in sol-gel matrix compared to the  $\Delta\lambda$  values in PVC matrix and in solutions. Kessler et al. have stated that the dye in a sol-gel matrix may undergo spectral shifts, and also that other polarity dependent

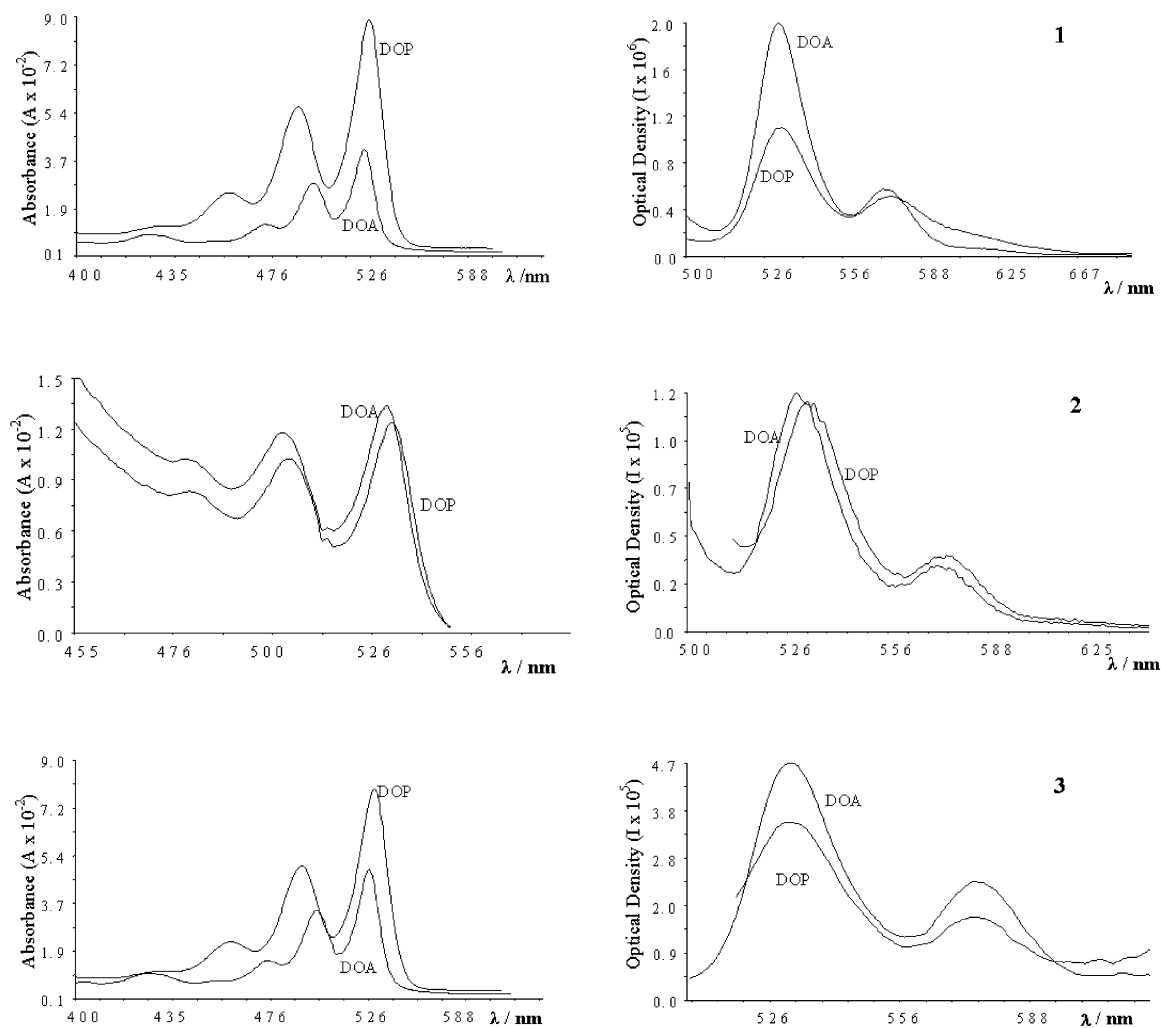


Fig. 1. The absorption and emission spectra of ABIPER (1), N-DODEPER (2) and PECA (3) PVC films that were plasticized with bis-(2-ethylhexyl)phthalate (DOP) and bis-(2-ethylhexyl)adipate (DOA).

parameters may change also, such as molar absorptivity constant and fluorescence quantum yield [27]. The observed red-shift of the absorption spectra in sol-gel host matrix of perylenediimide derivatives, compared to the spectra in both solution and PVC, can be explained by the polar environment of the dye molecules within the silica cage (Fig. 2).

Burgdorff et al. have reported that perylenediimide derivatives in a sol-gel matrix show broad and structureless fluorescence spectra in thin films that are similar to the spectra observed in highly concentrated solutions and to “excimer

like” emission; they reported the lifetime of the excimer as 12 ns [21]. Although the fluorescence emission spectra obtained for each of the three derivatives under investigation in the sol-gel matrix were broad and structureless, in neither of them was the lifetime higher than 4 ns. At high concentrations, interactions between the dye molecules, such as the formation of dimers and excimers, can be expected and deviations from the linearity of Lambert–Beer law may occur. Biju et al. have reported that aggregated molecules may be separated into single molecules by reducing the concentration as well as by mixing the dye solu-

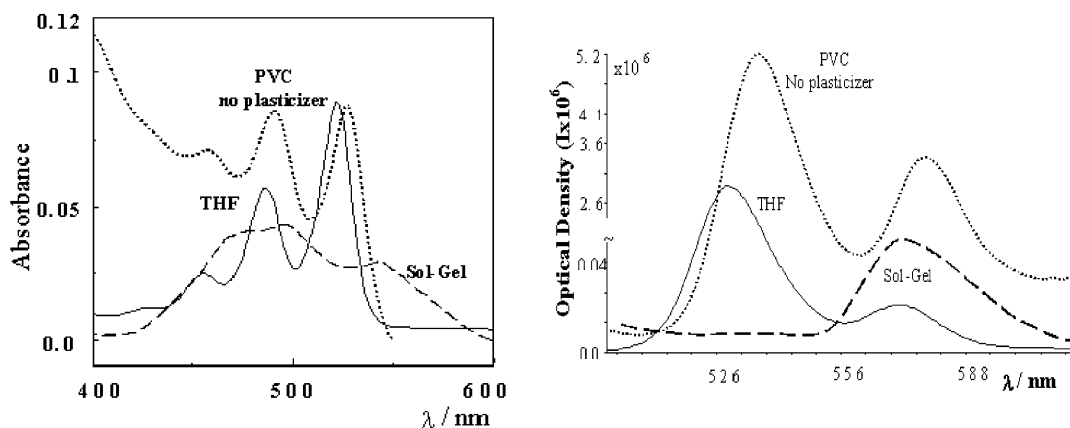


Fig. 2. The absorption and fluorescence emission spectra of ABIPER in THF solution, PVC film without plasticizer and sol-gel matrices.

tion in a polymer solution [1]. Absorption values were tried to be maintained below 0.1 not only for the solution phase studies but also for the immobilized host matrices, in order to avoid these kinds of complications.

### 3.2. Fluorescence quenching with cobalt ions

Perylenediimides are known to be both electron acceptors [28] and electron donors [18,19,29]. The quenching process for all of the three host matrices obeyed the Stern–Volmer relation [30] (2).

$$I_0/I = 1 + k_q \tau_0 [Q] \quad (2)$$

where  $I_0$  and  $I$  represent the fluorescence intensity of dyes in the absence and presence of quencher cobalt ions, of concentration  $[Q]$  and  $\tau_f$  is the radiative lifetime in the absence of the quencher. The values of fluorescence quenching rate constants,  $k_q$ , were calculated using the Stern–Volmer plots shown in Fig. 3.

In THF solution, the Stern–Volmer plots yielded quenching rates of  $4 \times 10^{11}$ ,  $3 \times 10^{11}$  and  $1.9 \times 10^{11}$  for ABIPER, *N*-DODEPER and PECA, respectively (Table 2). These  $k_q$  values are above the diffusion rate limit of  $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  reported for perylenediimides [29]. High quenching rates indicate towards the tendency of electron transfer process, although quenching rates, for a perylenediimide derivative with  $\pi$ -electron donors,

have been reported as  $10^{11}$ – $10^{14}$ , which are also above diffusion rate limits [28]. We [19] have reported the  $k_q$  value of quenching of the fluorescence emission of PECA with  $\text{Co}^{+2}$  in  $\text{H}_2\text{O}$  as  $2.3 \times 10^{12}$ . High  $k_q$  values can be attributed to an electron transfer mechanism in aqueous solution. The high quenching rate values obtained in the present study may be due to, an interaction between the polar oxygen atom of THF and perylenediimide.

Higher concentrations of  $\text{Co}^{+2}$  were needed to impart a quenching effect in the immobilized phases. In neither of them was the diffusion rate limit exceeded and there were no significant differences between the  $k_q$  values (Table 2). All of the calculated  $k_q$  values were approximately 10 times lower than those obtained the case in solution phase. One may suggest that immobilization of the dye inhibits the energy transfer process. The effect of increasing the concentration of  $\text{Co}^{+2}$  on the fluorescence emission of the dyes in both the solution phase and the immobilized host matrices is illustrated in Fig. 3.

## 4. Conclusions

It has been found that the characteristics of the host matrix have a marked on the photophysical and photochemical properties of the dye. DOP acted as a quencher for the perylenediimide

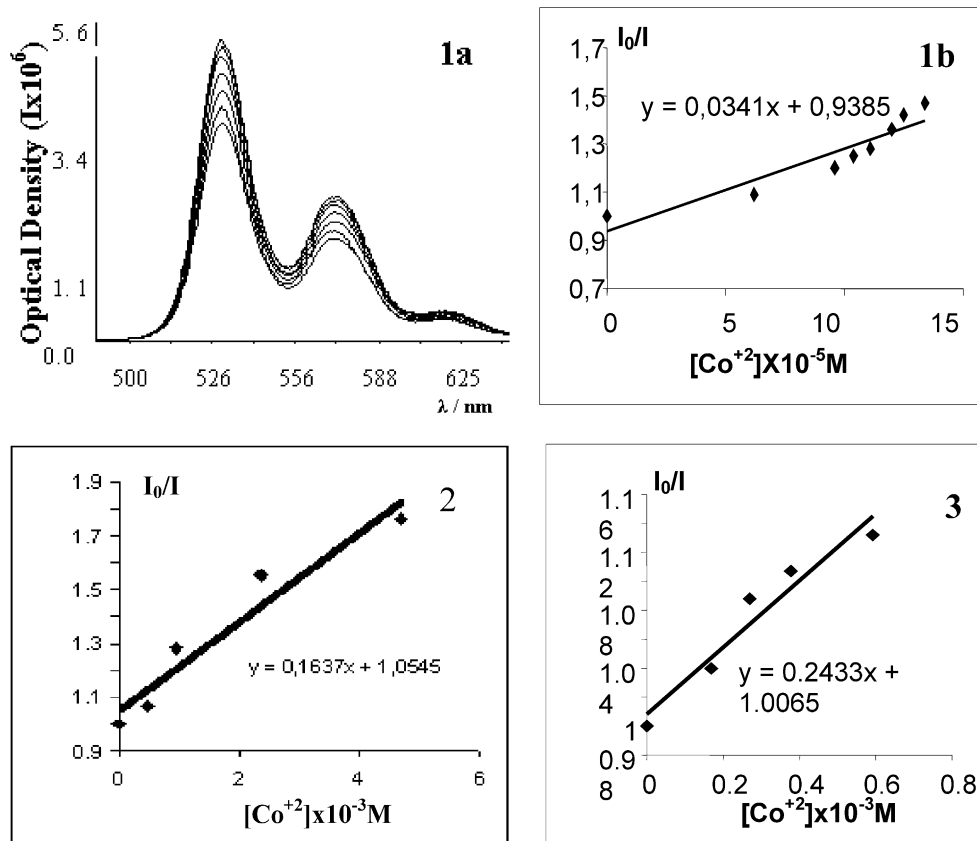


Fig. 3. Fluorescence emission quenching of PECA in THF solution, with increasing  $\text{Co}^{+2}$  concentration (1a) and corresponding Stern–Volmer plot (1b). Stern–Volmer plot of *N*-DODEPER in sol-gel matrix (2) and ABIPER in PVC film plasticized with DOA (3).

derivatives with aromatic substituents; this is a finishing which had not been previously reported. We also found that where usage of plasticizer supports the interaction of dye molecule and  $\text{Co}^{+2}$ , the glassy structure of the sol-gel matrix inhibits this interaction.

### Acknowledgements

We acknowledge the project support funds of Research Fund Center of Ege University (AFS), Alexander von Humboldt Foundation (AvH) and of the Scientific Research Council of Turkey (TUBITAK). We are also indebted to Dr. Kadriye Ertekin for her generosity in sharing her knowledge about film preparation and Alper Toker, Du

Pont representative in Turkey, for providing us polyester support material, respectively.

### References

- [1] Biju V, Yamauchi M, Ishikawa M. Distribution of single molecules in polymer thin films. *Journal of Photochemistry and Photobiology A: Chemistry* 2001;140:237–41.
- [2] Brusatin G, Guglielmi M, Bozlo R, Meneghetti M, Signorini R, Maggini M, Scorrano G, Prato M. Preparation of fullerenes containing sol-gel glass. *Journal of Sol-Gel Science and Technology* 1997;8:609–13.
- [3] Shortreed M, Monson E, Kopelman R. Lifetime enhancement of ultrasmall fluorescent liquid polymeric film based optodes by diffusion-induced self-recovery after photobleaching. *Analytical Chemistry* 1996;68(22):4015–9.
- [4] Ertekin K, Alp S, Karapire C, Yenigül B, Henden E, İçli S. Fluorescence emission studies of an azlactone derivative



- embedded in polymer films: An optical sensor for pH measurements. *Journal of Photochemistry and Photobiology A: Chemistry* 2000;137:155–61.
- [5] Hong Chan W, Lee AWM, Kwong DWJ, Tam WL, Wang KM. Potassium ion-selective optodes based on the calix[6]arene hexaester and application in human serum assay. *Analyst* 1996;121:531–4.
- [6] Papkovsky DB, Mohr GJ, Wolfbeis OS. New polar plasticizers for luminescence-based sensors. *Analytica Chimica Acta* 1997;337:201–5.
- [7] Avnir D, Kaufman VR. Alcohol is an unnecessary additive in the silicon alkoxide sol-gel process. *Journal of Non-Crystalline Solids* 1987;192:180–2.
- [8] Lobnik MA. Optical characterization of sol-gels and their application to chemical sensors. PhD thesis, University of Graz, Germany, 1998.
- [9] Sakka SJ. Glasses and glass-ceramics from gels. *Non-Crystalline Solids* 1985;73:651–60.
- [10] Angadi MA, Gosztola D, Wasielewski MR. Organic light emitting diodes using poly(phenylenevinylene) doped with perylene diimide electron acceptors. *Materials Science and Engineering* 1999;B56:191–4.
- [11] Gosztola D, Niemczyk MP, Svec W, Lucas AS, Wasielewski MR. Excited doublet states of electrochemically generated aromatic imide and diimide radical anions. *Journal of Physical Chemistry* 2000;A104:6545–51.
- [12] Cormier RA, Gregg BA. Synthesis and characterization of liquid crystalline perylene diimides. *Chemistry and Materials* 1998;10:1309–19.
- [13] Cormier RA, Gregg BA. Self-organization in thin films of liquid crystalline perylene diimides. *Journal of Physical Chemistry B* 1997;101:11004–6.
- [14] Içil H, Arslan E. Synthesis and spectroscopic properties of highly pure perylene fluorescent dyes. *Spectroscopy Letters* 2001;34(3):355–63.
- [15] Içil H, Arslan E. Synthesis and spectroscopic characterization of water soluble perylene tetracarboxylic diimide derivatives. *Spectroscopy Letters* 2001;34(5):605–14.
- [16] Kalinin S, Speckbacher M, Langhals H, Johansson LBA. A new and versatile fluorescence standard for quantum yield determination. *Phys Chem Chem Phys* 2001;3:172–4.
- [17] El-Daly SA, Okamoto M, Hirayama S. Fluorescence quenching of N,N'-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylenebis(dicarboximide) (DBPI) by molecular oxygen. *J Photochemistry and Photobiology A: Chemistry* 1995;91:105–10.
- [18] Içil H. Energy transfer studies with perylene bis-diimide derivatives. *Spectroscopy Letters* 1998;31(4):747–55.
- [19] Içli S, Demiş S, Dindar B, Doroshenko AO, Timur C. Photophysical and photochemical properties of a water soluble perylene diimide derivative. *Journal of Photochemistry and Photobiology A: Chemistry* 2000;136:14–23.
- [20] Gregg BA, Sprague J, Peterson MW. Long-range singlet energy transfer in perylene bis(phenethylimide) films. *J Physical Chemistry B* 1997;101:5362–9.
- [21] Burgdorff C, Löhmansröben HG, Reisfeld R. A perylene dye in sol-gel matrices: photophysical properties of N,N'-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylene-bis(dicarboximide) in glasses and thin films. *Chemical Physics Letters* 1997;197:358–63.
- [22] El-Daly SA. Spectral, lifetime, fluorescence quenching, energy transfer and photodecomposition of N,N'-bis(2,6-dimethyl phenyl)-3,4,9,10-perylene tetracarboxylic diimide (DXP). *Spectrochimica Acta Part A* 1999;55:143–52.
- [23] Içli S, Içil H. A thermal and photostable reference probe for  $\phi_f$  measurements: chloroform soluble perylene 3,4,9,10-tetracarboxylic acid-bis-N,N'-dodecyl diimide. *Spectroscopy Letters* 1996;29(7):1253–7.
- [24] Içil H, Içli S, Sayıl Ç. Synthesis and properties of a new photostable soluble perylene dye: N,N'-di-(1-dehydroabietyl)perylene-3,4,9,10-bis(dicarboximide). *Spectroscopy Letters* 1998;31(8):1643–7.
- [25] Price GJ, Wallance ENK, Patel AM. In: Jones RG, editor. Silicon-containing polymers. The Royal Society of Chemistry; 1995. p. 146–155.
- [26] Turro NJ. *Molecular photochemistry*. London: Benjamin; 1965.
- [27] Kessler MA, Wolfbeis OS. New highly fluorescent ketocyanine polarity probes. *Spectrochimica Acta Part A: Molecular Spectroscopy* 1991;47(2):187–92.
- [28] Içli S, Içil H, Gürol İ. High rates of fluorescence quenching between perylene dodecyldiimide and  $\pi$ -electron donors. *Turkish Journal of Chemistry* 1997;21(4):363–8.
- [29] El-Daly SA. Fluorescence quenching of N,N'-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylenebis(dicarboximide) (DBPI) by  $\text{Co}^{2+}$  ion. *Journal of Photochemistry and Photobiology A: Chemistry* 1992;68:51–8.
- [30] Lakowicz JR. *Principles of fluorescence spectroscopy*, part 8. New York: Kluwer Academic/Plenum Publisher; 1999.