

# Comparative Study of Commercially Available Fluorescers Versus bis(2,4,5-trichloro-6-carbobutoxyphenyl) oxalate

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*The quantum yield of a photoluminescent substance provides a direct measure of the efficiency of the conversion of absorbed photons into emitted photons. In the present study, the emphasis was to determine the fluorescence quantum yield of five commercial fluorescers under the same conditions: peri-dinaphthalene (perylene), 5,6,11,12-tetraphenyltetracene (rubrene), 9,10-diphenylanthracene, 9,10-bis(phenylethynyl)-anthracene, 1-chloro-9,10-bis(phenylethynyl)-anthracene, in comparison with synthesized bis(2,4,5-trichloro-6-carbobutoxyphenyl) oxalate. The quantum yields and the maximum wavelengths of these fluorescers are very important for practical applications, where scotopic visual sensitivity intervenes.*

**Keywords:** quantum yield, luminescence, oxalate, rubrene, perylene

Luminescent substances have found important application potential due to their emission spectra, such as multicolor emission [1-2], biological and medical use in cell luminescence imaging, light-emitting devices, color displays, chemosensors, lasers, etc. [3-9]. Such substances may be constituted by organic or inorganic molecules, such as NaF complexes [1], calix[4]arenes [10], pyrene-derivatives [11], rhodamine-derivatives [12], or anthracene-derivatives [2].

Among these classes of substances, ester-oxalates present some key advantages, the system including it being the only chemiluminescent reaction involving a mechanism with demonstrated high quantum yields, i.e. an intermolecular chemically initiated electron exchange luminescence (CIEEL) [13-14]. This major advantage conducted to their synthesis and use in chemiluminescent (CL) mixtures, in order to obtain high light capacities (> 500 lumens-hour/liter) in case of TCCBPO, high luminous flux in short time, longer lasting life (over 12 hrs. in case of TCCBPO), superior performances at low temperatures [15-16].

The quantum yield of a photoluminescent substance ( $\Phi_f$ ) is one of its fundamental properties, providing a direct measure of the efficiency of the conversion of absorbed photons into emitted photons. Thus, the measurement of  $\Phi_f$  is a key step in the characterization of any photoluminescent species. The reliable determination of  $\Phi_f$  is challenging, since it is affected by many different parameters, such as temperature, environment (solvent and viscosity), and concentration. The most elementary method for the determination of  $\Phi_f$  involves the comparison of the fluorescence intensity of a dilute fluorophore solution with that of a solution of a  $\Phi_f$  standard of known  $\Phi_f$  under identical measurement conditions using conventional absorption and fluorescence spectrometers [17-20].

In order to demonstrate their applicative potential, the present study focused on materials which were submitted to various tests, in order to determine their photoluminescent properties, by using the absolute method for  $\Phi_f$  measurement under unified conditions (temperature, concentration, and measurement method). This method is widely used and is important for the examination of

emission properties and mechanisms in order to predict the photophysical properties,  $\Phi_f$ , the band shape and position of emission and excitation spectra.

The emphasis was on the  $\Phi_f$  determination for five commercial fluorescers under the same conditions, in comparison with a synthesized ester-oxalate. For some of them,  $\Phi_f$  has not been reported previously, while for others,  $\Phi_f$  was reported in different solvents under different experimental conditions or using different instruments/methods, without giving a consistent comparison among their applicative performances.

The maximum wavelengths of the fluorescers dissolved in various media, together with the solubility of the CL system components, present remarkable importance for practical applications, streamline of these factors leading to improvement of the light capacity.

## Experimental part

### Materials and methods

Bis(2,4,5-trichloro-6-carbobutoxyphenyl) oxalate (TCCBPO) was synthesized in two steps, accordingly to [15-16] with 99.7% purity, from 2,4,5-trichlorosalicylic acid and n-butyl alcohol, obtaining 2,4,5-trichlorosalicylate, in a first step, and further from this latter reaction with oxalyl chloride.

All the other reagents were purchased from Sigma-Aldrich, analytical grade, and used without any further purification: peri-dinaphthalene (perylene), 5,6,11,12-tetraphenyltetracene (rubrene), 9,10-diphenylanthracene (DPA), 9,10-bis(phenylethynyl)-anthracene (BPEA), 1-chloro-9,10-bis(phenylethynyl)-anthracene (ClBPEA). Dibutylphthalate (DBP) 99% was employed as inert solvent for the achievement of ester-oxalate based CL mixtures. All the solutions analyzed had  $4 \cdot 10^{-3}$  mole/L concentrations and were studied in triplicate (table 1) under nitrogen flow, due to the fact that oxygen is known to be a strong dynamic quencher of fluorescers luminescence [21].

Fluorescence determinations were performed on a UNICAM Helios absorption spectrometer, and a JASCO FP-6300 spectrofluorimeter within the range 220-750 nm. Fluorescence emission and excitation analyses were performed at room temperature using a Jasco FP-6500 Spectrofluorimeter provided with a Xe-450 W excitation lamp. The parameters employed were: band width (ex/

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em) - 3 nm; response - 1 s; data pitch - 1 nm; scanning speed - 200 nm/min. The fluorescence was measured at 90° to the incident excitation beam. The fluorescence intensity at a certain wavelength was calibrated against the detector response and the excitation light intensity. The relative intensities of fluorescence of these substances are listed in table 1.

The  $\Phi_f$  of the materials considered was determined using equation (1), in comparison with perylene, which has an absolute quantum yield  $\Phi_f = 0.94$  [22]:

$$\Phi_f = \Phi_f^0 \times \frac{I_{f_s}}{I_{f_0}} \times \frac{A_0 n_s^2}{A_s n_0^2} \quad (1)$$

where  $I_f$  is the fluorescence intensity,  $A$  is the absorbance at the excitation wavelength,  $n$  is the refractive index of DBP, the subscript 0 stands for a reference compound and  $s$  represents the sample. Several measurements of the  $\Phi_f$  were performed and averaged by choosing different concentrations and excitation wavelengths [17-20].

Further, steady-state fluorescence analysis was performed based on the relationship intensity versus wavelength.

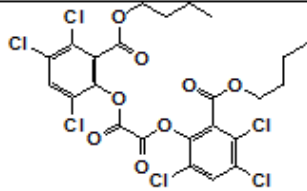
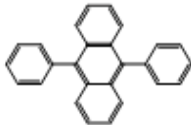
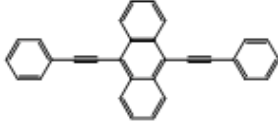
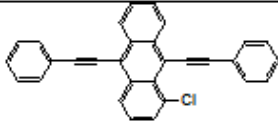

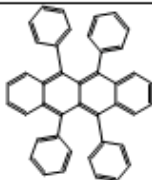
## Results and discussions

UV-vis absorption and steady-state fluorescence measurements are important tools for the emphasis of the effect of the materials structure on the absorption and fluorescence properties. Consequently, tests were performed and a comprising study of the influence of the absorption wavelength and the intensity of fluorescence on the materials performances was achieved. Experimental tests were performed in order to establish the influence of fluorescers on practical applications of CL systems, such as light-emitting devices in the visible spectrum, along with the efficiency of scotopic visual sensitivity.

### UV-Vis absorption analysis

The compounds implied in the present study exhibit substantial differences in their experimental UV-vis absorption spectra by characteristic bands variations in shape and position. These modifications of the absorption bands, next to the values of the molar extinction coefficient, give evidence for the influence of the aromatic substitution.

For CIBPEA, the substitution effect of phenyl ring by the Chlorine atom on the spectroscopic properties has been evidenced versus the compound with the unsubstituted

Compound	Molecular structure	$I_f$ , a.u.
TCCBPO		441/111
DPA		553/140 364/396 412/428 878/901 859/879
BPEA		796/355/103
CIBPEA		387/228
perylene		748/423/101
rubrene		16/145/42

**Table 1**  
FLUORESCERS USED DURING THE  
STUDY AND THEIR  $I_f$

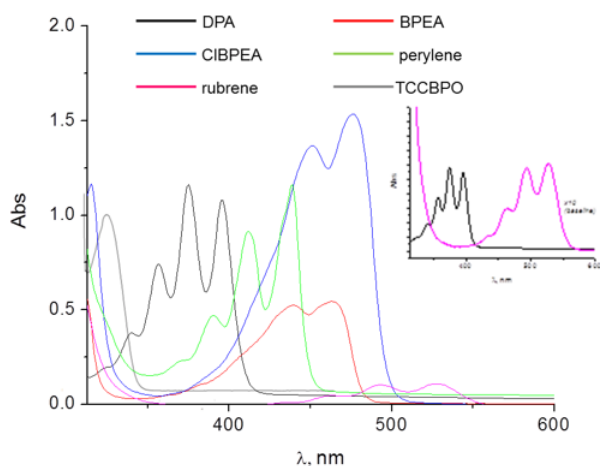


Fig. 1. Absorption spectra of the fluorescers in DBP

phenyl group, BPEA. The bathochromic shift, of about 12 nm, observed for the absorption spectra (fig. 1), may indicate that the lower energy absorption band ( $S_0 \rightarrow S_1$  transition) of anthracene shows an electronic structure that is lost upon substitution of the phenyl ring by the Chlorine atom. Also, the extent of the p-electrons conjugation is taken into consideration. In direct comparison with

perylene, a slight overlapping of the absorption bands between 350-450 nm has been observed.

The spectra of the fluorescers considered are given in figure 1. In the detail, figure 1 shows a comparison between two different electronic structures: DPA (313-425 nm) and rubrene (425-600 nm).

The absorption maxima of the compounds and the corresponding molar extinction coefficients ( $\epsilon$ ) obtained are summarized in table 2.

#### Steady-state fluorescence analysis

All the compounds present intense fluorescence, with high  $\Phi_f$  values (table 3). Since an extended p conjugation can exert a significant influence on the physical properties, figure 2 presents comparatively the fluorescence emission and excitation spectra of BPEA, CIBPEA, perylene, rubrene and TCCBPO. For example, the emission spectra of BPEA and CIBPEA consist in two structure bands, at 476 and 508 nm in the case of BPEA, and 491 and 525 nm respectively, for CIBPEA. In the latter case, the red-shifted emission without the emission band at 545 nm, was found. As regarding the excitation spectra, no significant changes were observed in the ground state properties, in comparison to those found in excited quantum state.

Compound	Spectral absorption parameters		
	$\lambda_{max}$ (nm)	Abs	$\epsilon$ ( $L \text{ mol}^{-1} \text{ cm}^{-1}$ )
TCCBPO	332	0.89	$0.6357 \times 10^4$
DPA	323	0.18	$0.08571 \times 10^4$
	339	0.37	$0.1761 \times 10^4$
	356	0.74	$0.3523 \times 10^4$
	375	0.86	$0.4523 \times 10^4$
	396	0.77	$0.4095 \times 10^4$
BPEA	440	0.52	$0.5360 \times 10^4$
	464	0.54	$0.5567 \times 10^4$
CIBPEA	415 (sh)	0.54	$1.0188 \times 10^4$
	451	0.96	$2.5660 \times 10^4$
	476	0.93	$2.8867 \times 10^4$
perylene	369	0.22	$0.2340 \times 10^4$
	390	0.47	$0.5000 \times 10^4$
	412	0.91	$0.9680 \times 10^4$
	439	0.86	$1.2340 \times 10^4$
rubrene	434	0.008	$0.0333 \times 10^4$
	463	0.046	$0.1916 \times 10^4$
	493	0.101	$0.5208 \times 10^4$
	528	0.108	$0.5500 \times 10^4$

**Table 2**  
ABSORPTION PARAMETERS OF  
THE FLUORESCERS USED

Compound	$\lambda_{ex}$ , nm	$\lambda_{em}$ , nm	$\Phi_f$
TCCBPO	330	447/527 (sh)	0.73
DPA	325	442/521(sh)	0.77
	339	412/433/466 (sh)	
	350	412/432/466 (sh)	
	375	411/432	
	395	412/432	
BPEA	425	476/508/545	0.81
	440	476/508/545	
	460	476/508/545	
CIBPEA	425	491/525	0.85
	453	491/525	
	480	491/525	
perylene	390	443/472/506	0.94 [14,21,29]
	412	443/472/506	
	439	443/472/506	
rubrene	461	552/596 (sh)	0.98 [30]
	496	552/596	
	531	552/596	

**Table 3**  
THE FLUORESCENCE EMISSION MAXIMA,  $\lambda_{em}$ , AND FLUORESCENCE QUANTUM YIELDS,  $\Phi_f$  OF THE FLUORESCERS

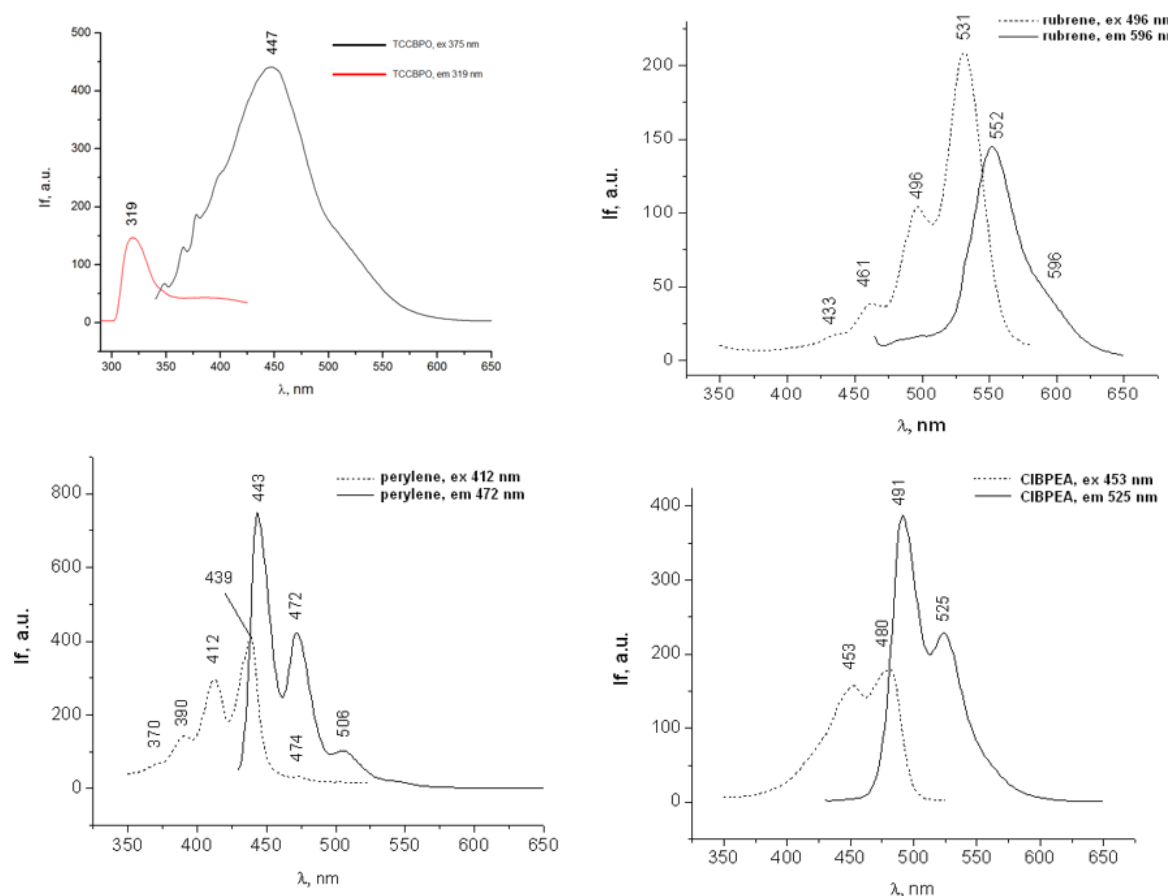


Fig. 2. Fluorescence emission and excitation spectra of BPEA, CIBPEA, perylene, rubrene and TCCBPO in DBP

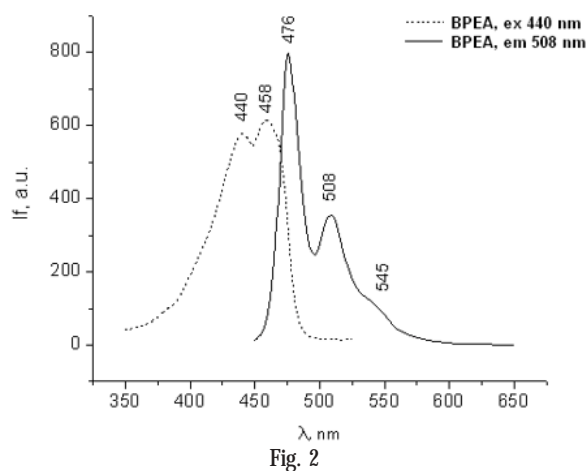


Fig. 2

Further, the fluorescence emission and excitation spectra of perylene and rubrene were plotted. The differences observed in the emission maxima are attributed to their various plotted conformations [22-28]. As regarding the excitation spectra of rubrene, only slight changes in excited state properties versus ground state are observed. For perylene, no changes were found.

Table 3 presents the differences observed in the fluorescence parameters (emission, excitation,  $\Phi_f$ ) of the studied compounds.

According to the  $\Phi_f$  determinations for fluorescers, besides perylene, the best results for the CL systems were obtained for compositions containing either CIBPEA or BPEA or rubrene.  $\Phi_f$  is higher as the oxidation potential of the fluorescer or the singlet excited state energy ( $E_s$ ) is lower. As regarding the peroxy-oxalate chemiluminescent systems, the electronic excited state can be generated while using fluorescers with  $E_s$  up to 105 kcal/mole.

## Conclusions

In the present study,  $\Phi_f$  and emission maxima of five fluorescers were measured under the same conditions in DBP. Based on the data obtained, the correlation between the substances structures and their fluorescence properties has been discussed.

The high  $\Phi_f$  ( $\Phi_f = 0.81..0.98$ ) and flexibility regarding the type and the concentrations of fluorescers represent determinant factors in using CL systems in practical and specific applications.

The emission maximum wavelengths of the fluorescers in DBP were determined (perylene - 443 nm; rubrene - 552 nm; CIBPEA - 491 nm and BPEA - 476 nm). The evaluation of fluorescer influence on the CL systems performances was necessary due to the fact that the maximum emission wavelengths, required for scotopic visual sensitivity assessment, are influenced by the solvent nature where the CL reaction occurs.  $\epsilon_{DPA}$  is the lowest and is considered to have no practical interest.

A set of consistent fluorescence data for commercially available dyes was provided. There were also advanced data on the TCCBPPO fluorescence. Though it appears to have the lowest  $\Phi_f$ , it presents important other properties that make it interesting for achieving various tasks in fluorescent systems. Moreover, these fluorescence data and related emission mechanism are useful for selecting

and designing new fluorescent materials and probes needed for various industrial applications.

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