Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photoluminescence and Electro-Optic Kerr Effect in Porphyrin Derivatives of C60

J. Niziol [a], M. Prato [b], C. Soombar [b], E. Vazquez [b], E. Gondek [c], I. Rau [d] & F. Kajzar [d] [e]

[a] AGH University of Science and Technology, Krakow, Poland
[b] Dipartimento di Scienze Farmaceutiche, Trieste University, Italy
[c] Cracow University of Technology, Krakow, Poland
[d] Politehnica University of Bucharest, Romania
[e] UFR Sciences, POMA Laboratory, Angers University, Angers, France

Version of record first published: 28 May 2010

To cite this article: J. Niziol, M. Prato, C. Soombar, E. Vazquez, E. Gondek, I. Rau & F. Kajzar (2010): Photoluminescence and Electro-Optic Kerr Effect in Porphyrin Derivatives of C60, Molecular Crystals and Liquid Crystals, 522:1, 191/[491]-202/[502]

To link to this article: http://dx.doi.org/10.1080/15421401003726956

Mol. Cryst. Liq. Cryst., Vol. 522: pp. 191/[491]–202/[502], 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421401003726956

Photoluminescence and Electro-Optic Kerr Effect in Porphyrin Derivatives of C60

J. NIZIOL,[1] M. PRATO,[2] C. SOOMBAR,[2] E. VAZQUEZ,[2]
E. GONDEK,[3] I. RAU,[4] AND F. KAJZAR[4,5]

[1]AGH University of Science and Technology, Krakow, Poland
[2]Dipartimento di Scienze Farmaceutiche, Trieste University, Italy
[3]Cracow University of Technology, Krakow, Poland
[4]Politehnica University of Bucharest, Romania
[5]UFR Sciences, POMA Laboratory, Angers University, Angers, France

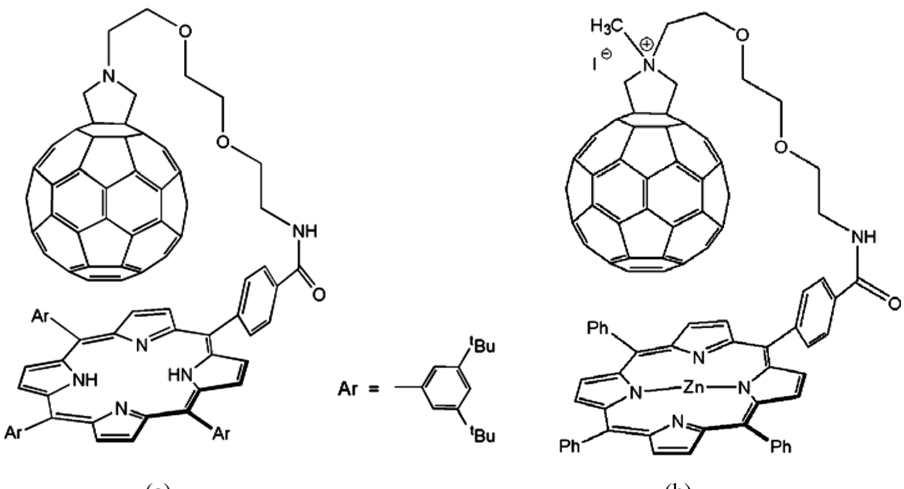
Photoluminescence and electro-optical properties of two C60 fullerene derivatives: with porphyrin ($C60\text{-}H_2P$) and of an iodide salt of Zn porphyrin $(C60\text{-}ZnP)^+I^-$ are reported. Both studies were done in solution. In the case of the ($C60\text{-}H_2P$) the photoluminescence spectra depend strongly on the solvent used and emission from B band is quenched in dioxane. For the idodide salt $[C60\text{-}ZnP]^+I^-$ both emissions from B and Q bands are observed. In all studied cases the photoluminescence at 650 nm is present, however it is excited in the iodide salt only for certain excitation energies. The EO Kerr effect measurements show a very slow rotation of molecules under the applied electric field. This rotation is more complex in the case of the iodide salt.

Keywords Electro-optic Kerr effect; fullerene derivatives; photoluminescence; porphyrin

Introduction

In the previous paper [1] we have reported on the chemical synthesis of two complexes of fullerene C60 molecule functionalized with the porphyrin molecule, whose chemical structures are shown in Figure 1. The first one denoted as C60-H2P (Fig. 1(a)) is a regular molecule whereas the second one ((Fig. 1(b)) is a C60-Zn porphyrin salt with iode as the counterion ($[C60\text{-}H2P]^+I^-$). Both compounds are soluble in several organic solvents. However the solubility of the iodide salt is much lower than that of C60-H2P. These compound show an interesting property to form regular, submicron size aggregates in thin films obtained by solution casting on glass substrates. The size of aggregates decreased when films were obtained from solutions of C60-H2P in polymer, PMMA in this case. In this paper we report on photoluminescence and nonlinear optical properties of these compounds.

Address correspondence to F. Kajzar, Angers University, POMA Laboratory, 2 bd Lavoisier, Angers 49045, France. Tel.: +40213154193; Fax: +40213154193; E-mail: frkajzar@yahoo.com



(a) (b)

Figure 1. Chemical structure of C60-H2P (a) and of the iodide salt $[\text{C60-ZnP}]^{+}\text{I}^{-}$ (b).

Fullerenes, representing electron accepting properties, while bound covalently with electron donors are good candidates for applications relying on converting the light into the electricity or vice-versa. Special place among variety of donors occupy porphyrins and derivatives because they let mimic naturally occurring processes like photosynthesis [2].

Photoluminescence is presently a very desired property motivated by a fast development of organic light emitting diodes (OLED's) [3,4]. and was already reported for a large class of porphyrins. OLED's, whose main advantage is their high quantum efficiency with law driving voltage, are at the same time source of photons, in contrary to liquid crystal (LC) display. They have already found several practical application in displays for mobile phones (Pioneer), TV sets (Sony, Samsung), car-radio (Pioneer), notebooks and laptops (Samsung), etc. However the largest application is expected in exploring white emission to replace the presently used incandescent bulbs or fluorescent tubes for home lightening. Due to the significantly better quantum efficiency it will decrease the lightening cost and make it more flexible in use. However to do it large emission spectra are required.

The photoluminescence of porphyrins was largely studied in past [5,6], and it was found that it depends strongly on the local environement. This property is already largely used in biosensors [7,8], and in chemiosensors [9].

Both compounds are very large, asymmetric molecules. Such large molecules should exhibit large Kerr electro-optic coefficient s_{3333}, as it was observed e.g., in rotaxane solutions [10]. The EO Kerr effect measurements, as function of the frequency of the applied external field give also information about their rotational mobility of molecules and, in general, on their third order nonlinear optical (NLO) properties.

Photoluminescence Spectroscopy in UV-VIS

The photoluminescence studies were done in function of the excitation wavelength in solution of studied compounds. According to the good laboratory practice the typical optical density of studied solutions was of 0.05. The studies were done using different solvents to check their influence on the photoluminescence spectra. In presented figures there are seen two inclined lines formed by trains of peaks. They come from dispersed light of the excitation wavelength and second order diffraction on the spectrometer grating. Therefore, physical meaning represent only the spectra appearing between these lines.

Photoluminescence in C60-H2P

Figures 2–5 shows the photoluminescence maps (intensity of emission wavelength dependence on the excitation wavelength) for solutions of C60-H2P in dioxane, 1,1,2-trichloroethylene, DMF and DMSO, respectively. It is seen that the emission spectrum depends strongly on the excitation wavelength and on the solvent used. The simplest situation is for the dioxane as solent. Only relatively week emission bands at 650 and 710 nm are observed (cf. Fig. 2) for the whole excitation wavelength spectrum 280–430 nm. The largest emission efficiency is observed when the exciting wavelength is within the Soret band, with no photoluminescence for excitation wavelengths larger of 430 nm. In contrary, the solution in 1,1,2-trichloroethane exhibit a strong photoluminescence, with a peak at slightly below the Soret band at 430 nm (cf. Fig. 3). A weak photoluminescence at around 700 nm is observed when excited in UV. The most complex fluorescent spectrum is observed for this molecule in DMF. There are four peaks in the photoluminescence spectrum at 400, 460, 545, and 650 nm (cf. Fig. 4). The most intense is emission at 545 nm. For the last studied solution in DMSO a strong photoluminescence at around 345 nm is observed and a significantly weaker one at 650 nm (cf. Fig. 5).

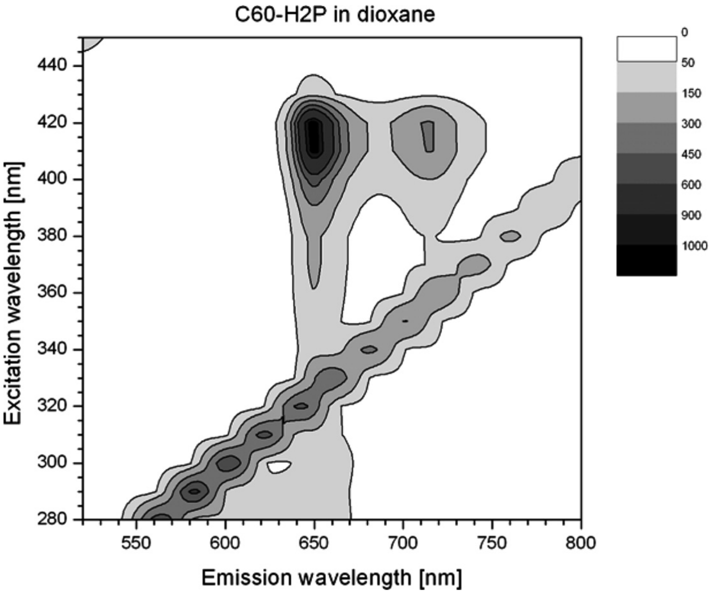


Figure 2. Photoluminescence excitation-emission map of C60-H2P in dioxane. Excitation wavelength ranges from 280 nm to 450 nm. Emission region shown from 520 nm. Any detectable signal was measured below this wavelength.

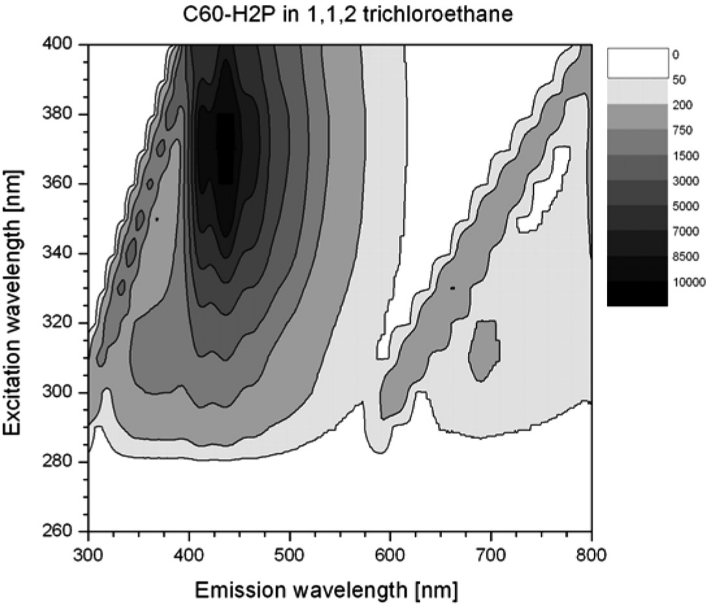


Figure 3. Photoluminescence excitation-emission map of C60-H2P in 1,1,2-trichloroethane. Excitation ranges from 260 nm to 400 nm.

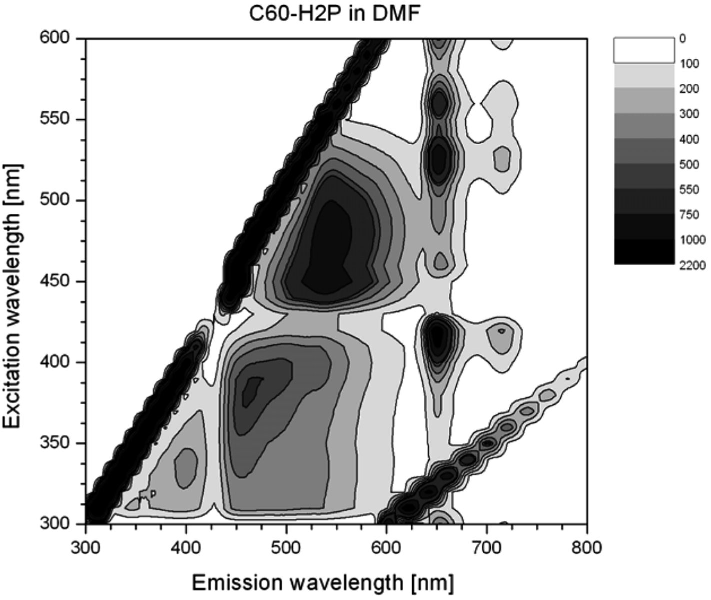


Figure 4. Photoluminescence excitation-emission map of C60-H2P in DMF. Excitation ranges from 300 nm to 600 nm.

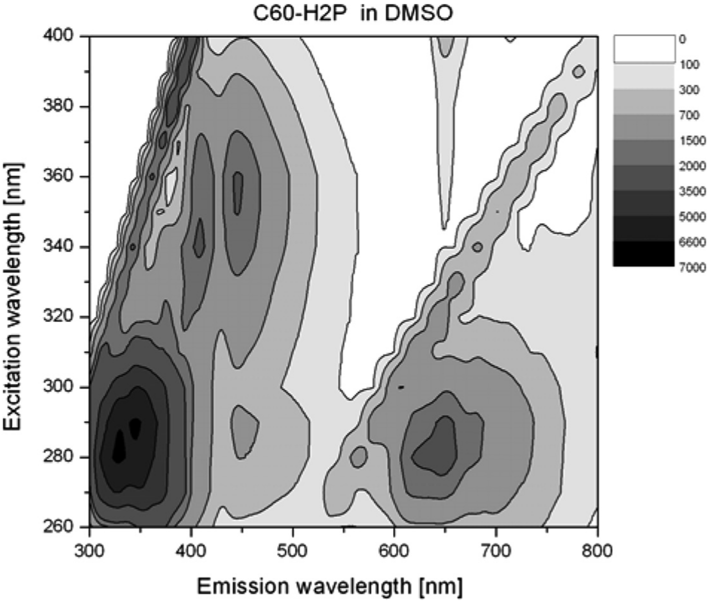


Figure 5. Photoluminescence excitation-emission map of C60-H2P in DMSO. Excitation ranges from 260 nm to 400 nm.

Photoluminescence in [C60-ZnP]$^+$I$^-$

Because of the limited solubility the photoluminescence of the iodide salt [C60-ZnP]$^+$I$^-$ was studied in toluene and in DMF only. In toluene the photoluminescence spectrum exhibit two relatively weak peaks at 420 and 710 nm (cf. Fig. 6), respectively. In fact the position of the first peak exhibits a red shift when the energy of exciting photons is decreasing and depends on their enrgy. Emission intensity at 710 nm depends on the wavelength too and is the largest one with the UV excitation. Smilarly as in the case of C60-H2P a complex photoluminescence spectrum is observed in DMF (cf. Fig. 7). There vare two strong emission bands located around 610 and 650. However there is a gap in the excitation spectrum between 440 and 480 nm. Another, weaker band, is present when the excitation takes place within the Soret band.

A common feature in all spectra is the presence of nearly excitation wavelength independent peak at about 650, with a difference concerning photoluminescence in DMF solution. The 650 nm and 710 nm peaks are visible only if the sample is excited at one of the absorption peaks. When sample was excited elsewhere, the photoluminescence spectrum changes dramatically. All these observation proves that C60-H2P strongly interact with the surrounding solvent environment. An exhausting explanation of recorded spectra needs however, further studies. It confirms the already observed solvatochromism in linear absorption spectra [1]. It shows also that this molecule may be interesting for second order NLO.

The dependence of photoluminescence on environment was already reported by Sapunov [11].

As already mentioned, the solubility of the iodide salt zinc porphyrin [C60-ZnP]$^+$I$^-$ is significantly smaller than of the compound therefore only a limited study was possible.

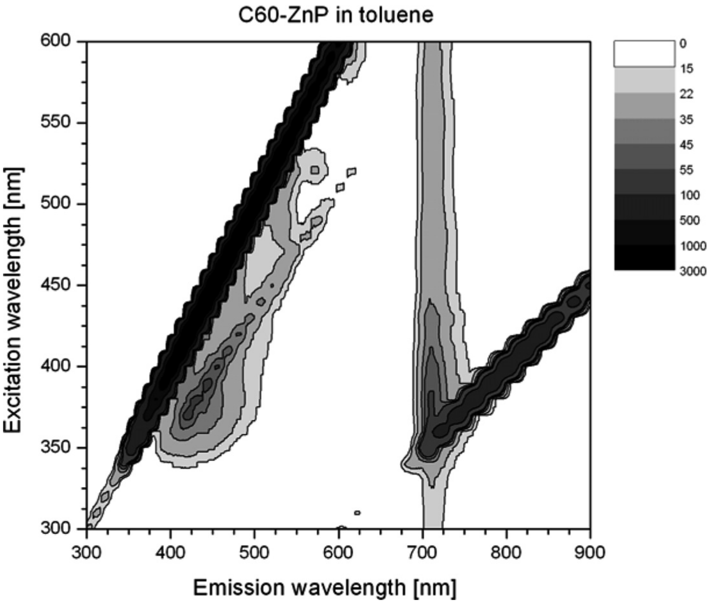


Figure 6. Photoluminescence excitation-emission map of the iodide salt [C60-ZnP]$^{+}$I^{-} in toluene. Excitation ranges from 260 nm to 400 nm.

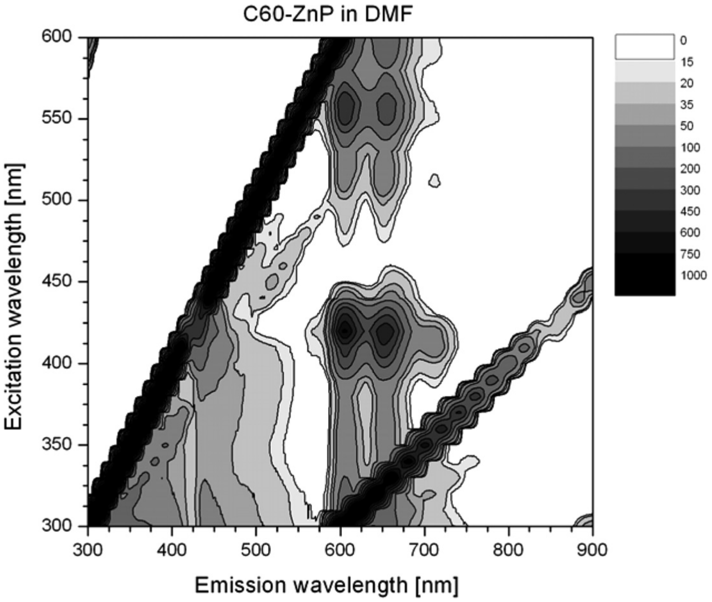


Figure 7. Photoluminescence excitation-emission map of the iodide salt [C60-ZnP]$^{+}$I^{-} in DMF. Excitation ranges from 260 nm to 400 nm.

The common feature of all observed spectra were emission lines at ca. 650 nm and 700 nm of varied intensity or sometimes in certain solvents even collapsed. Porphyrine [12] and native fullerene. photoluminescence at the same time cover this band. Effects like that have already been mentioned in numerous similar dyads. More intriguing is emission between 300 nm and 500 nm, which strongly depends on solvent polarity and excitation. This phenomenon requires however, a more detailed study.

Electro-Optic Kerr Effect Studies

The electro-optic Kerr effect, discovered by John Kerr in 19 teen centaury [13]. address the medium refractive index variation under the applied low frequency (Ω) (or constant) electric field E, which varies quadratically with its strength

$$\Delta n = \lambda s E^2 \tag{1}$$

where λ is the wavelength of the propagating beam and r is the electro-optic Kerr effect coefficient. Kerr has done the observation in an isotropic medium (isotropic liquid). In a crystal or any anisotropic medium the EO Kerr coefficient is a fourth rank 3D s_{ijkl} tensor with 81 components. Due to the material symmetry components these number is strongly reduced. In specific experiments, choosing adequately direction of the electric and optical fields some tensor components may be selected, contributing to the refractive index variation. In fact, the variation of the medium refractive index can is a result of the variation of its polarization. In the general case the ith component of medium polarization is given by

$$\mathrm{P_I}(\omega, \Omega, \mathrm{E}_\Omega, \mathrm{E}_\omega) = P_I + \varepsilon_0 \left\{ K_1 \chi^{(1)}_{IJ} E_J + K_2 \chi^{(2)}_{IJK} E_J E_K + K_3 \chi^{(3)}_{IJKL} E_J E_K E_L + \cdots \right\} \tag{2}$$

where Einstein's notation is used, $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$ are, respectively, the linear, the quadratic and the cubic susceptibilities of the medium, $\mathrm{P_I}$ is the Ith component of permanent polarization, $\mathrm{K_I}$ are coefficients arising from conventions and degeneration in the frequencies (see e.g., Rau *et al.* [14].)

$$E_I = E^I_\Omega \cos \Omega t + E^I_\omega \cos \omega t \tag{3}$$

where ω and Ω are frequencies of the propagating wave and of the applied external field, respectively.

Limiting to isotropic, media, as it is the case of measurements in solution, we have for Eq. (2) the following formula

$$\mathrm{P} \approx \varepsilon_0 \left\{ \chi^{(1)} + 3\chi^{(3)} E^2(\Omega) \right\} E(\omega) = \varepsilon_0 \left\{ n^2(E(\Omega)) - 1 \right\} \tag{4}$$

from which we can easily derive dependence of refractive index on the strength of the applied electric field

$$\Delta n = n(E(\Omega)) - n_0 = \frac{3\chi^{(3)}_{EO}(-\Omega; \omega, -\omega, \Omega)}{\varepsilon_0 c n_0^2} \tag{5}$$

where n_0 is the medium refractive index at zero field and c is the light velocity in vacuum Comparing Eq. (5) with Eq. (1) we obtain for an isotropic medium the following formula for the Kerr constant:

$$s = \frac{3\chi^{(3)}_{EO}(-\Omega; \omega, -\omega, \Omega)}{2\lambda} \tag{6}$$

The tensor $\chi^{(3)}_{EO}(-\Omega; \omega, -\omega, \Omega)$ in general contains three different contributions with different response times.

$$\begin{aligned} \chi^{(3)}_{EO}(\Omega; \omega, -\omega, -\Omega) &= \chi^{(3)}_{el}(\Omega; \omega, -\omega, -\Omega) + \chi^{(3)}_{vib}(\Omega; \omega, -\omega, -\Omega) \\ &\quad + \chi^{(3)}_{orient}(\Omega; \omega, -\omega, -\Omega) \end{aligned} \tag{7}$$

The fastest is the electronic contribution $\chi^{(3)}_{el}(\Omega; \omega, -\omega, -\Omega)$ arising from the polarization of electronic cloud. Significantly slower are vibronic $\chi^{(3)}_{vib}(\Omega; \omega, -\omega, -\Omega)$ and orientational $\chi^{(3)}_{orient}(\Omega; \omega, -\omega, -\Omega)$ contributions. The last contribution depends on the size of molecule. It can be very fast, as it was observed e.g., in CS_2 [15,16] or very slow in the case of large molecules. In fact in his pioneering work Kerr observed only the orientational part of $\chi^{(3)}$. The measurements of electronic and vibronic contributions were possible only after invention of powerful and monochromatic light sources which are laser. Orientational contribution is usually very large and can be measured with relatively low intensity monochromatic light source. Here we expect that the orientational contribution $\chi^{(3)}_{orient}(\Omega; \omega, -\omega, -\Omega)$ is largely prevailing.

Experiment

The bexperimental setup used in electro-optical Kerr effect measurements is shown schematically in Figure 8. It consists of a cw laser. It consists of a cw laser emitting a monochromatic collimated light, polarizer, Soleil-Babinet compensator, thermostated sample holder, analyzer, photomultiplier (PMT), alternating voltage source, lock-in amplifier and osciloscope. The sample is placed between two ITO coated glasses (semi transparent electrodes). Polarization planes of the polarizer and the analyzer are orthogonal and make an angle of 45° with the vertical direction.

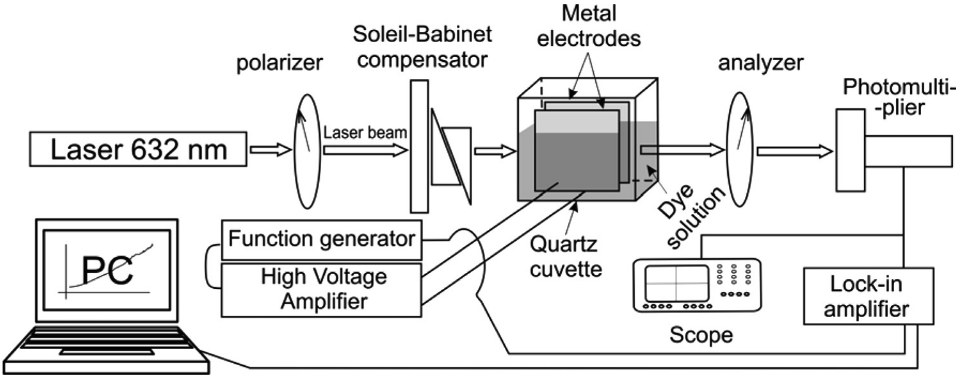


Figure 8. Schematic representation of the experimental setup used for electro-optic Kerr effect measurements.

The Soleil-Babinet compensator introduces a phase shift between components of of the optical electric of probing laser beam parallel and perpendicular to the applied electric field. To break the symmetry, the sample is twisted vertically by 45°. The largest modulation signal is observed when the convenient phase difference between these components is $\pi/2$ or $3\pi/2$ [17]. Such choice offers also a simple dependence between the AC field amplitude, the induced phase difference and the modulation amplitude at 2Ω frequency of the probing beam intensity (further referred as the EO Kerr signal) [18]. It simplifies significantly the determination of the EO Kerr constant s (cf. Eq. (1)).

In the present study we used the electro-optic Kerr effect mainly as a diagnostic tool to study the mobility of these big molecules in solution. Therefore the knowledge of exact value of the Kerr constant is not as important as we were interested only in its relative variations.

External Electric Field Dependence

First of all we have checked the dependence of the EO Kerr signal on the applied external field, which is shown in Figures 9 and 10 for the iodide salt $[C60\text{-}ZnP]^+I^-$ in toluene and the porphyrin C60-H2P in dioxane, respectively. The choice of solvent was dictated by the solubility of molecules. Dioxane as an nonpolar solvent was preferred when it was possible. First of all we observed the quadratic dependence of the EO Kerr signal on the applied AC field, it is shown in Figures 9 and 10. For C60-H2P, due to a better solubility, we were able to measure the concentration dependence of EO Kerr signal, which is shown in Figure 10. As it is easily seen the EO Kerr signal doesn't scale linearly with it. The reason for that is most likely the mentioned already aggregation of these molecules, which dependes obviously on concentration.

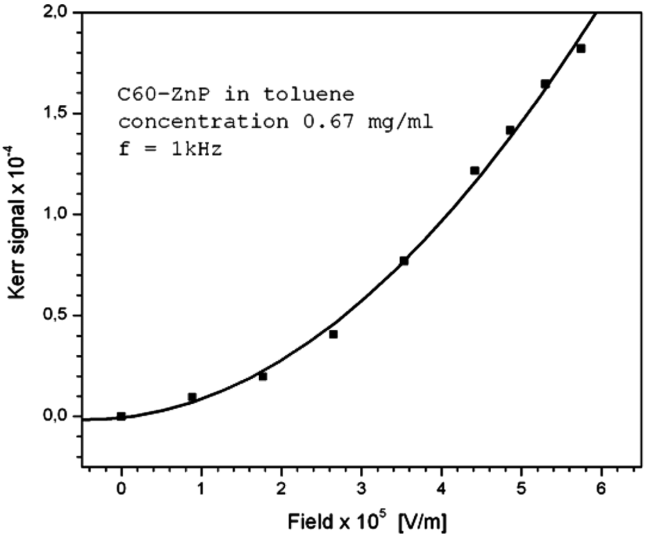


Figure 9. External electric field dependence of EO Kerr signal for $[C60\text{-}ZnP]^+I^-$ in toluene. The solute concentration is of 0.67 mg/ml. Solid line show a parabolic curve fit whereas squares are the measured values. The frequency of external field is of 1 kHz.

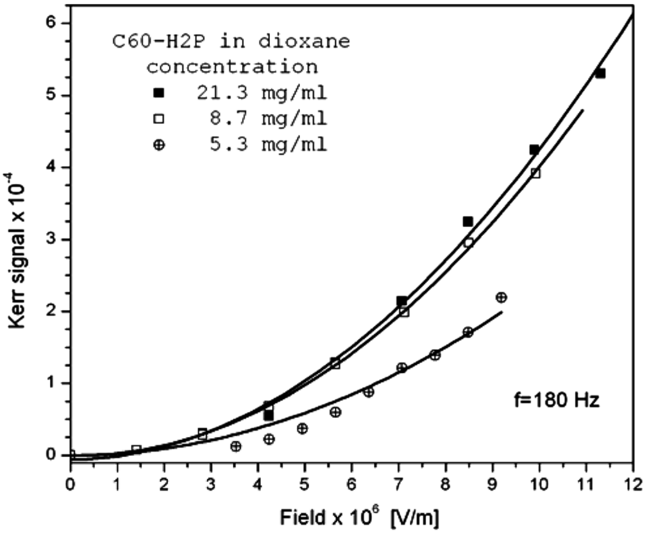


Figure 10. External electric field dependence of EO Kerr signals for two concentrations of C60-H2P in dioxane: 5.3 mg/ml and 8.7 mg/ml. Solid line show a parabolic curve fit whereas squares are the measured values. The frequency of external field is of 180 Hz.

Frequency Dependence

The frequency dependent measurements in EO Kerr effect give information about the rotational mobility of molecules. Figure 11 shows such a dependence for three concentrations of C60-H2P in dioxane. Three observations can me made here:

(i) There is a maximum in EO Kerr signal at very low frequency of the applied electric field, i.e., about 10 Hz. This result can be interpreted as corresponding

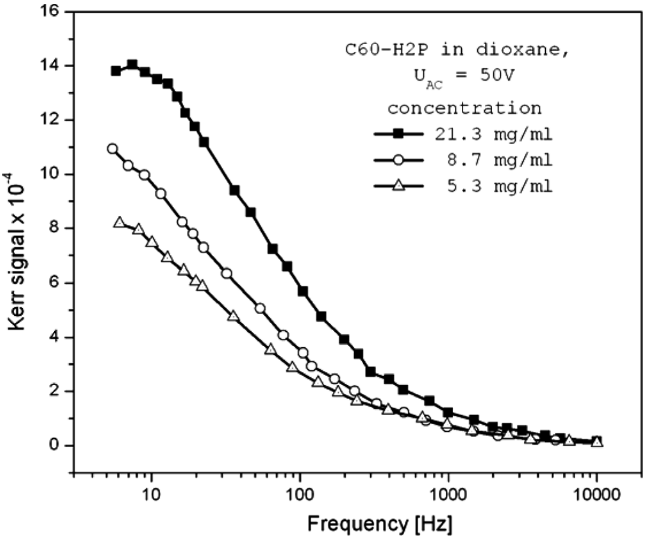


Figure 11. The observed external field frequency dependence of EO Kerr signal for three solution concentrations of C60-H2P in dioxane: 5.3 mg/ml, 8.7 mg/ml and 21.3 mg/ml.

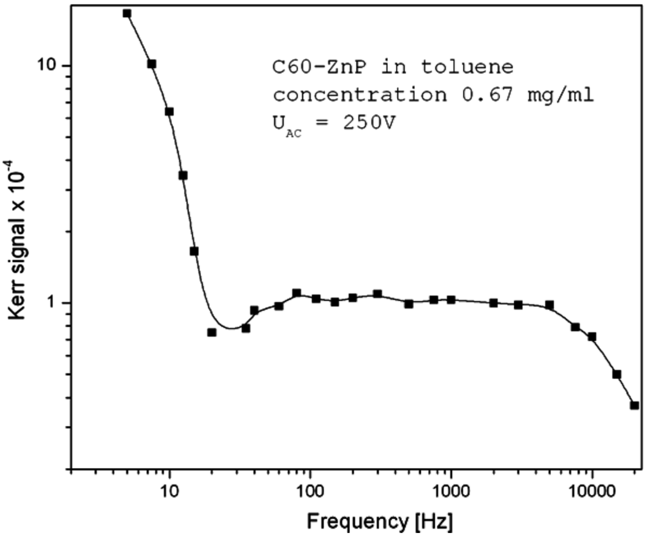


Figure 12. The observed external field frequency dependence of EO Kerr signal for [C60-ZnP]$^+$I$^-$

to the frequency of rotation of this molecule. Its very low value is not strange considering the form and the size of these molecule.

(ii) The EO Kerr signal for a given frequency doesn't follow the concentration, as we already discussed. It confirms the already discussed phenomenon of aggregation of these molecules.

(iii) At higher frequencies the EO Kerr signal is the same for all studied concentrations. It means the lack of rotational contribution of individual molecules about a certain frequency limit.

In the case of the iodide salt [C60-ZnP]$^+$I$^-$ the observed frequency dependence of the EO Kerr signal is more complex than that for C60-H2P (Fig. 12). There are two distinct resonances: at low frequency, below 10 Hz, similar as in the former molecule and a broad one at higher frequencies. The second one is very broad. If the first one we can attribute to the individual molecules, in analogy to C60-H2P, the second one, very broad, arises most likely from the aggregates.

Conclusions

The photoluminescence and the EO Kerr effect were studied in solution for two C60 complexes with porphyrin: C60-H2P and an iodide salt [C60-ZnP]$^+$I$^-$.

Both molecules are photoluminescent, however the strength and the spectrum of photoluminescent depend on the excitation wavelength and on the solvent used.

The EO Kerr effect study shows that both molecules rotate slowly under the applied electric field. In the case C60-H2P a broad rotation speeds distribution is observed with a maximum at the frequency of about 10 Hz. In the case of the iodate salt [C60-ZnP]$^+$I$^-$ the rotation spectrum is much complex. It means that rotationas movements of these molecules in solution are complex. Possible explanation may come from the aggregation of these molecules.

The concentration dependence measurements performed for C60-H_2P sows that the EO Kerr effect signa doesn't follow linearly the solute concentration. This result can be again tentatively explained by the phenomenon of aggregation.

References

[1] Niziol, J., Prato, M., Soombar, C., Vazquez, E., Gondek, E., & Rau, I. *Mol. Cryst. Liq. Cryst., this issue*.

[2] Imahori, H. & Fukuzumi, S. (2004). *Adv. Funct. Mater.*, *14*, 525.

[3] Tang, C. W. & VanSlyke, S. A. (1987). Organic electroluminescent diodes. *Appl. Phys. Lett.*, *51*, 913.

[4] Nalwa, H. S. (Ed.). (2008). *Handbook of Organic Electronics and Photonics*, ASP: Vol. 3, ISBN 1-58883-098-5.

[5] Polo, C. F., Frisardi, A. L., Resnik, E. R., Schoua, A. E., & Batlle, A. M. (1988). *Clinical Chemistry*, *34*, 757–760.

[6] Guilbault, G. G. (1990). In: *Assay of Organic Compounds, in Practical Fluorescence*, Guilbault, G. G. (Ed.), Modern Monographs in Analytical Chemistry/3, CREC Press, Science: Boca Raton, 231–366.

[7] Lundvall, O. & Enerbäck, L. (1969). *J. Clin. Pathol.*, *22*, 704–709.

[8] Easson, Michael W., Fronczek, Frank R., Jensen, Timothy, Graça, M., & Vicente, H. (2008). *Bioorg. Med. Chem.*, *16*(6), 3191–3208.

[9] D'Souza, F., Deviprasad, G. R., & Hsieh, Yi-Ying. (1997). *Chem. Commun.*, 533–534.

[10] Bermudez, V., Capron, N., Gase, T., Gatti, F. G., Kajzar, F., Leigh, D. A., Zerbetto, F., & Zhang, S. (2000). Influencing submolecular motion with an alternating electric field. *Nature*, *406*, 608.

[11] Sapunov, V. V. (2000). *Journal of Applied Spectroscopy*, *67*, 21–25.

[12] Monti, D., Nardis, S., Stefanelli, M., Paolesse, R., Natale, C., & D'Amico, A. (2009). *Journal of Sensors*, Article ID 856053, doi:10.1155/2009/856053.

[13] Kerr, J. (1877). *Phil. Mag.*, *3*, 321; (1878). *Ibid.*, *5*, 161.

[14] Rau, I., Kajzar, F., Luc, J., Sahraoui, B., & Boudebs, G. (2008). *J. Opt. Soc. Am. B*, *25*(10), 1738–1747.

[15] Halbout, J. M. & Tang, C. L. (1982). *Appl. Phys. Lett.*, *40*, 765–767.

[16] Kalpouzos, C., Lotshaw, W. T., McMorrow, D., & Kenney, G. A. (1987). *J. Phys. Chem.*, *91*, 2028–2030.

[17] Sandalphon, G., Kippelen, B., Meerholz, K., & Peyghambarian, N. (1996). *Appl. Opt.*, *35*, 2346–2354.

[18] Niziol, J. & Kajzar, F. (2006). *Mol. Cryst. Liq. Cryst.*, *447*, 105–114.