

## Mixtures of synthetic organic dyes in a photoelectrochemical cell

Danuta Wróbel<sup>a,\*</sup>, Andrzej Boguta<sup>a</sup>, Rodica M. Ion<sup>b</sup>

<sup>a</sup> Institute of Physics, Poznan University of Technology, Piotrowo 3, 60-965 Poznań, Poland

<sup>b</sup> ZECASIN S.A. Photochemistry Department, Splaiul Independentei 202, 79 611 Bucharest, Romania

Received 19 June 2000; received in revised form 23 June 2000; accepted 21 September 2000

### Abstract

Spectroscopic and photoelectric properties of phthalocyanine (Pc), tetranaphtyloporphyrin (TNP) and merocyanine (Me) and their mixtures have been studied. Dyes dissolved in polyvinyl alcohol in dimethylsulfoxide were immersed in a semiconducting/metallic photoelectrochemical cell. Absorption, fluorescence and photoacoustic spectroscopies have been used as methods to follow deactivation pathways of radiative and non-radiative processes of excited states as a competitive processes to charge separation process. The dependence of photovoltage signal on excitation wavelength (photovoltage action spectrum), kinetics of photocurrent rise and decay in second time scale have been presented. Electric parameters of the photoelectrochemical cell with dyes (conductivity, capacitance) and their mixtures in the dark and upon illumination have been estimated. It was shown that all investigated dyes are able to generate photosignal but the values of photocurrent generated were dependent on the dye used in the experiment. The complexity of photoconversion process in the electrochemical cell fulfilled with the dye mixtures has been discussed. The presence of Me dye was found to improve TNP photovoltaic effect, whereas weak enhancement of photoeffects were observed in photoelectrochemical cell based on Me and Pc. This different tetraphenylporphyrin and Pc conversion effectiveness in the presence of Me was discussed in aspects of various mechanisms of interaction between dyes. It has been indicated that dye aggregation, energy transfer, charge recombination and other processes can lead to improvement or inhibition of the photovoltaic effects and of the conversion effectiveness depending on the composition of dyes embedded in an electrochemical cell. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Absorption; Current–voltage characteristics; Deactivation processes; Merocyanine; Light energy conversion; Phthalocyanine; Porphyrin; Photoelectrochemical cell

### 1. Introduction

Porphyrins, phthalocyanines (Pc) and merocyanines (Me) are synthetic organic dyes which can find a lot of applications in photodynamic therapy of cancer, in laser technology, as radiation power indicators and as photosensitizers in light to electric energy conversion process.

In our previous investigations [1,2] and in other papers it has been shown that some organic porphyrin dyes and their chemical analogues [3,4] can be attractive candidates for photovoltage/photocurrent signal generation when embedded in a specially constructed semiconducting/metallic electrochemical cell.

Porphyrins resemble Pc in their structure and contain four pyrrole rings linked by methine carbon bridges, whereas Pc are composed of four indole units (pyrrole ring conjugated with benzene ring). A large group of Pc and porphyrin derivatives can be chemically made by attaching the peripheral group to the outer ring of the isoindols and methine bridges, respectively. Me differ from porphyrins and Pc in its chemical structure. The differences in the molecular structure of dyes lead to the distinct photophysical properties. Porphyrin, Pc and Me are characterised by significant visible light absorption but each dye absorbs in different spectral region and covers only part of solar light spectrum. Thus the use of a mixture composed of various dyes instead of one dye will cover almost whole solar spectrum and could lead to improvement of the photovoltaic effects in an electrochemical cell and in consequence the effectiveness of solar energy conversion.

The general idea of this paper is to follow photoelectric properties of three different dyes: tetranaphtyloporphyrin (TNP) complexed with magnesium (MgTNP),

\*Corresponding author.

E-mail address: wrobel@phys.put.poznan.pl (D. Wróbel).

Abbreviations: DMSO, dimethylsulfoxide; ET, energy transfer; Me, merocyanine; Pc, phthalocyanine; TNP, tetranaphtyloporphyrin; PAS, photoacoustic signal/spectrum; PVA, polyvinyl alcohol

phthalocyanine (MgPc) and Me and their various compositions: MgPc–Me, MgTNP–Me, MgTNP–MgPc and MgTNP–MgPc–Me when dissolved in polyvinyl alcohol–dimethylsulfoxide (PVA–DMSO) solution and then embedded in an electrochemical cell. Photovoltaic signal as a function of excitation wavelength in the range of dye absorption (photovoltaic action spectrum) and kinetics of photocurrent rise and declining in the second time range were monitored. Electric parameters of systems in the dark and under illumination were determined from current–voltage characteristics. Photoelectric and electric measurements were accompanied with spectroscopic studies to follow the fate of energy absorbed by dyes. In such investigation the radiative and non-radiative processes of the dye molecule excited states deactivation as competitive processes with respect to charge separation can be followed. Absorption, fluorescence and photoacoustic spectroscopies have been used to find deactivation pathways which compete with charge separation process and to establish interaction between dye molecules (aggregation, energy transfer (ET), etc.) which can influence the effectiveness of photoconversion. The kinetics of photocurrent was found to be dependent on dye composition and possible processes leading to the improvement (or inhibition) of photoconversion in the electrochemical cell with dye mixture are discussed.

## 2. Materials and methods

MgPc and MgTNP dyes have been synthesised and their purity checked according to the methods described in [5–9]. The synthesis of Me used in this paper was described in [10]. Molecular structures of dyes used in this paper are shown in Fig. 1. Dyes were dissolved in PVA with DMSO.

Absorption spectra have been monitored with Specord 40 (Carl-Zeiss, Jena) in the range 350–800 nm. Steady-state fluorescence spectra were collected with a standard home-made apparatus for the dye — PVA/DMSO solution in quartz cuvette (in the range 450–800 nm depending on the dye). Photoacoustic measurements (in the range 350–800 nm) were done with one beam spectrometer described elsewhere [11]. One modulation frequency –12 Hz was used at the constant phase shift ( $\varphi = -80$  grad). The sample was embedded in a photoacoustic cell and the signal was detected with a very sensitive microphone. The black-body was used to correct photoacoustic spectra for device response.

For photovoltaic and photocurrent measurements dyes in PVA with DMSO (PVA/DMSO) were immersed in a sandwich-like photoelectrochemical cell constructed with semiconducting ( $\text{In}_2\text{O}_3$ ) and gold (Au) electrodes distanced with 60  $\mu\text{m}$  Teflon spacer. The scheme of photovoltaic arrangement is described in [12,13]. The following measurements have been done with automatic Potentiostat–Galvanostat (Complex 2, Poland) device: photovoltaic action spectra (the

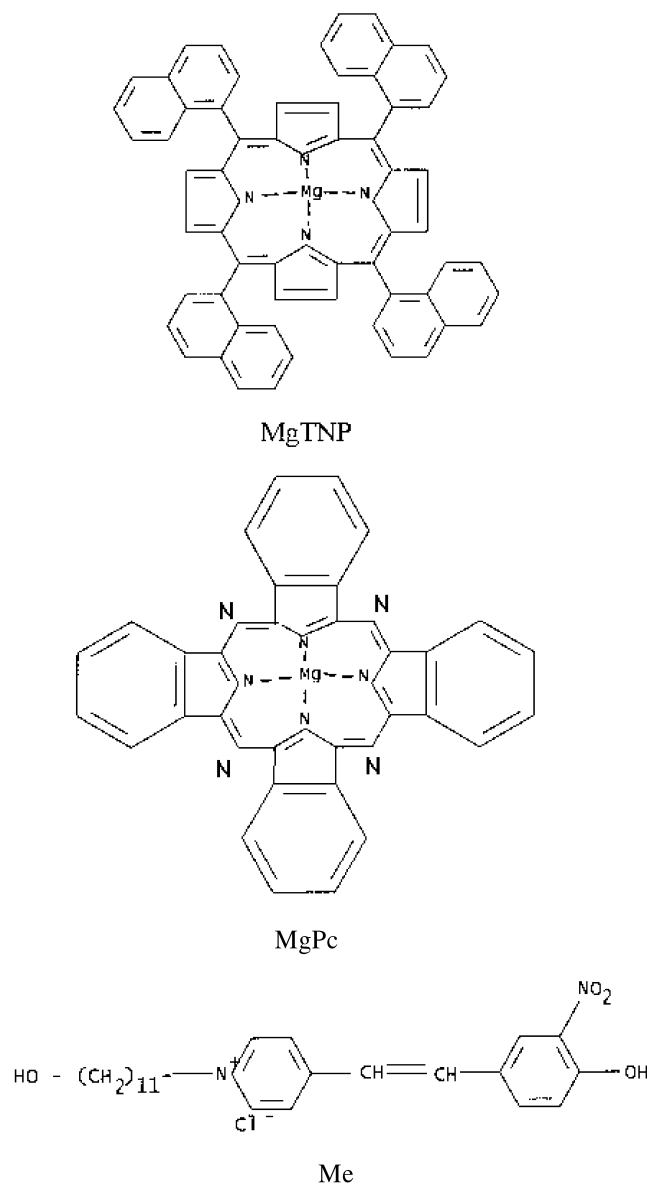


Fig. 1. Chemical structure of tetraphtylporphyrin (MgTNP), phthalocyanine (MgPc) and Me used in the experiment.

dependence of photovoltaic signal as a function of excitation wavelength), kinetics of photocurrent in the short circuit, current–voltage characteristics  $I(V)$ . Photovoltaic action spectra were corrected for a number of incident photons.

Dye concentrations were  $10^{-5}$  M for fluorescence measurements. The  $10^{-3}$  M samples were used for absorption, photoelectric and  $I(V)$  measurements in electrochemical cell. A stock solution of  $10^{-3}$  M was used for dye mixtures. The following dye mixtures in PVA/DMSO were prepared: MgTNP–Me, MgPc–Me, MgTNP–MgPc and MgTNP–Me–MgPc in various ratios: 1:1, 2:1 and 1:2 (v/v). Composition of three dyes: MgTNP–Me–MgPc was prepared from stock solution in proportion of 1:1:1 (v/v/v).

### 3. Results

#### 3.1. TNP, Pc and Me

Fig. 2 presents the absorption spectra of magnesium tetranaphthylporphyrin (MgTNP), magnesium phthalocyanine (MgPc) and Me in PVA/DMSO solution. MgTNP shows very intensive Soret band in the range of about 426 nm and less intensive Q-bands in the long wavelength region. Me absorption spectrum is very broad and is extended from about 400 to 600 nm. Two bands with maxima at 446 and 514 nm arrive. Pc is a dye whose Soret band is shifted to the short wavelength region (up to almost 350 nm — not shown) and the last band in the “red” region is clearly seen at about 671 nm. The difference between dye spectra is due to the existence of pyrrole rings and indole groups in porphyrin and Pc, respectively. Fig. 2A shows that the absorption regions of the dyes used in the experiment cover almost the spectral distribution of the visible light.

Fluorescence spectra of MgTNP, MgPc and Me shown in Fig. 2B unambiguously indicate intensive fluorescence of all dyes. Me is characterised by one broad band with maximum at 575 nm, whereas MgTNP and MgPc have two bands at 625 and 668 nm as well as at 692 and 748 nm, respectively. Moreover, the analysis of absorption and fluorescence spectra of dyes can lead to the conclusion about the possible ET process which can occur when dyes are mixed together. Following pairs as energy donors and energy acceptors can be taken into account: Me–MgPc (donor–acceptor), MgTNP–MgPc (donor–acceptor) and Me–MgTNP (donor–acceptor). Fig. 3 presents the overlapping of the fluorescence and absorption bands of mentioned dye pairs and shows in this way the most effective ET for the composition of MgTNP and Me. Otherwise rather low ET could be expected for the MgPc–Me mixture.

Photoacoustic spectra (PAS) — Fig. 2C — clearly shows that part of energy absorbed by dyes is changed into heat as a result of non-radiative processes of excited states. The comparison of absorption spectra and PAS evidently shows that thermal deactivation of Me is most effective. Some spectroscopic characterisation of Me, Pc and porphyrins is also presented in [2,14,15] but a little is found in the literature about their photothermal behaviour. The result presented in Fig. 2A–C confirms the participation of MgTNP, Me and MgPc in radiative and non-radiative deactivation processes which can influence their photoelectric properties when measured in an electrochemical cell.

Photovoltage spectroscopy (the dependence of the photovoltage signal on the wavelength — photovoltaic action spectrum) is presented in Fig. 4A. The coincidence of these spectra with absorption ones confirms that MgTNP and MgPc are able to generate photovoltage when immersed in the electrochemical cell. MgTNP shows the highest signal which reaches the value of 1474  $\mu\text{V}$ , whereas MgPc is much less effective in photoconversion and shows only photovoltage of 245  $\mu\text{V}$ . This observation has been confirmed

by kinetics of photocurrent rise and declining in second time scale as shown in Fig. 4B–D. All photocurrent signals are recalculated taking into account numbers of incident photons and they can be compared directly one to each other. Moreover, the highest photocurrent was obtained in the electrochemical cell with MgTNP and it reaches almost 100 nA, the twice lower signal is observed for MgPc and Me gives very low, noisy signal which approaches merely 10 nA. For other porphyrins with metal incorporated in the core and dissolved in liquid crystal and monitored under the same condition the photocurrent signal was found to reach value of ca. 40 nA [1–3,15]. In the paper dealing with other types of Me this value was found to be ca. 1 nA [16]. Photocurrent measurements have been performed with white light as a source. It allows us to compare the results of photocurrent generation for only one dye in the electrochemical cell with those for the dye mixtures.

Current–voltage characteristics are shown in Fig. 5 for investigated dyes in the electrochemical cell in the dark and after illumination. The character of the I(V) loop for MgTNP and MgPc is as expected and found previously in our previous papers for porphyrins in nematic liquid crystal [1,2]. The I(V) dependence for Me differs very markedly from that obtained for other dyes studied. On the basis of the results presented in Fig. 5 electric parameters: conductivity and capacitance have been determined and data are gathered in Table 1. As seen after illumination the electric parameters of the electrochemical cell are changed — the conductivity and capacitance slightly increase for MgTNP and MgPc what can indicate difference in distribution of charges due to charge separation process upon illumination and it can suggest that dyes can play the role of electron donors. Opposite behaviour is observed for Me and it shows rather the acceptor feature of this dye.

#### 3.2. Mixtures of MgPc–Me, MgTNP–Me and MgPc–MgTNP

The set of the absorption spectra of dye mixtures are presented in Fig. 6A–C for various dye concentration ratios. The intensity of each band rises or decreases depending on the concentration ratio of the dye in the mixtures. The contribution of each dye in absorption spectra is evidently seen but from the comparison of Figs. 2 and 6 the mixture absorption spectra are not ideal superposition of those for individual dyes most probably due to the creation of some aggregated forms of the dye molecules. In the case of MgPc and MgTNP mixture even the “red” band shift of MgPc in the long wavelength region of absorption spectra (Fig. 6C) is observed when compared with the MgPc analogue spectrum (Fig. 2C). It confirms the existence of some aggregated forms of dyes.

Photothermal feature of the dye mixtures are shown in Fig. 7A–C. In Fig. 7A which shows PAS for the mixture of MgPc and Me, the signal intensities in the absorption range of Me (450–555 nm) and in the “red” region of MgPc

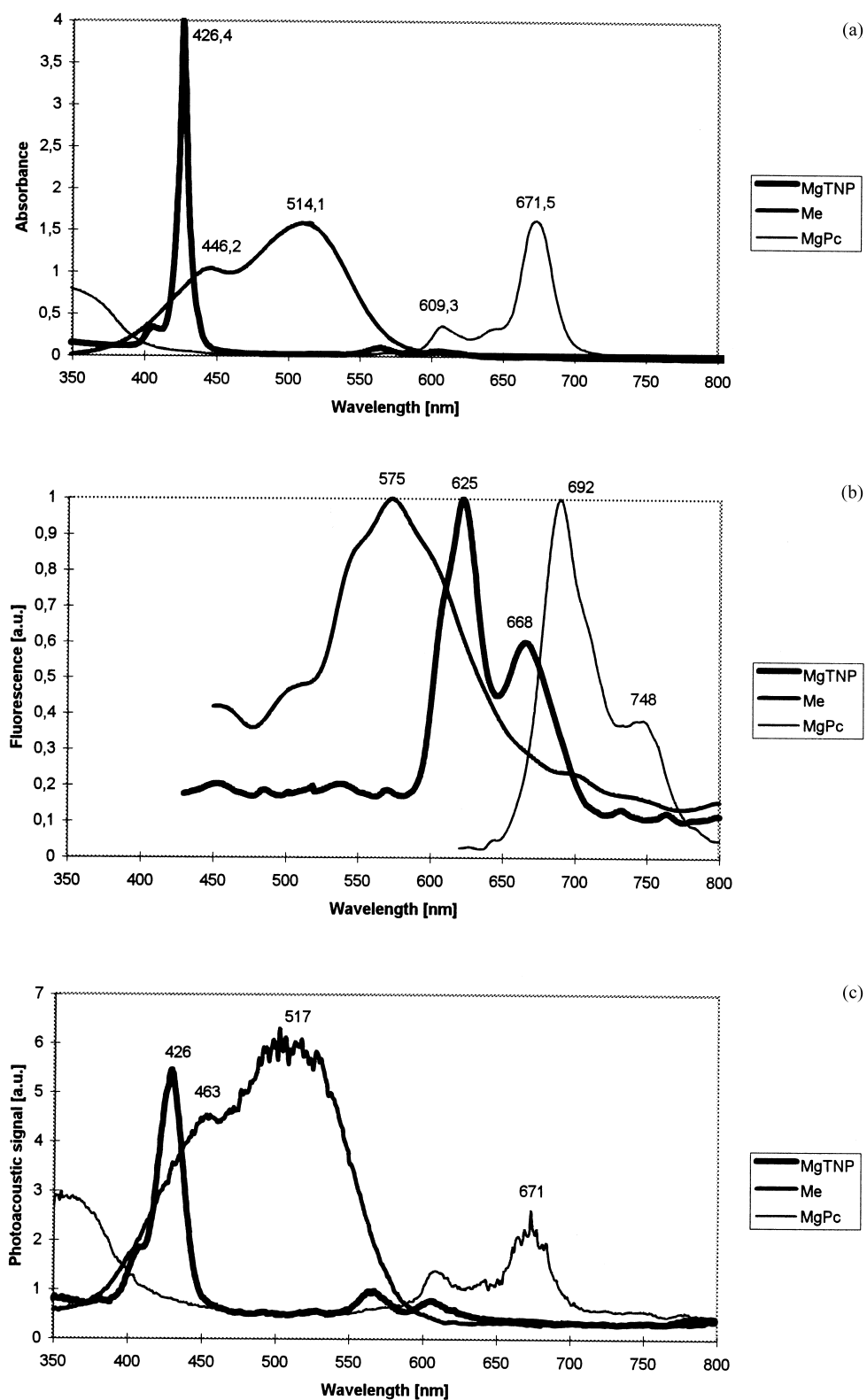


Fig. 2. Absorption (A), normalised fluorescence (B) and photoacoustic (C) spectra of MgTNP, Me, Pc-Mg.

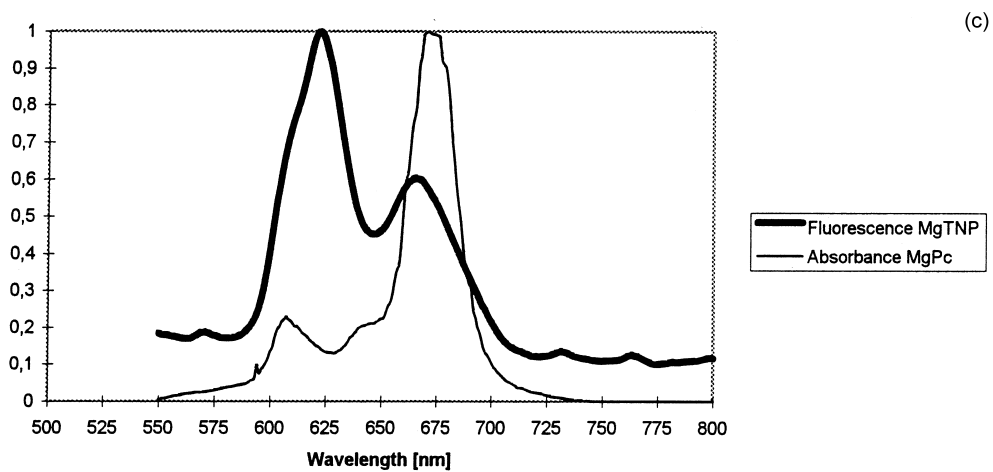
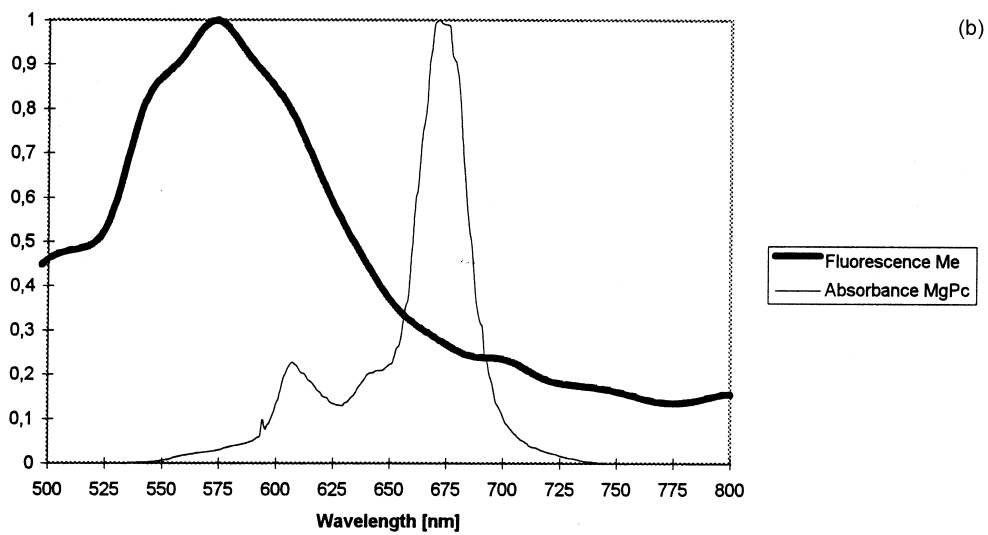
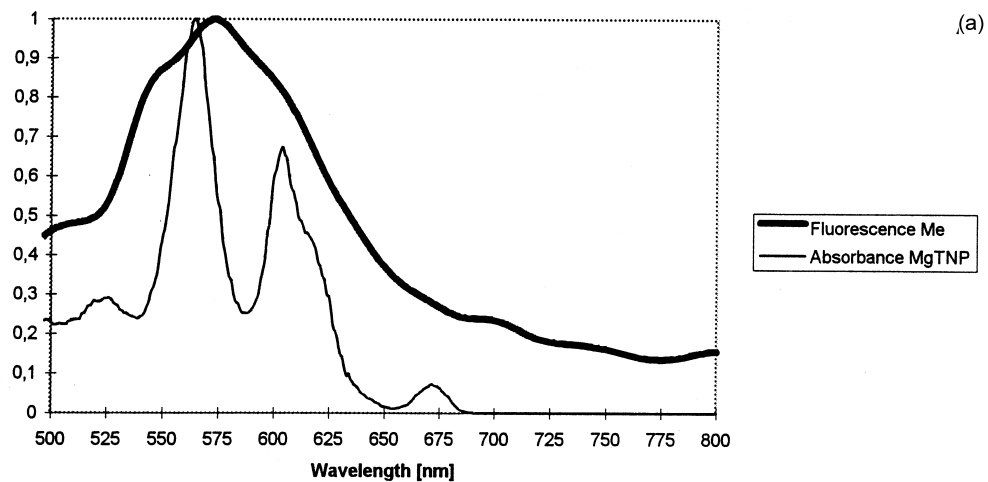


Fig. 3. Normalised absorption and fluorescence spectra of dyes mixtures.

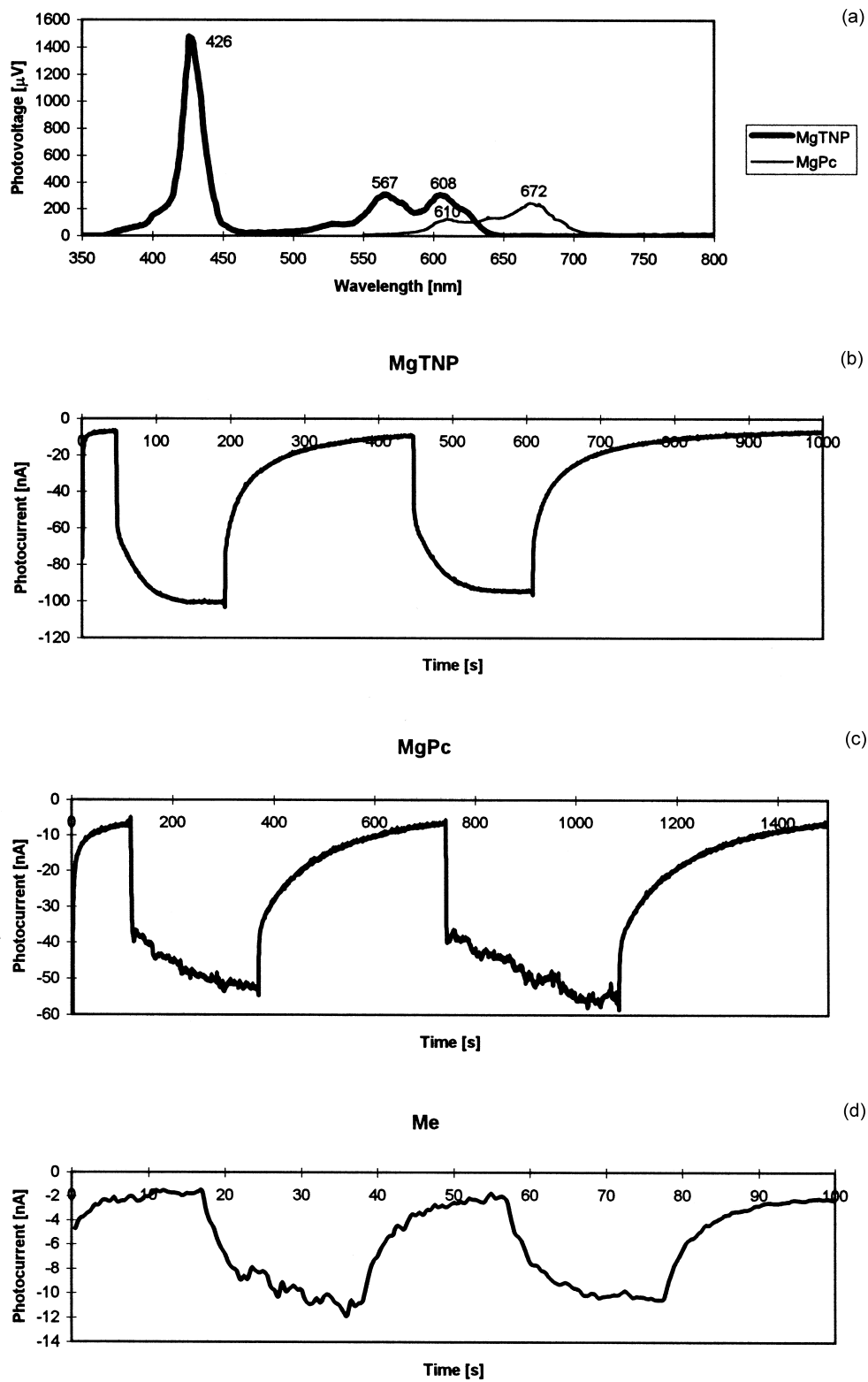


Fig. 4. Photovoltaic spectra of MgTNP and MgPc (A), and photocurrent kinetics of MgTNP (B), MgPc (C) and Me (D).

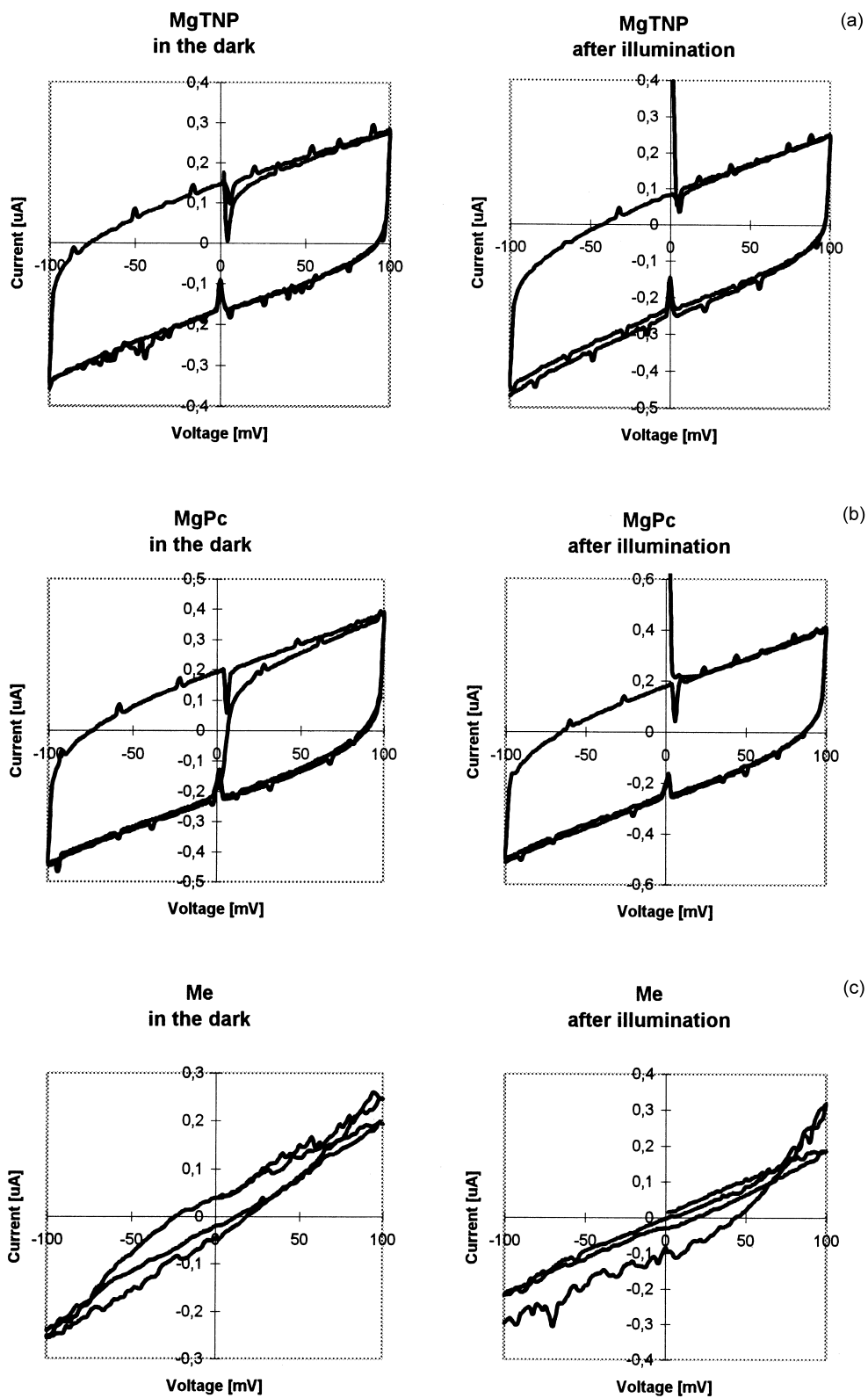


Fig. 5. Current–voltage characteristics for MgTNP (A), MgPc (B) and Me (C) in the dark (left column) and after illumination (right column).

Table 1  
Conductivity and capacitance of the electrochemical cell with dyes and their mixtures in the dark and after illumination

Dyes and mixtures	Conductivity in the dark, $\sigma \times 10^{-6}$ (1/ $\Omega$ )	Conductivity after illumination, $\sigma \times 10^{-6}$ (1/ $\Omega$ )	Capacitance in the dark, C (nF)	Capacitance after illumination, C (nF)
MgTNP	1.55	1.59	30.3	30.8
MgPc	2.26	2.61	38.7	42.1
Me	2.28	1.78	16.1	13.1
MgPc:Me, 1:1	2.15	2.13	38.4	39.7
MgPc:Me, 1:2	2.12	1.85	40.8	46.7
MgPc:Me, 2:1	2.08	1.94	34.8	37.9
MgTNP:Me, 1:1	0.98	1.47	53.0	54.3
MgTNP:Me, 1:2	1.01	1.68	30.4	30.5
MgTNP:Me, 2:1	1.26	1.66	27.9	31.2
MgPc:MgTNP, 1:1	1.85	1.68	28.7	30.7
MgPc:MgTNP, 1:2	1.89	1.37	26.0	28.9
MgPc:MgTNP, 2:1	2.34	2.22	41.5	43.6
MgTNP:MgPc:Me, 1:1:1	2.00	1.81	37.3	40.8

absorption are very similar. Low intensity of Me absorbance in the MgPc–Me mixtures (Fig. 6A) and similar PAS intensities of both dyes clearly demonstrates the high yield of thermal deactivation and domination of Me in thermal processes as it was observed for individual Me dye (Fig. 2B). This result let us to presume the weak contribution of Me in direct photovoltage generation in MgPc–Me mixtures. It is confirmed by photovoltaic spectroscopy presented in Fig. 8 (photovoltage action spectra). On the other hand the contribution of Me to thermal deactivation in the mixture of Me and MgTNP is rather low as follows from PAS (Fig. 8B) and absorption spectrum (Fig. 6B). On the basis of the fluorescence spectrum of Me and absorption spectrum of MgTNP the effective ET between Me and MgTNP can be expected. Energy transferred to MgTNP can be utilised for charge separation process. For MgTNP–MgPc mixtures the intensive participation of MgTNP in non-radiative thermal deactivation processes is clear as follows from Figs. 6C and 7C.

The results of photovoltaic action spectra are shown in Fig. 8A–C for three dye mixtures: MgPc–Me, MgTNP–Me and MgPc–MgTNP, respectively. In each spectrum of these series the signal originating from Me dye is not practically observed what confirms that this dye does not participate in the direct charge separation process including the dye mixtures. From the comparison of the photovoltaic action spectra obtained for the dye mixtures with those for the individual dyes it has been shown that MgTNP photoactivity increases and MgPc photoconversion is almost not altered in the presence of Me.

Photocurrent kinetics of the dye mixtures are illustrated in Fig. 9. In the case of MgPc (Fig. 9A) the presence of Me, influences slightly the MgPc photoactivity. Opposite result has been observed when Me is mixed with MgTNP (Fig. 9B). The intensity of photocurrent signal for MgTNP when mixed with Me increases several times with respect to individual MgTNP. In the light of our absorption and fluorescence measurements (large overlapping of Me fluorescence and MgTNP absorption) as well as from PAS results (low contribution of Me in thermal deactivation) we can suggest

very effective excitation ET from Me to MgTNP. Thanks to this process energy transferred to TNP is used by TNP for intensive photocurrent generation.

The most interesting photoelectric behaviour has been observed for the MgTNP and MgPc. Photovoltaic action spectra of these mixtures show the distinct decreasing of the signal when compared with those for individual dyes both in the region of MgTNP absorption (426 nm) and of absorption of MgPc (672 nm). The value of photocurrent generated in the electrochemical cell with MgTNP and MgPc mixture is much lower than that for individual dyes (Fig. 9C). Moreover, kinetics of photocurrent are found to be very complex and different from those for individual dyes and other investigated dye mixtures. Dissimilarity of kinetics for MgTNP with MgPc mixture when compared with other mixtures kinetics could be explained as a result of several molecular processes occurring between MgTNP and MgPc.

The data of I(V) characteristics for all mixtures are gathered in Table 1. The shapes of the I(V) loops are very similar to those presented in Fig. 5A and B for individual MgTNP and MgPc. As follows from Table 1, the conductivity of electrochemical cell with MgPc–Me decreases upon illumination, whereas conductivity for individual MgPc increases. These results indicate again that Me in the mixtures with MgPc can act as an acceptor of negative carriers. Otherwise MgTNP in the presence of Me shows rather strong donor features. The rise of the conductivity and capacitance under illumination indicates that the donor properties of MgTNP are stronger than the acceptor properties of Me. The data for MgTNP–MgPc mixtures show the increase of capacitance with the simultaneous declining of conductivity. This result indicates the fast recombination process between MgTNP and MgPc.

### 3.3. Mixtures of MgTNP–Me–MgPc

Fig. 10 shows the spectroscopic and photoelectric results for the mixture of three investigated dyes: MgTNP–Me–MgPc in concentration ratio 1:1:1 (v/v/v). The absorption



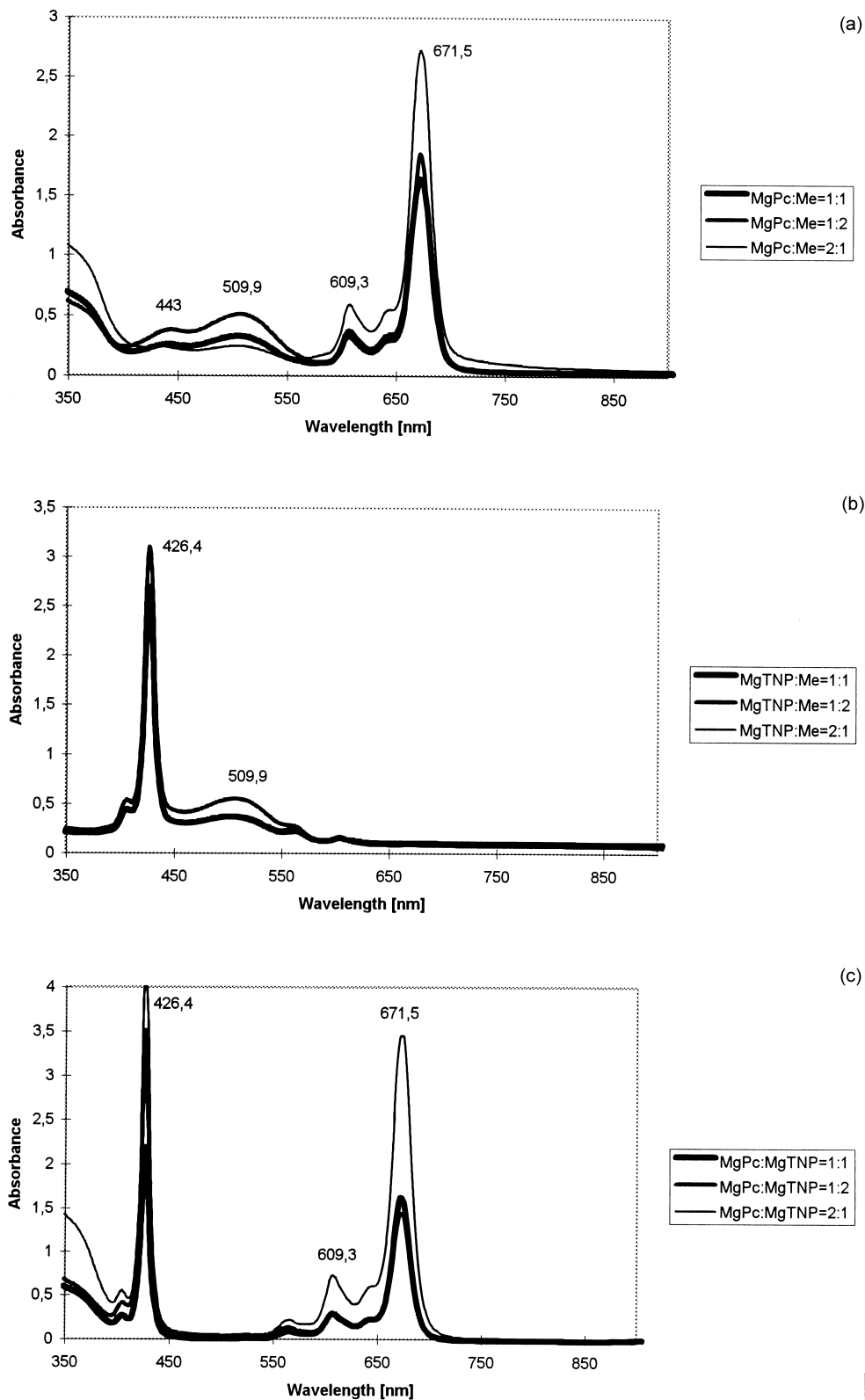


Fig. 6. Absorption spectra of dye mixtures: MgPc-Me (A), MgTNP-Me (B), MgPc-MgTNP (C) for different concentration ratios.

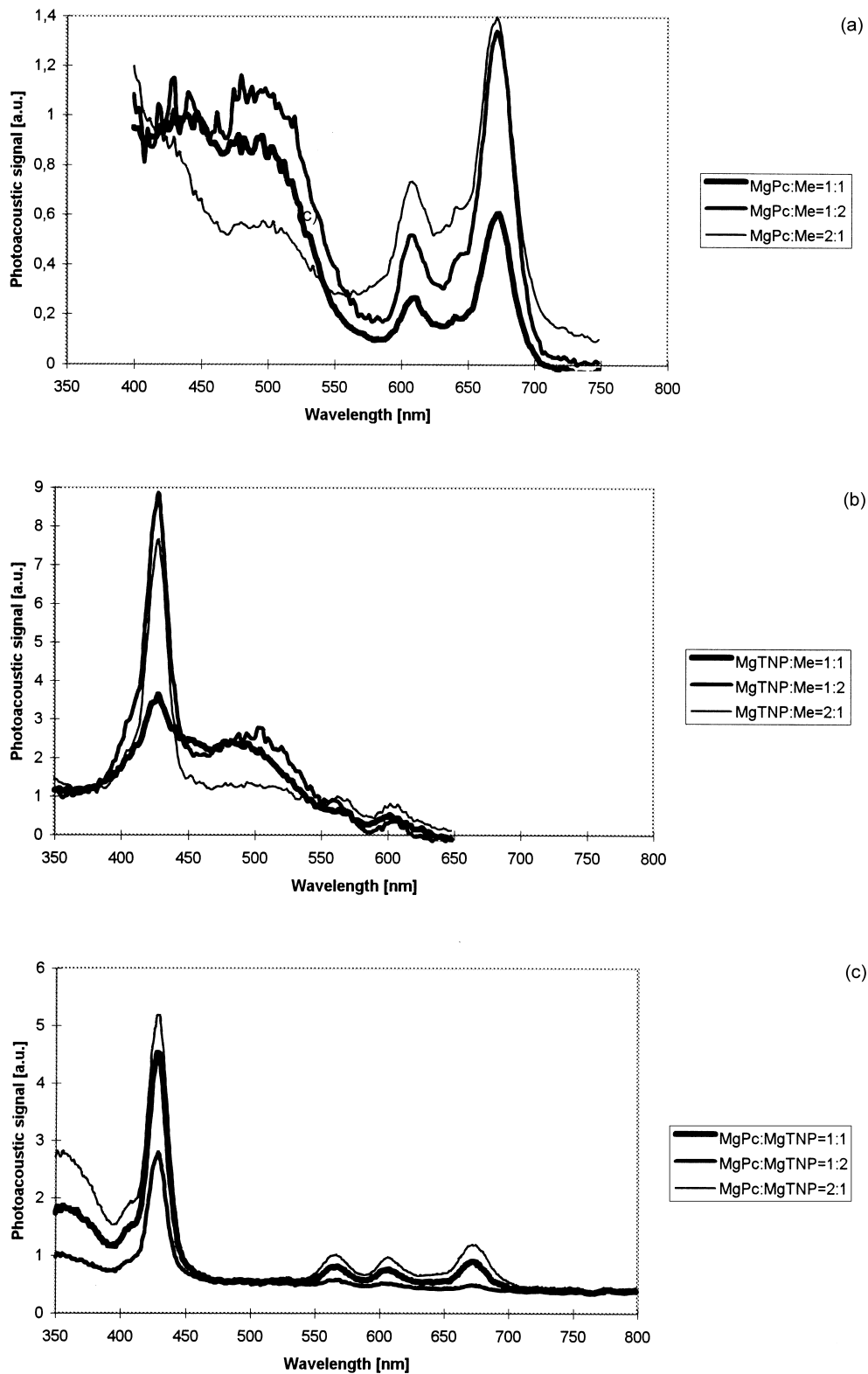


Fig. 7. Photoacoustic spectra of dye mixtures: MgPc–Me (A), MgTNP–Me (B), MgPc–MgTNP (C) for different concentration ratios.

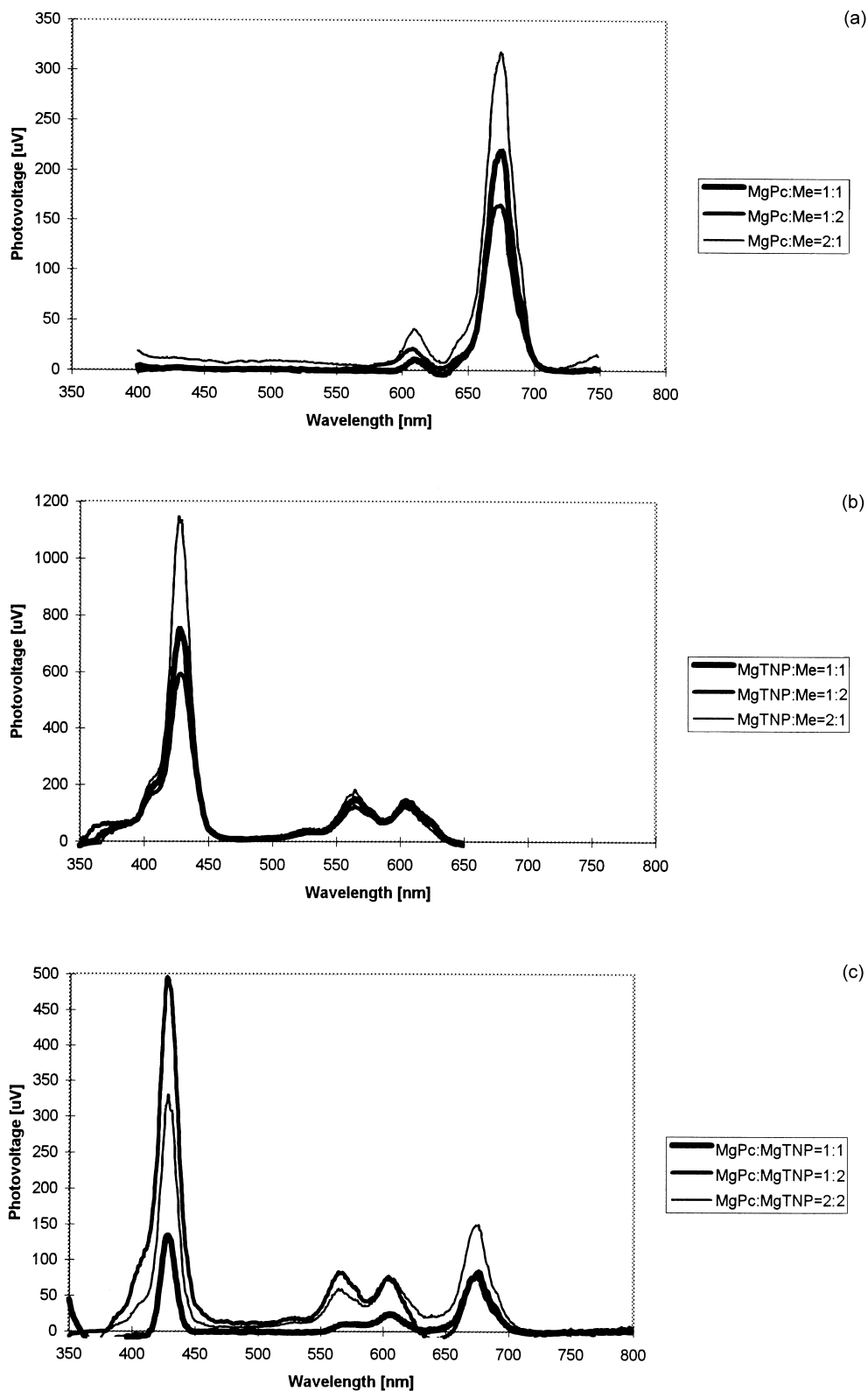


Fig. 8. Photovoltaic action spectra of dye mixtures: MgPc–Me (A), MgTNP–Me (B), MgPc–MgTNP (C) for different concentration ratios.

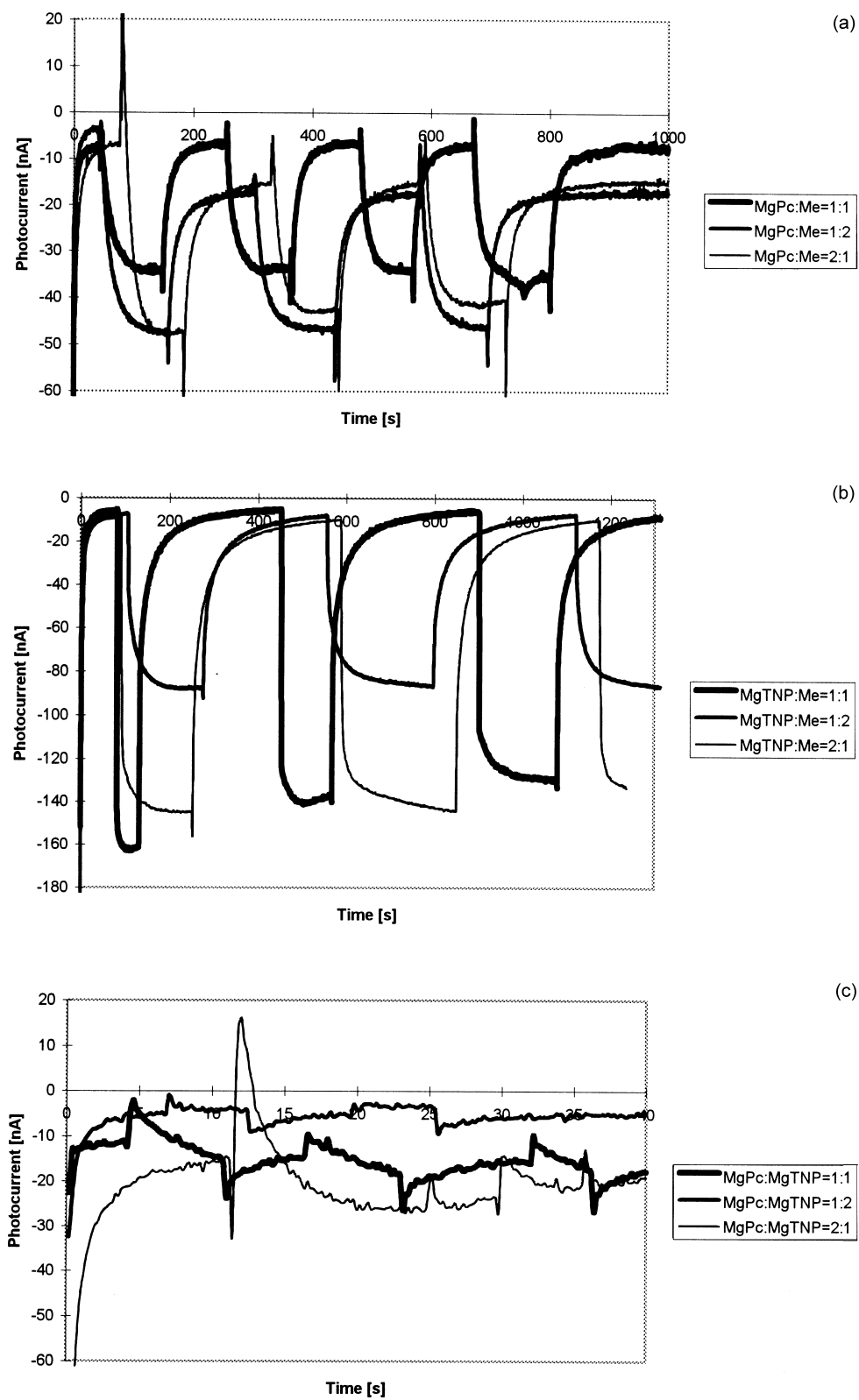


Fig. 9. Photocurrent kinetics of dye mixtures: MgPc-Me (A), MgTNP-Me (B), MgPc-MgTNP (C) for different concentration ratios.

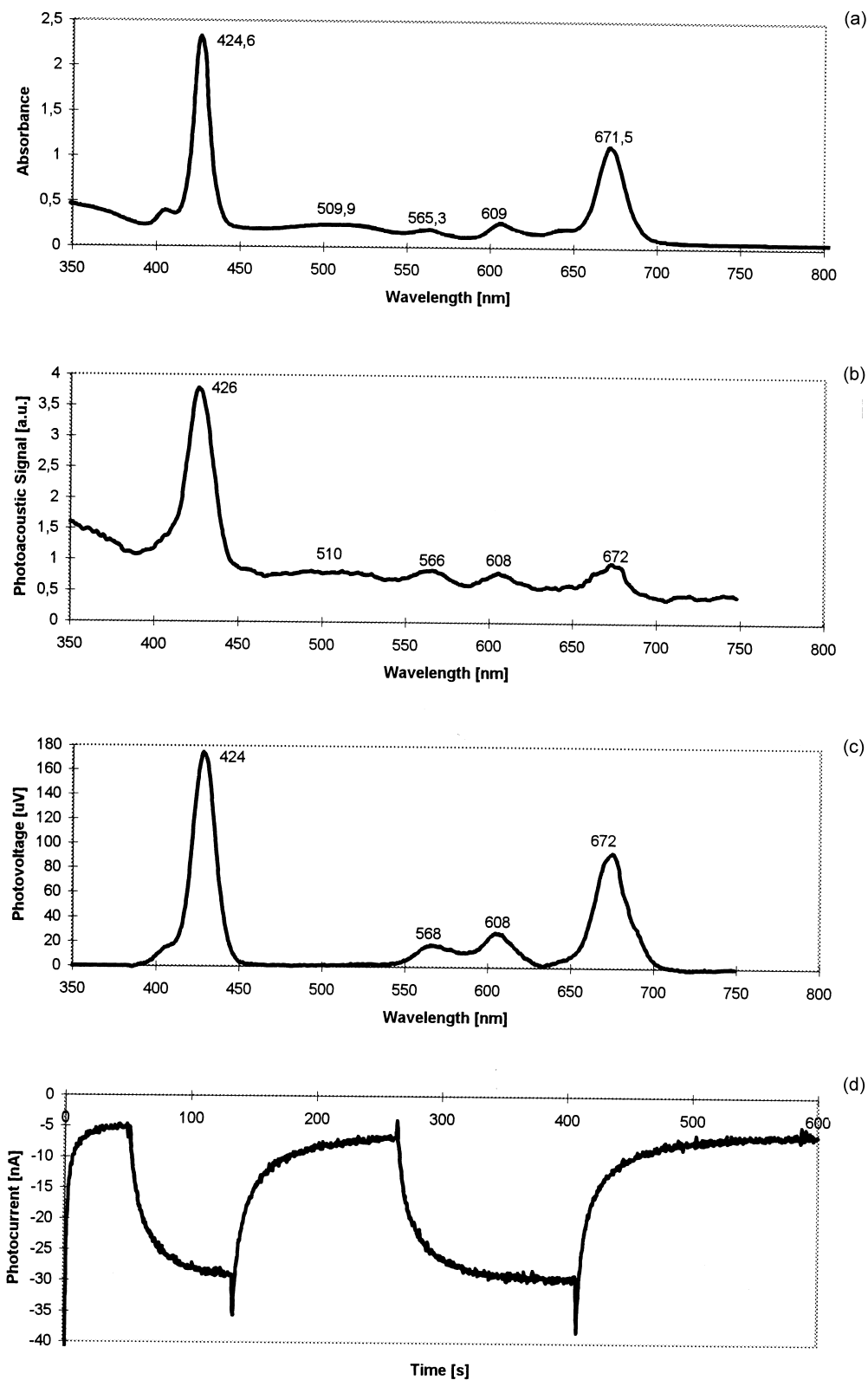


Fig. 10. Absorption spectra (A), photoacoustic spectra (B), photovoltaic action spectra (C) and photocurrent kinetics (D) for dye mixture: MgPc–MgTNP–Me (concentration ratio: 1:1:1, v/v/v).

spectra (Fig. 10A) and the photovoltaic action spectra (Fig. 10C) show the contributions from MgTNP and MgPc and confirm the participation of these dyes in photovoltage generation, whereas Me does not take part in direct photovoltage generation. Me behaviour in photovoltaic generation confirms our previous observation described in the previous chapter. Low PAS observed for Me (Fig. 10B) is due to ET to MgTNP as we have discussed for the MgTNP–Me mixture.

On the basis of the results in Fig. 10D which show the photocurrent kinetics for mixing dyes we can conclude that the mixture of the dyes: TNP–Me–Me–MgPc does not enhance the photoconversion effectiveness in the electrochemical cell. The value of photovoltage (Fig. 10C) is much lower than for individual MgTNP, Me and MgPc. Photocurrent signal of MgTNP–Me–MgPc mixture (about 30 nA) does not reach the values observed for individual MgTNP and MgPc (which are 100 and 50 nA, respectively). Thus photocurrent signal is lower than expected. This observation could be explained in the light of the possible processes occurring between dye molecules and discussed above (dye aggregation, ET and charge recombination).

#### 4. Discussion

The objective of this paper is to study organic dyes and their mixtures as photoconverters in an electrochemical cell. As we have shown above mixtures of investigated dyes have different spectroscopic properties to individual dyes. Moreover, it has been shown that the spectral behaviour of investigated dye mixtures influences strongly their photoactivities in energy conversion.

The interaction between dyes in the mixtures can lead to ET and to aggregation formation [20,21] and thus influence photocurrent generation. Such a supposition found the confirmation in our absorption/fluorescence/PAS measurements and photovoltaic spectroscopy.

On the basis of absorption and fluorescence spectra of individual dyes we can conclude on the ET process occurring between pair of dyes when they are mixed together. According to Förster theory [22] the ET efficiency depends on the mutual overlapping to the donor fluorescence and acceptor absorption spectra. The Förster radius  $R_0$  can be determined experimentally from those dye spectra in homogeneous solvent. We have used the similar procedure as was described in [23] for chlorophyll in PVA/DMSO.

For mixture of dyes examined in this paper these values are as follows:  $R_0 = 9.2, 4.4$  and  $7.1$  nm for Me–MgTNP, Me–MgPc and MgTNP–MgPc, respectively. Such  $R_0$  values (between 5 and 10 nm) are typical for numerous of organic dyes for which ET can be described by mechanism proposed by Förster [22]. The Förster radius  $R_0$  obtained for the pairs of dyes investigated in our experiment are in good agreement with those found previously in organic solvent for other porphyrin-like dyes [20,23]. In the light of our results we can conclude that the most effective intermolecular ET

operates between Me and MgTNP. On the other hand much less effective ET is expected to occur between two pairs of dyes: Me–MgPc and MgTNP–MgPc.

First we will discuss the spectroscopic and photoelectric differences between the two pairs of dyes: Me–MgTNP and Me–MgPc. The effective ET process between Me and MgTNP is supported by our PAS measurements. For Me–MgTNP mixtures very weak thermal deactivation is observed in the range of Me absorption, although individual Me exhibits efficient TD. This observation indicates that energy absorbed by Me dye is very fast transferred to MgTNP. For Me–MgPc mixtures, spectroscopic features are found to be different from those of Me–MgTNP. The results for Me–MgPc composition indicate strongly that Me takes part very actively in TD rather than in ET to MgPc as follows from absorption/fluorescence overlapping and PAS measurements.

Such a difference in spectroscopic behaviour of the two investigated mixtures: Me–MgTNP and Me–MgPc leads to the difference in photoactivity of both mixtures in photocurrent generation. In both cases Me does not participate (or very weakly) in direct charge separation process as it has been shown for individual Me when immersed in the electrochemical cell. However, when Me is in a company of a good excitation energy acceptor, energy absorbed by Me can be utilised by this acceptor for charge separation due to ET provided that Me does not lose its exceeding energy by TD. In this way Me can be indirectly involved in generation of photosignal thanks to excitation ET. Photovoltaic spectroscopy and photocurrent generation confirm such a supposition. For Me–MgTNP mixtures addition of Me to MgTNP enhances the photocurrent signal, whereas only weak or non-alternation in photosignal generation is observed in the Me–MgPc mixtures. Such a variation in Me–MgTNP and Me–MgPc mixtures photoresponses results in competition between thermal deactivation in Me and ET from Me to MgTNP. Remarkably, and in contrast to the behaviour of MgTNP in mixtures with Me, the photoelectric activity of MgTNP is altered in the presence of MgPc.

The very complex result in photocurrent creation has been found for MgTNP–MgPc mixtures. On the ground of Förster theory [22] and our experimental data ET between MgTNP and MgPc cannot be excluded. Nevertheless singlet states of MgPc excited indirectly via ET from MgTNP are de-excited in non-radiative dissipative processes as shown by our photoacoustic spectroscopy. Thus part of absorbed energy can be lost in thermal processes rather than in charge separation process. Contrary to expectation ET between MgTNP and MgPc does not increase photocurrent generation. Moreover, in all samples with MgPc the drastic jump of photocurrent was always observed under light-off and light-on conditions. This effect was also observed in the literature for native whole cells of green bacteria [13,17–19]. The sign of the jump which is called by us as a “light shock” is always opposite to the generated photocurrent. Such a complex photocurrent signal rise and declining can occur as a result of at least two

effects: very fast charge separation occurring immediately after light absorption and much slower migration of charge carriers in the electrochemical cell [17]. Moreover, charge separation process competes with fast charge recombination and the latter one can lead to decreasing of generated photocurrent. Fast recombination process in MgTNP–MgPc sample was confirmed by I(V) characteristics by simultaneous increase of capacitance and decreasing conductivity of the electrochemical cell under light illumination.

The question now remains as to the possible influence of aggregation on the photoelectric responses in the dye mixtures. A large variety of aggregates and complexes of porphyrin and Pc are known to exist and have been studied extensively in different media [24–26]. Heterodimers of charged porphyrin and Pc have been intensively examined by Agirtas et al. [26]. Some porphyrin dyes (e.g. chlorophyll, pheophitin) when dissolved in PVA/DMSO are found to form stacked forms as shown in [27]. However, in spite of using DMSO as a solvent the creation of aggregated forms of uncharged dyes at high concentration cannot be excluded. We would like to underline, however, that the structure of aggregates cannot be determined from our experiments alone. Finally we want to establish how aggregation formation can affect photocurrent generation.

We have found significant differences in the formation of MgTNP–MgPc heteroaggregates from that of either MgTNP–Me or MgPc–Me. The analysis of the difference spectra (calculated as the difference between absorption spectrum of dye mixture minus a sum of absorption spectra of individual dyes — data not shown) evidently show the existence of MgTNP–MgPc complex in the dye mixture. Almost flat difference spectra showed distinct aggregation behaviour of Me–MgPc and MgTNP–Me mixtures. The high ability of MgTNP and MgPc for aggregated complex creation could be explained by the structure of their porphyrin rings. The observation that Me creates complexed forms with MgTNP and MgPc can hardly be attributed to the weak interaction between Me chain and porphyrin rings. Otherwise porphyrin and Pc can form stacks as a result of the strong interaction between their  $\pi$ -orbitals in similar way as we have found previously for pheophitin pigment in PVA/DMSO [27].

The weak photocurrent of MgTNP–MgPc mixture can be attributed to non-radiative deactivation channels of the excited states as we have monitored by photoacoustic spectroscopy. Although ET between MgTNP and MgPc cannot be neglected, energy transferred to MgPc is lost in non-radiative dissipative processes. The competition between ET and heat dissipation depends strongly on the aggregated form formation and in consequence influence other deactivative processes. Taking into account all our results and observations it is believed that the drastic declining of photocurrent value in the electrochemical cell fulfilled with MgTNP–MgPc mixtures is due to the several processes: MgPc thermal deactivation, MgTNP–MgPc aggregation and fast charge recombination. Finally photocurrent kinet-

ics and I(V) measurements also reveal distinct behaviour for different mixtures. The rise of conductivity and capacitance under illumination indicates strong donor properties of MgTNP while Me is believed to be rather an acceptor for negative carriers.

We have therefore every reason to believe that when three dyes are together in the mixture, ET between Me and MgTNP as a process which enhances photoconversion in the electrochemical cell is not the only one which occurs. In the investigated mixture ET process is accompanied with thermal deactivation, aggregation of dyes and charges recombination which can decrease the effectiveness of photoconversion.

## 5. Conclusions

Taking into account the results presented in this paper, we can summarise and draw the following conclusions:

1. The region of light absorption by dyes is not the only criterion for effective solar energy conversion into electric energy even when dye absorption bands cover almost whole solar spectrum.
2. All dyes used in our experiments are able to generate photovoltage and photocurrent: most effectively MgTNP and Me rather ineffectively.
3. Increasing of generated photosignal in the electrochemical cell with MgTNP with Me is caused by effective ET between dyes, whereas Me does not create the increase of photocurrent when mixed with MgPc.
4. Me used in our experiment is not useful dye in photoconversion because of its high thermal deactivation which occurs to be the dominant process. Thus this dye does not participate in direct charge separation but can be useful when transfers excited energy to other dye molecules and in this way can take part in indirect charge separation process.
5. Creation of aggregated dye forms inhibits the photoconversion processes.
6. We have evidently shown that the photoelectric property studies must be accompanied with spectroscopic measurements in order to determine the way of energy deactivation of excited states of dye molecules as a competitive processes to charge separation process which determine the effective photoconversion of light to electric energy.

## Acknowledgements

The paper was supported by Poznan University of Technology, grant DPB 62–168.

## References

- [1] D. Wróbel, J. Goc, R.M. Ion, *J. Mol. Struct.* 450 (1998) 239–246.
- [2] D. Wróbel, J. Łukasiewicz, A. Waszkowiak, R.M. Ion, *J. Mol. Struct.* (2000), in press.

- [3] D. Wöhrle, *Chimia* 45 (1991) 307–310.
- [4] N. Naser, A. Planner, D. Frąckowiak, *J. Photochem. Photobiol. A* 113 (1998) 279–282.
- [5] T. Tanno, D. Wöhrle, A. Yamada, *Ber. Bunsenges. Phys. Chem.* 84 (1980) 1032–1034.
- [6] J.R. Darwent, P. Douglas, A. Harriman, G. Porter, M.C. Richoux, *Coord. Chem. Rev.* 44 (1982) 83–126.
- [7] A.D. Adler, *J. Org. Chem.* 37 (1967) 467–470.
- [8] R.M. Ion, *Rom. J. Biophys.* 8 (1998) 50–55.
- [9] R.M. Ion, A. Stîrbet, C. Mandravel, *Rev. Chim. (Bucharest)* 49 (1998) 121–127.
- [10] I. Gruda, F. Bolduc, *J. Org. Chem.* 49 (1984) 3300–3305.
- [11] D. Ducharme, A. Tessier, R.M. Leblanc, *Rev. Sci. Instrum.* 50 (1979) 1461–1462.
- [12] A. Ptak, E. Chrzumnicka, A. Planner, D. Frąckowiak, *Biophys. Chem.* 65 (1997) 165–170.
- [13] A. Ptak, A. Dudkowiak, D. Frąckowiak, *J. Photochem. Photobiol. A* 115 (1998) 63–68.
- [14] J. Goc, D. Frąckowiak, *J. Photochem. Photobiol. A* 59 (1991) 233–241.
- [15] D. Wróbel, A. Boguta, R.M. Ion, *Int. J. Photoenergy*, submitted for publication.
- [16] N. Naser, A. Planner, D. Frąckowiak, *Acta Phys. Polon.* 92 (1997) 535–542.
- [17] A. Ptak, A. Der, R. Toth-Boconadi, N. Naser, D. Frąckowiak, *J. Photochem. Photobiol. A* 104 (1997) 133–139.
- [18] D. Frąckowiak, A. Ptak, *Curr. Top. Biophys.* 21 (2) (1997) 123–129.
- [19] D. Frąckowiak, M. Romanowski, S. Hotchandani, L. LeBlanc, R. Leblanc, I. Gruda, *Bioelectrochem. Bioenerg.* 19 (1998) 371–387.
- [20] R.S. Knox, in: Govindjee (Ed.), *Bioenergetics in Photosynthesis*, Academic Press, New York (1975), pp. 183–222.
- [21] M. Kasha, H.R. Rawls, M. Ashraf El-Bayoumi, *Pure Appl. Chem.* II (1965) 371–392.
- [22] T. Förster, *Ann. Phys.* 2 (1948) 55–73.
- [23] D. Wróbel, M.A.M.J. van Zandvoort, P. Lettinga, G. van Ginkel, Y.K. Levine, *Photochem. Photobiol.* 62 (1995) 290–298.
- [24] I. Rosenthal, *Photochem. Photobiol.* 43 (1986) 691–699.
- [25] D. Wróbel, I. Hanyz, R. Bartkowiak, R.M. Ion, *J. Fluorescence* 8 (1998) 191–198.
- [26] S. Agirtas, R.M. Ion, O. Bekaroglu, *Mater. Sci. Eng. C* 7 (2000) 105–110.
- [27] M.A.M.J. Zandvoort, D. Wróbel, P. Lettinga, G. van Ginkel, Y.K. Levine, *Photochem. Photobiol.* 62 (1995) 279–289.