FULL PAPER

### Phenoxazine Dyes for Dye-Sensitized Solar Cells: Relationship Between Molecular Structure and Electron Lifetime

### Karl Martin Karlsson,<sup>[a]</sup> Xiao Jiang,<sup>[b]</sup> Susanna K Eriksson,<sup>[c]</sup> Erik Gabrielsson,<sup>[a]</sup> Håkan Rensmo,<sup>[d]</sup> Anders Hagfeldt,<sup>[c]</sup> and Licheng Sun<sup>\*[a]</sup>

**Abstract:** A series of metal-free organic dyes with a core phenoxazine chromophore have been synthesized and tested as sensitizers in dye-sensitized solar cells. Overall conversion efficiencies of 6.03-7.40 % were reached under standard AM 1.5G illumination at a light intensity of 100 mW cm<sup>-2</sup>. A clear trend in electron lifetime could be seen; a dye with a furan-conjugated linker showed a shorter lifetime relative to dyes with the acceptor group directly attached to the phenoxazine. The addition of an extra donor unit, which bore insulating alkoxyl chains, in the 7position of the phenoxazine could increase the lifetime even further and,

**Keywords:** charge transfer • dyes/ pigments • energy conversion • sensitizers • solar cells together with additives in the electrolyte to raise the conduction band, an open circuit voltage of 800 mV could be achieved. From photoelectron spectroscopy and X-ray absorption spectroscopy of the dyes adsorbed on  $TiO_2$ particles, it can be concluded that the excitation is mainly of cyano character (i.e., on average, the dye molecules are standing on, and pointing out, from the surface of TiO<sub>2</sub> particles).

### Introduction

Recently, concern for the usage of classical energy sources, such as fossil fuels, has readily increased due to environmental and long-term shortage issues.<sup>[1]</sup> Research into alternative energy sources is currently receiving extensive attention all around the world. The abundance of energy coming from the sun makes solar cells a very attractive alternative for the major sources used today. However, the production cost of the currently used crystalline silicon-based solar cells is still

- [a] K. M. Karlsson, E. Gabrielsson, Prof. L. Sun Organic Chemistry School of Chemical Science and Engineering Royal Institute of Technology (KTH) 10044 Stockholm (Sweden) Fax: +(46)8-761-2333 E-mail: lichengs@kth.se [b] Dr. X. Jiang Inorganic Chemistry School of Chemical Science and Engineering Royal Institute of Technology (KTH) 10044 Stockholm (Sweden) [c] S. K. Eriksson, Prof. A. Hagfeldt Department of Physical and Analytical Chemistry Uppsala University 75105 Uppsala (Sweden) [d] Dr. H. Rensmo Molecular and Condensed Matter Physics Department of Physics and Astronomy Uppsala University, Box 516
- Supporting information (experimental data for the synthesis of the dyes; dye loadings; and the structure of **D5**) for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201003730.

too high to be able to really compete with the conventional energy sources in the market. Dye-sensitized solar cells (DSCs) could be a very attractive choice to potentially lower production costs. A typical DSC consists of a wide bandgap semiconductor photoanode, an anchored molecular sensitizer, a redox electrolyte, and a counter electrode.<sup>[2-6]</sup> Among these components, the sensitizing dye plays a vital role in the light-harvesting efficiency (LHE). The development of new sensitizers for DSCs is very important to improve of the overall efficiency of the cell through a better understanding about the function of the cell and its limitations. During the early years of DSC research the focus was mainly on metal complexes as sensitizers. Lately more attention has been paid to metal-free organic dyes due to their high molar-extinction coefficients, easy synthesis and structural modification, as well as lesser environmental concerns compared to the heavy-metal-based complexes. So far, metal-free organic dyes show lower performance than their metal-based analogues because of lower LHE in the visible and near-infrared (NIR) regions. However, due to heavy research within this field, the metal-free organic sensitizers have now gained promising solar energy-to-electricity conversion efficiencies  $(\eta)$ . With top efficiencies reaching 10%,<sup>[7,8]</sup> the distance to the best inorganic dyes—with efficiencies of approximately 11%<sup>[9,10]</sup>—should not be unreachable anymore. Many different kinds of chromophores have been examined in DSCs (such as porphyrin,<sup>[11,12]</sup> phthalocyaindoline,<sup>[14,15]</sup> nine,[13] perylene,<sup>[16]</sup> triphenylamine (TPA),<sup>[7,8,17-22]</sup> and hetero-anthracene)<sup>[23-27]</sup> and give efficiencies in the range of 5-11%. Recently, TPA-based chromophores have gained great attention due to their potential as electron donors. We have compared the effect of different electron donors in DSCs and showed that sensitizers with a

Chem. Eur. J. 2011, 17, 6415-6424

75120 Uppsala (Sweden)



phenothiazine (PTZ) electron-donating unit gave promising efficiencies, with even better performance than the TPAbased dyes.<sup>[24]</sup> This is because the PTZ unit displayed a stronger electron-donating ability than the TPA unit (0.848 and 1.04 V vs. the normal hydrogen electrode (NHE), respectively).<sup>[28]</sup> Phenoxazine (POZ) shows similar structural and electrochemical properties to PTZ (0.880 V vs. NHE),<sup>[28]</sup> which implies that POZ could also be incorporated as a dye sensitizer. Despite this, most of the previous work has focused on PTZ as the donor.<sup>[23,26,29,30]</sup> In 2009, we published two dyes based on POZ, TH301 and TH305, which gave efficiencies up to 7.7%,<sup>[25]</sup> and the panchromatic dye TH304 with absorption into the NIR region.<sup>[27]</sup> A comparison between POZ- and PTZ-based sensitizers showed that the POZ-based dye TH301 gave an efficiency of 6.2% and the structurally similar PTZ-based T2-1 showed an efficiency of 5.5% under similar conditions.<sup>[25,26]</sup>

POZ dyes have been used in other applications, such as laser dyes,<sup>[31]</sup> indicators,<sup>[32]</sup> biological stains,<sup>[33]</sup> anticancer agents,<sup>[34]</sup> hole-transporting materials,<sup>[35]</sup> and in host–guest systems.<sup>[36]</sup>

There are some general considerations to take into account for the design of a sensitizer for DSCs: 1) strong and broad light absorption for efficient light harvesting, 2) appropriate energy levels for efficient electron injection and dye regeneration, and 3) easy and reliable synthesis with cheap, nontoxic materials suitable for future large-scale production.

An important feature of POZ is the easy structural modification on both sides of the core to tune the properties of the dye. To further evaluate the role of the POZ unit in sensitizers, a series of dyes were designed (Scheme 1) and synthesized (Schemes 2 and 3). The absorption properties can be modified by different approaches, which include extending the conjugation,<sup>[21]</sup> increasing the electron-donating abilities of the donor,<sup>[19,37]</sup> or enhancing the electron-withdrawing abilities of the acceptor.<sup>[26,27,38]</sup> By extending the conjugation with a furan ring linker (MP08) the absorption spectrum can be redshifted.<sup>[39,40]</sup> The introduction of an additional electron donor in the 7-position on the POZ (MP03, MP05) will increase the energy levels, mostly affecting the HOMO, which

will be lifted towards a more negative value to generate a bathochromic shift. The influence of insulating alkyl chains has been shown to be beneficial for the performance of the cell due to decreased aggregation, increased solubility, and surface protection that will depress the recombination of the injected electron with the oxidized dye or the redox species in the electrolyte. Therefore, a long hydrophobic chain was introduced as substituent on the POZ nitrogen atom for three of the dyes (MP03, MP08, MP13). By changing this chain for a hexyloxy-substituted benzene ring (MP05, MP12), a structure that resembles the TPA structure is obtained. This extra ring could increase the donating properties of the dye even further and, because it will not be coplanar with the POZ core, it could also decrease dye aggregation. 2-Cyanoacrylic acid was used as the acceptor and anchoring group for all the dyes. The strong electron-donating property of POZ will not only increase the energy of the HOMO significantly, but also increase the energy of the LUMO of the dye. This presents the possibility to increase the conduction band of TiO<sub>2</sub> with additives such as 4-tert-butylpyridine, to improve the voltage and total efficiency. The LUMO lifting effect is more relevant if the donor is close to the acceptor. Photoelectron spectroscopy (PES) and X-ray absorption spectroscopy (XAS) can, because of the surface sensitivity of these techniques, be used to study the binding geometry of the dye to the semiconductor surface and also to study the energy of the HOMO versus the semiconductor and unoccupied levels in the dye. In this study the best performing dye (MP05) was chosen to investigate this aspect further.

To estimate the energy levels and spectral properties of the dyes, density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were carried out for all the molecules prior to the synthesis.

### **Results and Discussion**

**Photophysical properties of the dyes**: To better understand the properties of the dyes, quantum chemical calculations were performed. The optimized geometries of the HOMO,



Scheme 1. Structures of the dye sensitizers.

6416 -

www.chemeurj.org

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

# **FULL PAPER**



Scheme 2. Synthesis of dyes MP03, MP13, and MP08.



Scheme 3. Synthesis of dyes MP05 and MP12.

LUMO, and HOMO-1 (Figure 1) show the dihedral angle between the aryl substituent on the POZ nitrogen atom and the plane of the POZ unit to be 90° (MP05, MP12). Because of this large dihedral angle, caused by steric effects, little overlap between the two  $\pi$  systems is expected, thus, the HOMO does not delocalize over the aryl substituent. A much smaller dihedral angle of about 45° is found between the POZ core and the substituent in the 7-position (MP03,



Figure 1. Frontier orbitals of the dyes, generated with an iso value of 0.02.

MP05), hence, delocalization of the HOMO over the substituent  $\pi$  system is enabled. TD-DFT calculations (Table 1) show that the first vertical transition for the dyes consists of 82–85% of a HOMO $\rightarrow$ LUMO excitation. One of the dyes, MP08, also shows a strong (oscillator strength (f)=0.87) ab-

Table 1. Calculated vertical transitions and energy levels for the different dyes.

Dye	Excited state 1		Excited state 2		Energy levels [V vs. NHE]		
	absorption peak [nm]	oscillator strength	absorption peak [nm]	oscillator strength	LUMO	НОМО	HOMO-1
MP03	504	0.41	332	0.26	-2.26	0.52	1.29
MP05	513	0.43	331	0.36	-2.36	0.37	1.23
MP08	523	0.49	366	0.87	-2.01	0.60	1.56
MP12	486	0.35	326	0.31	-2.27	0.60	1.97
MP13	473	0.33	326	0.16	-2.16	0.78	2.13

sorption peak around 350 nm. This is expected to give a higher LHE at short wavelengths compared to the other dyes. From the calculations, it is also found that dye MP08, with its extended conjugated system, has an absorption maximum at the longest wavelength of the series. Due to the small overlap between the POZ unit and N-aryl substituent in MP05 and MP12 there is very little difference in the calculated absorption spectra (Figure 2) compared to the related alkyl-substituted chromophores (MP03 and MP13, respectively). There is, however, a small redshift for these N-aryl-substituted dyes. As discussed above, substitution at the 7-position does not suffer from inefficient overlap of the  $\pi$  systems and, hence, results in redshifted absorption spectra of MP03 and MP05 versus MP13 and MP12, respectively.



Figure 2. Calculated gas-phase absorption spectra of the dyes ( $\blacksquare$ =MP03,  $\blacktriangle$ =MP05,  $\forall$ =MP08,  $\times$ =MP12,  $\bigstar$ =MP13).

The absorption spectra of the different dyes in  $CH_2Cl_2$ were measured and are shown in Figure 3; the corresponding experimental absorption data are listed in Table 2. As can be seen from Scheme 1, the alkyl-chain substituent on the nitrogen atom in MP03 is replaced by a 4-hexyloxyphenyl unit in MP05, with the intention to improve the light harvest in the visible region. However, this exchange does not make a contribution to an improved absorption property. The absorption spectrum of MP05 is slightly blueshifted compared to MP03. The same trend can be found in the comparison between dyes MP12 and MP13. Based on the above DFT study, the adverse contribution of the aryl unit is mainly due to its perpendicular relationship to the POZ

> core. This gives a poor orbital overlap, which leads to inefficient conjugation. Because the side chain located on the POZ nitrogen atom did not improve the light harvest, the modification on the 7-position of POZ was made to further investigate the effect of substitution on the absorption property of the dyes. Compared with MP13, the extinction coefficient of MP03 is distinctly increased by the introduction of a 7-(2,4-dibutoxyphenyl) unit onto the POZ and the absorption spectrum of MP03 is shifted to the longer wavelength region. Compared with



Figure 3. Absorption spectra of the dyes in CH<sub>2</sub>Cl<sub>2</sub> ( $\bullet = MP03$ ,  $\blacktriangle = MP05$ ,  $\forall = MP08$ ,  $\times = MP12$ ,  $\bigstar = MP13$ ).

Table 2. Absorption, emission, and electrochemical properties of the dyes in CH<sub>2</sub>Cl<sub>2</sub>.

Dye	Abs <sub>max</sub> <sup>[a]</sup> [nm]	$Abs_{max}$ on TiO <sub>2</sub> film <sup>[a]</sup> [nm]	$arepsilon$ $[10^4\mathrm{m^{-1}cm^{-1}}]$	Em <sub>max</sub> <sup>[a]</sup> [nm]	E <sub>(S+/S)</sub> <sup>[b]</sup> [V vs. NHE]	$E_{(0-0)}^{[c]}$ [eV]	<i>E</i> <sub>(S+/S*)</sub> <sup>[d]</sup> [V vs. NHE]
MP03	506	456	2.22	627	0.962	2.17	-1.208
MP05	500	455	2.03	625	0.967	2.19	-1.223
MP08	518	448	1.92	626	0.918	2.16	-1.242
MP12	486	451	1.98	601	1.133	2.27	-1.137
MP13	491	448	1.88	607	1.090	2.25	-1.160

[a] Absorption (*Abs*) and emission (*Em*) data of dyes in CH<sub>2</sub>Cl<sub>2</sub>. [b] The ground-state oxidation potential of the dyes was measured under the following conditions: Pt working electrode and Pt counter electrode; electrolyte, tetrabutylammonium hexafluorophosphate (0.05 m) in CH<sub>2</sub>Cl<sub>2</sub>. Potentials measured vs. Fc<sup>+</sup>/Fc were converted to potentials vs. NHE by the addition of +0.63 V. [c] 0–0 transition energy,  $E_{(0-0)}$ , estimated from the intercept of the normalized absorption and emission spectra in ethanol. [d] Estimated LUMO energies (*E*(LUMO) vs. NHE) from the difference between the estimated highest occupied molecular orbital (HOMO) energies obtained from the ground-state oxidation potential and the 0–0 transition energy,  $E_{(0-0)}$ .

MP12, MP05 also shows a redshifted absorption spectrum and enhanced extinction coefficient due to the introduction of the 2,4-dibutoxyphenyl unit. Although there is a dihedral angle between the POZ core and the 2,4-dibutoxyphenyl substituent, shown in Figure 1, the orbital overlap between the two moieties is still favorable for the absorption properties of the dyes. The effect of the addition of an electron-donating substituent in the 7-position of POZ is consistent with earlier results.<sup>[25]</sup> In addition, it was found that MP08, with a furan ring linker, shows the most redshifted and broadest absorption spectrum of all of the dyes, due to its efficient conjugation system. All dyes show relatively low extinction coefficients with values around 20000 m<sup>-1</sup> cm<sup>-1</sup>. When adsorbed onto the  $TiO_2$  film, the absorption spectra (Figure 4, < Table 2) for all dyes are blueshifted compared to those in solution (Figure 3, < Table 2). This could be an effect of dye aggregation<sup>[41]</sup> and/or deprotonation of the carboxylic acid groups upon adsorption to the TiO<sub>2</sub> surface, which decreases the strength of the electron acceptor.<sup>[42,43]</sup>

**Electrochemical study**: The electrochemical properties of the sensitizers are shown in Table 2. The oxidation potentials of these dyes were measured by cyclic voltammetry.



Figure 4. Absorption spectra of the dyes on TiO<sub>2</sub> film ( $\blacksquare$ =MP03,  $\blacktriangle$ =MP05,  $\checkmark$ =MP08, ×=MP12,  $\bigstar$ =MP13).

Chem. Eur. J. 2011, 17, 6415-6424

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

- 6419

Due to the electron-donating properties, the introduction of a 2,4-dibutoxyphenyl substituent at the 7-position of the POZ (MP03, MP05) lifts both the

7-position of the POZ (MP03, MP05) lifts both the HOMO and LUMO energy levels of the dyes relative to unsubstituted MP13 and MP12. The shift is larger for the HOMO, which results in the redshifted absorption illustrated in Figure 3, due to the smaller energy-level gap. As seen from Table 2, the excited-state oxidation potentials (LUMO levels) of these dyes are more negative than the conductionband edge (CB) of  $TiO_2$  (approximately -0.5 V vs. NHE), which means that the electrons could be efficiently injected into the TiO<sub>2</sub> conduction band from the excited dyes and simultaneously oxidized dyes are formed. The large difference between the TiO<sub>2</sub> CB and the LUMO of the dye suggests that a high concentration of additive (e.g. 4-tert-butylpyridine) in the electrolyte could be used to increase the CB to yield a higher open-circuit photovoltage  $(V_{oc})$ . On

the other hand, the ground-state oxidation potentials (HOMO levels) are more positive than the iodide/tri-iodide redox potential (0.4 V vs. NHE), which indicates that the oxidized dyes could be efficiently regenerated by the electrolyte.

Figure 5 shows the incident photon-to-current conversion efficiency (IPCE) as a function of light excitation wavelength. The onsets of the IPCE spectra increase in the order MP12 < MP13 < MP05 < MP03 < MP08, which is in good agreement with the absorption spectra for all of the dyes.



Figure 5. IPCE for POZ-based DSCs ( $\blacksquare$  =MP03,  $\blacktriangle$  =MP05,  $\forall$  =MP08, × =MP12,  $\bigstar$  =MP13).

**Photovoltaic performance**: The photovoltaic performance characteristics of DSCs based on the POZ sensitizers, under standard AM 1.5G illumination ( $100 \text{ mW cm}^{-2}$ ) are summarized in Table 3 and the current–voltage characteristics are shown in Figure 6. One can see from Scheme 1 that MP13 is the basic structure, and three different kinds of structural modification on the different positions of POZ core have been selected to examine the substituent effects on the photovoltaic performance of DSCs. First, a hexyloxy-substituted phenyl unit was introduced to replace the long alkyl chain

## **FULL PAPER**

A EUROPEAN JOURNAL

Table 3. Photovoltaic performance of DSCs based on the different dyes.

Dye	$J_{\rm sc}  [{ m mA}{ m cm}^{-2}]$	$V_{ m oc}$ [V]	Fill Factor	η [%]
MP03	14.38	0.78	0.64	7.17
MP05	13.09	0.80	0.70	7.40
MP08	14.22	0.70	0.60	6.03
MP12	10.67	0.77	0.74	6.07
MP13	12.25	0.76	0.72	6.70



Figure 6. Current-voltage characteristics of DSCs based on dyes MP03–MP13 under 100 mW cm<sup>-2</sup> AM 1.5G illumination ( $\blacksquare$ =MP03,  $\bullet$ =MP05,  $\blacktriangle$ =MP08,  $\blacktriangledown$ =MP12,  $\bullet$ =MP13).

located on the POZ nitrogen atom (MP12). It was expected that the electron reservoir of the benzene ring would contribute to better conjugation for MP12 and, hence, yield enhanced photovoltaic behavior. The photocurrent however, decreased significantly with an almost unchanged photovoltage. This is mainly due to the disadvantageous absorption properties of MP12 relative to MP13. According to the DFT study (Figure 1), the phenyl substituent is almost perpendicular to the POZ core, which leads to poor orbital overlap. As a result the benzene ring cannot be of benefit to the conjugated system. It was confirmed that the introduction of phenyl unit not only blueshifted the absorption spectrum, but also lowered the extinction coefficient (discussed above). In addition, the presence of the relatively large hexyloxy-phenyl unit decreases the dye loading on the TiO<sub>2</sub> surface (see the Supporting Information, Table S1). As a result, the photocurrent of MP12 dropped greatly due to the inefficient light harvest (Table 3). The same effect is observed on comparison of MP05 with MP03.

Because the hexyloxy-phenyl unit on the nitrogen atom was not in favor of high LHE, a 7-(2,4-dibutoxyphenyl) unit was introduced onto the POZ moiety (MP03, Scheme 1). The photovoltage of MP03-based DSCs is slightly higher than those based on MP13 (Table 3). This is probably due to the enhanced surface protection caused by the presence of a large substituent at the end of molecule, which inhibits the recombination of electrons in TiO<sub>2</sub> with oxidized species in the electrolyte to a certain extent. This can be confirmed by consideration of electron lifetime as a function of  $V_{oc}$  of the DSC (Figure 7). According to the DFT study (Figure 1), although there is a slight dihedral angle, MP03 still shows a relatively planar structure. Therefore, the electron can be



Figure 7. Electron lifetime  $(J_{sc})$  as a function of open-circuit voltage  $(V_{oc})$  for DSCs ( $\bullet = MP03$ ,  $\blacktriangle = MP05$ ,  $\checkmark = MP08$ , + = MP12,  $\bigstar = MP13$ ).

delocalized across the whole donor at the HOMO level. This increases the conjugation and strengthens the electrondonating ability of the donor in MP03. It was observed that the presence of a 2,4-dibutoxyphenyl unit in MP03 shifts the absorption maximum to the longer wavelength region and broadens the spectrum (Figure 3). At the same time, the extinction coefficient was also enhanced. As a result, the photocurrent of DSCs based on MP03 is increased greatly due to the advantageous absorption properties compared to MP13. The same trend can also be found for MP05 compared to MP12.

The effect of a linker unit on the photovoltaic performance of DSCs was also examined. It was found that MP08 shows a higher photocurrent than MP13 due to the extended conjugation system, which produces a broader, redshifted absorption spectrum and a higher extinction coefficient. However, the photovoltage of MP08-based DSCs is much lower than all the other dyes. As illustrated in Figure 7, MP08 shows quite a short electron lifetime at a certain voltage, which is mainly responsible for the lower  $V_{oc}$ . It is known that a short electron lifetime usually results from pronounced electron recombination with the electrolyte. It has been observed in previous studies that iodine has the tendency to form iodine-electron donor complexes with atoms that contain lone-pair electrons, such as oxygen, nitrogen, and sulfur. Therefore, it is possible for MP08 to form dye-iodine complexes due to the presence of the furan ring. This would cause an increased concentration of tri-iodide near the TiO<sub>2</sub> surface and subsequently result in an enhanced electron recombination compared to the dyes without a furan ring.<sup>[44-46]</sup> This problem can be avoided by the use of alternative redox systems, without iodine. It could also be an effect of the longer distance between the insulating alkyl chains and the TiO<sub>2</sub> surface, which leads to a less protected surface and hence a shorter lifetime. The extended  $\pi$  conjugation can also lead to an increased intermolecular  $\pi$ - $\pi$  interaction, which can explain the higher dye loading for MP08 (see the Supporting Information, Table S1) compared to the other dyes.<sup>[41]</sup> This extended conjugation can also enhance the charge recombination and result in a lower  $V_{oc}$ <sup>[47]</sup> These results are consistent with those pub-

# **FULL PAPER**

lished for PTZ-based dyes.<sup>[23,26]</sup> The fairly low currents measured for all of the dyes are probably a result of absorption at short wavelengths, which affects the LHE of the solar cell. For better LHE, the absorption properties of the dyes need to be improved; a broader, redshifted spectrum and also an increase in extinction coefficients are desirable. With  $J_{\rm sc}$ =13.09 mA cm<sup>-2</sup> and  $V_{\rm oc}$ =0.80 V, together with a fill factor of 0.70, MP05 is the best dye in the series, with a solar energy-to-electricity conversion efficiency of 7.4%. As a comparison, previously reported dye TH305 showed 7.3% efficiency under the same working conditions.<sup>[48]</sup>

**PES and XAS**: The performance of the DSC largely depends on the electronic and molecular surface structure. PES techniques are well-suited to study such characteristics.<sup>[49–51]</sup> PES and XAS were, therefore, specifically used in the present study to investigate the surface structure of the most efficient interface, MP05/TiO<sub>2</sub>.

Figure 8 shows the N1s spectra of MP05, measured with 758 and 535 eV photon energy. Each asymmetric spectrum can be fitted with two components that originate from the nitrogen atom in the cyano (CN) group (398.8 eV) and the nitrogen atom in the POZ group (400.0 eV), respectively.<sup>[49]</sup> When the intensities from the different peaks are compared, the ratios between the intensity of the peaks that correspond to the CN and POZ nitrogen atoms are found to be 0.31 and 0.46 at photon energies of 535 and 758 eV, respectively. Because the surface sensitivity is strongly dependent on the kinetic energy of the emitted electrons, the spectrum measured at 535 eV is more surface sensitive than the spectrum measured at 758 eV.<sup>[49,51]</sup> This indicates that the CN group is

closer to the TiO<sub>2</sub> surface than the POZ group. The ratios are similar to those of adsorbed dye D5 (see the Supporting Information for the structure of D5)<sup>[49,50]</sup> and, therefore, indicate that, on average, the molecules are aligned on the surface with the POZ group pointing out, as illustrated in Figure 9.



Figure 9. Illustration of MP05 standing on the  $TiO_2$  surface. Nitrogen atoms are highlighted in blue.

In Figure 10 (left), the valence electronic spectrum for MP05 on TiO<sub>2</sub> is shown. The contribution from the TiO<sub>2</sub> valence electronic structure is mainly located at binding energies higher than 3 eV and the spectral features observed below 3 eV are totally dominated by contributions from the dye.<sup>[50]</sup> In this outermost valence structure region, a peak positioned at 1.4 eV binding energy is observed, which originates from the HOMO-level of the dye adsorbed to TiO<sub>2</sub>. The HOMO peak measured for D5 in our earlier report is positioned at 1.6 eV and the value for N3 is about the same as for MP05.<sup>[50,51]</sup> Although the theoretical modelling dis-



Figure 8. N1s spectra measured with different photon energies. The smaller feature is from the CN group, the larger from the POZ group. When PES is used, the mean free path of the emitted electrons depends on the kinetic energy of the electrons. Therefore, measurements with lower photon energy will be more surface sensitive compared to measurements with higher photon energy.



Figure 10. Left: Part of the valence spectrum of MP05/TiO<sub>2</sub>. The HOMO level is found at 1.4 eV binding energy. Right: N1s-XAS spectrum, in which a large resonance is seen at 399.9 eV photon energy.

Chem. Eur. J. 2011, 17, 6415-6424

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

- 6421

Figure 10 (right) shows the N1s XAS spectrum of MP05 on TiO2. Two sharp resonances can be seen at 398.7 and 399.9 eV. These resonances originate from the CN unit and the structures at higher energy are from the POZ unit.<sup>[50]</sup> The XAS spectra can be used to shed some light on the nature of the excitation; this is of importance in UV-Vis absorption. There are large differences in the electronic relaxation that determines the valence- and core-excitation energies. When an electron is emitted, a core-hole potential is created and the relaxation of the occupied orbitals will, therefore, be different. When positioning the XAS spectrum by subtracting the energy of the corresponding core level this contribution partly cancels out. By using this procedure, the energy position of the valence- and core-excitations will mainly differ in how the excited electrons couple to the valence- or core-hole, respectively. The two unoccupied states with CN character were found 1.5 and 2.7 eV, respectively, from the HOMO peak. The UV-Vis absorption shows a maximum peak at 2.72 eV, which is in agreement with the XAS data. One can compare data from other dyes, in this case D5, to see relative differences. The unoccupied state at the CN moiety in D5 is located 2.8 eV from the HOMO level and the corresponding absorption peak in the UV-Vis spectrum is found at 2.6 eV. These data are measured on dry films (both D5 and MP05) but the electrochemistry is performed in solution, in which other effects have to be considered. However, the measurements support the theoretical conclusion that the absorption transition at 2.72 eV in MP05 is a charge-transfer excitation with the accepting orbital partly located at the CN moiety.

### Conclusion

A series of five metal-free organic dyes, based on the phenoxazine structure, have been synthesized. By using standard conditions, the solar cells based on these sensitizers with liquid electrolyte gave overall conversion efficiencies of 6.03-7.40%. The difference in performance could be explained by the different absorption properties and electron lifetimes for the cells. The power-conversion efficiency increased with increasing electron lifetime, which yielded higher  $V_{\rm oc}$  values. From data obtained by PES, it can be concluded that the excitation in MP05 (studied with UV-Vis absorption) is of mainly CN character. Additionally, the dye molecules are, on average, standing on, and pointing out, from the TiO<sub>2</sub> surface.

#### **Experimental Section**

Synthesis: The dyes were synthesized as shown in Schemes 2 and 3, from a commercially available phenoxazine precursor. The N-alkylation to give 1 was performed in acetone with 1-bromo-octane, NaOH, and palmityl trimethyl ammonium bromide as a phase-transfer catalyst. For the 4hexyloxyphenyl-substituted phenoxazines, MP12 and MP05, the initial arylation to give 7 followed a procedure reported by Buchwald and coworkers.<sup>[52,53]</sup> Formylation of 1 and 7 was accomplished by the Vilsmeyer-Haack reaction. Higher yields of 4 and 8 were obtained by heating the reaction mixture to reflux in CHCl<sub>3</sub> overnight, compared to heating in pure dimethylformamide (DMF).[25] Bromination of 1, 4, and 8 with Nbromosuccinimide (NBS) provided the coupling reaction precursors 2, 5, and 9 in good yield, however, for the unformylated phenoxazine 2 a mixture of mono- and dibrominated products was formed. It was possible to separate the products by chromatography, but the yield of the desired compound 2 was lower than desired. The Suzuki reactions<sup>[54]</sup> of 2, 5, and 9 were carried out with unprotected 5-formyl-2-furanboronic acid and 2,4-dibutoxyphenylboronic acid by using palladium bis(diphenylphosphino)ferrocene (Pd(dppf)Cl<sub>2</sub>) as a catalyst. The final step in the synthesis for each dye was Knoevenagel condensation of the respective aldehydes (3, 4, 6, 8, or 10) with 2-cyanoacetic acid, in the presence of piperidine. All of the dyes and intermediate compounds were characterized by NMR spectroscopy. The dyes were also characterized by HRMS. Full experimental data is provided in the Supporting Information.

General procedure for the preparation of solar cells: Fluorine-doped tin oxide (FTO) glass plates (Pilkington-TEC15) were cleaned sequentially with detergent solution, water, and ethanol in an ultrasonic bath overnight. The conducting glass substrates were immersed into aqueous TiCl4 solution (40 mm) at 70 °C for 30 min and washed with water and ethanol. The screen-printing procedure was repeated (layers  $\approx 4 \,\mu m$ ) with TiO<sub>2</sub> paste (≈18 nm colloidal particles, Dyesol LTD.) to obtain a transparent nanocrystalline film (thickness  $\approx 12 \,\mu\text{m}$ ; area = 0.25 cm<sup>2</sup>). A scattering layer (≈3 µm, PST-400C, JGC Catalysts and Chemicals LTD) was deposited and a final thickness of  $15.7\pm0.5\,\mu m$  was attained. The TiO\_2 electrodes were gradually heated in an oven (Nabertherm Controller P320) following a temperature gradient program through four levels: 180°C (10 min), 320 °C (10 min), 390 °C (10 min), and 500 °C (60 min). After sintering, the electrodes once again passed a post-TiCl4 treatment, as described above. A final sintering, at 500 °C for 30 min, was performed. When the temperature had decreased to 70 °C, the electrodes were immersed into a solution of the dye (0.2 mm) and coadsorbent, chenodeoxycholic acid, (6 mm) in EtOH (99.5%). The electrodes were left in solution for 18-19 h, in the dark, at room temperature. After adsorption of the dyes, the electrode was rinsed with EtOH. The electrodes were assembled with a platinized counter electrode by using a hot-melt Surlyn film. The redox electrolyte, which consisted of I<sub>2</sub> (99.9%, 0.04 M), LiI (99.9 %, 0.06 M), 4-tert-butylpyridine (99%, 0.4 M), and 3-hexyl-1,2-dimethylimidazolium iodide (98%, 0.6м) in acetonitrile, was introduced through a hole drilled in the back of the counter electrode. Finally, the hole was sealed with the Surlyn film.

**Photocurrent density-voltage** (*J-V*) measurements: The prepared solar cells were characterized by current-voltage characteristics and incident photon-to-current conversion efficiency (IPCE). Current-voltage characteristics were carried out with an AM 1.5G solar simulator, 300 W xenon (ozone free). The incident light intensity was 1000 W m<sup>-2</sup> calibrated with a standard Si solar cell. For the *J-V* curves, the solar cells were evaluated by using a black mask on the cell surface to avoid diffusive light (cell area = 0.25 cm<sup>2</sup>, aperture area = 0.49 cm<sup>2</sup>).<sup>[55]</sup> IPCE measurements were carried out with a computerized set-up, which consisted of a xenon arc lamp (300 W Cermax, ILC Technology), followed by a 1/8 m monochromator (CVI Digikrom CM 110). The data collection was performed with a Keithley 2400 source/meter and a Newport 1830-C power meter with 818-UV detector head.

**Photophysical measurements:** The UV-Vis absorption spectra of the dyeloaded transparent film and the dye solution  $(1 \times 10^{-5} \text{ M in CH}_2 \text{Cl}_2)$  were recorded on a Lambda 750 spectrophotometer by using a normal quartz sample cell (1 cm path length). The fluorescence spectra of the dye solu-

6422 -

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Chem. Eur. J. 2011, 17, 6415-6424

tions were recorded on Cary Eclipse fluorescence spectrophotometer at the same concentration as the UV-Vis measurement.

**Electrochemical measurements**: Electrochemical experiments were performed with a CH Instruments electrochemical workstation (model 660 A) with a conventional three-electrode electrochemical cell. Measurements were obtained from a solution of dye in CH<sub>2</sub>Cl<sub>2</sub>  $(1 \times 10^{-3} \text{ M})$  with tetrabutylammonium hexafluorophosphate (0.05 m) as the supporting electrolyte. A glass carbon disk was used as the working electrode was utilized as a reference electrode, and the scan rate used was 100 mVs<sup>-1</sup>. All redox potentials were calibrated versus a normal hydrogen electrode (NHE) by the addition of ferrocene as an internal standard ( $E^{\circ}$ (Fc/Fc<sup>+</sup>)=630 mV vs. NHE).

**Measurement of dye-loadings**: The preparation and sensitization of the  $TiO_2$  films was by the procedure described above. The adsorbed dyes were then desorbed in solution of  $(CH_3)_4$ NOH in acetonitrile (0.1 M) and the dye loading on the  $TiO_2$  film was estimated by UV-Vis absorption spectroscopy (see the Supporting Information, Table S1).

**PES and XAS**: A thin layer ( $\approx 1~\mu m$ ) of nanostructured TiO<sub>2</sub> was doctorbladed on conductive glass and heated for 30 min at 450 °C. The films were sensitized for 2 h in a dye bath of **MP05** in EtOH (0.2 mM). The PES and XAS measurements were performed by using synchrotron radiation at BL I411 at the Swedish National Laboratory MAX-Lab in Lund. The electron take-off angle was 70° and the electron take-off direction was collinear with the e-vector of the incident photon beam. The kinetic energy of the photoelectrons was measured with a Scienta R4000WALanalyzer. The N1s XAS spectra were recorded by detection of secondary electrons in partial-yield mode and were intensity normalized versus the number of incident photons. The PES spectra were energy calibrated by setting the Ti2p substrate signal to 458.56 eV.<sup>[51]</sup> The N1s XAS spectra were energy calibrated by measuring the Ti3p peak with first- and second-order light.<sup>[49]</sup>

**Molecular orbital calculations**: The structural and electronic properties of the dyes were calculated with the B3LYP hybrid functional at the 6–31G(d) level in gas phase by using the Gaussian 03 program package.<sup>[56]</sup> TD-DFT was employed at the same level to calculate the vertical transitions. The UV-Vis spectra were calculated by using the GaussSum program, revision 2.2.3, with a 3000 cm<sup>-1</sup> FWHM bandwidth.<sup>[57]</sup>

#### Acknowledgements

We acknowledge the Swedish Research Council, Swedish Energy Agency and the Knut & Alice Wallenberg foundation for financial support. We also thank Bao-Lin Lee at Stockholm University for help with the HRMS measurements and Dr. Haining Tian for the helpful discussions.

- N. Armaroli, V. Balzani, Angew. Chem. 2007, 119, 52; Angew. Chem. Int. Ed. 2007, 46, 52.
- [2] M. Grätzel, Nature 1991, 353, 737.
- [3] A. Hagfeldt, M. Grätzel, Chem. Rev. 1995, 95, 49.
- [4] A. Hagfeldt, M. Grätzel, Acc. Chem. Res. 2000, 33, 269.
- [5] M. Grätzel, Inorg. Chem. 2005, 44, 6841.
- [6] A. Mishra, M. K. R. Fischer, P. Bäuerle, Angew. Chem. 2009, 121, 2510; Angew. Chem. Int. Ed. 2009, 48, 2474.
- [7] W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F. Wang, C. Pan, P. Wang, *Chem. Mater.* 2010, 22, 1915.
- [8] G. Zhang, H. Bala, Y. Cheng, D. Shi, X. Lv, Q. Yu, P. Wang, Chem. Commun. 2009, 2198.
- [9] Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, L. Y. Han, Jpn. J. Appl. Phys. Part 2 2006, 45, L638.
- [10] M. K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru, M. G. Gratzel, *J. Am. Chem. Soc.* 2005, *127*, 16835.

- [11] W. M. Campbell, K. W. Jolley, P. Wagner, K. Wagner, P. J. Walsh, K. C. Gordon, L. Schmidt-Mende, M. K. Nazeeruddin, Q. Wang, M. Gratzel, D. L. Officer, J. Phys. Chem. C 2007, 111, 11760.
- [12] T. Bessho, S. Zakeeruddin, C. Y. Yeh, E. G. Diau, M. Grätzel, Angew. Chem. 2010, 122, 6796; Angew. Chem. Int. Ed. 2010, 49, 6646.
- [13] S. Eu, T. Katoh, T. Umeyama, Y. Matano, H. Imahori, *Dalton Trans.* 2008, 5476.
- [14] S. Ito, S. M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, M. K. Nazeeruddin, P. Péchy, M. Takata, H. Miura, S. Uchida, M. Grätzel, *Adv. Mater.* **2006**, *18*, 1202.
- [15] S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Pechy, M. Graetzel, *Chem. Commun.* 2008, 5194.
- [16] C. Li, J.-H. Yum, S.-J. Moon, A. Herrmann, F. Eickemeyer, N.G. Pschirer, P. Erk, J. Schöneboom, K. Müllen, M. Grätzel, M. K. Nazeeruddin, *ChemSusChem* 2008, 1, 615.
- [17] Y. Liang, B. Peng, J. Liang, Z. Tao, J. Chen, Org. Lett. 2010, 12, 1204.
- [18] J. H. Yum, D. P. Hagberg, S. J. Moon, K. M. Karlsson, T. Marinado, L. C. Sun, A. Hagfeldt, M. K. Nazeeruddin, M. Gratzel, *Angew. Chem.* 2009, 121, 1604; *Angew. Chem. Int. Ed.* 2009, 48, 1576.
- [19] D. P. Hagberg, J. H. Yum, H. Lee, F. De Angelis, T. Marinado, K. M. Karlsson, R. Humphry-Baker, L. C. Sun, A. Hagfeldt, M. Gratzel, M. K. Nazeeruddin, J. Am. Chem. Soc. 2008, 130, 6259.
- [20] H. Choi, C. Baik, S. O. Kang, J. Ko, M. S. Kang, M. K. Nazeeruddin, M. Gratzel, Angew. Chem. 2008, 120, 333; Angew. Chem. Int. Ed. 2008, 47, 327.
- [21] D. P. Hagberg, T. Marinado, K. M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt, L. Sun, J. Org. Chem. 2007, 72, 9550.
- [22] D. P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt, L. C. Sun, *Chem. Commun.* 2006, 2245.
- [23] W. Wu, J. Yang, J. Hua, J. Tang, L. Zhang, Y. Long, H. Tian, J. Mater. Chem. 2010, 20, 1772.
- [24] H. Tian, X. Yang, J. Cong, R. Chen, C. Teng, J. Liu, Y. Hao, L. Wang, L. Sun, *Dyes Pigm.* 2010, 84, 62.
- [25] H. N. Tian, X. C. Yang, J. Y. Cong, R. K. Chen, J. Liu, Y. Hao, A. Hagfeldt, L. C. Sun, *Chem. Commun.* 2009, 6288.
- [26] H. Tian, X. Yang, R. Chen, Y. Pan, L. Li, A. Hagfeldt, L. Sun, *Chem. Commun.* 2007, 3741.
- [27] H. N. Tian, X. C. Yang, R. K. Chen, A. Hagfeldt, L. C. Sun, *Energy Environ. Sci.* 2009, 2, 674.
- [28] X. Q. Zhu, Z. Dai, A. Yu, S. A. Wu, J. P. Cheng, J. Phys. Chem. B 2008, 112, 11694.
- [29] T.-Y. Wu, M.-H. Tsao, F.-L. Chen, S.-G. Su, C.-W. Chang, H.-P. Wang, Y.-C. Lin, W.-C. Ou-Yang, I.-W. Sun, *Int. J. Mol. Sci.* 2010, 11, 329.
- [30] S. S. Park, Y. S. Won, Y. C. Choi, J. H. Kim, *Energy Fuels* 2009, 23, 3732.
- [31] T. G. Pavlopoulos, Appl. Opt. 1997, 36, 4969.
- [32] V. H. J. Frade, P. J. G. Coutinho, J. C. V. P. Moura, M. S. T. Gonçalves, *Tetrahedron* 2007, 63, 1654.
- [33] B. C. Channu, H. N. Kalpana, G. B. Eregowda, C. Dass, P. J. Houghton, K. N. Thimmaiah, J. Pharm. Biomed. Anal. 1999, 21, 775.
- [34] N. Miyano-Kurosaki, K. Ikegami, K. Kurosaki, T. Endo, H. Aoyagi, M. Hanami, J. Yasumoto, A. Tomoda, J. Pharmacol. Sci. 2009, 110, 87.
- [35] R. Paspirgelyte, J. V. Grazulevicius, S. Grigalevicius, V. Jankauskas, Synth. Met. 2009, 159, 1014.
- [36] H. Maas, A. Khatyr, G. Calzaferri, *Microporous Mesoporous Mater*. 2003, 65, 233.
- [37] D. P. Hagberg, X. Jiang, E. Gabrielsson, M. Linder, T. Marinado, T. Brinck, A. Hagfeldt, L. C. Sun, J. Mater. Chem. 2009, 19, 7232.
- [38] T. Marinado, D. P. Hagberg, M. Hedlund, T. Edvinsson, E. M. J. Johansson, G. Boschloo, H. Rensmo, T. Brinck, L. C. Sun, A. Hagfeldt, *Phys. Chem. Chem. Phys.* 2009, 11, 133.
- [39] J. T. Lin, P. C. Chen, Y. S. Yen, Y. C. Hsu, H. H. Chou, M. C. P. Yeh, Org. Lett. 2009, 11, 97.

www.chemeurj.org

## **FULL PAPER**

### CHEMISTRY

**A EUROPEAN JOURNAL** 

- [40] R. Li, X. Lv, D. Shi, D. Zhou, Y. Cheng, G. Zhang, P. Wang, J. Phys. Chem. C 2009, 113, 7469.
- [41] K. Hara, Z.-S. Wang, T. Sato, A. Furube, R. Katoh, H. Sugihara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, J. Phys. Chem. B 2005, 109, 15476.
- [42] Z.-S. Wang, H. Sugihara, *Langmuir* 2006, 22, 9718.
- [43] M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Gratzel, J. Am. Chem. Soc. 2001, 123, 1613.
- [44] H. Tsubomura, R. P. Lang, J. Am. Chem. Soc. 1961, 83, 2085.
- [45] T. Marinado, K. Nonomura, J. Nissfolk, M. K. Karlsson, D. P. Hagberg, L. Sun, S. Mori, A. Hagfeldt, *Langmuir* 2009, 25, 2592.
- [46] B. C. O'Regan, I. Lopez-Duarte, M. V. Martinez-Diaz, A. Forneli, J. Albero, A. Morandeira, E. Palomares, T. Torres, J. R. Durrant, J. Am. Chem. Soc. 2008, 130, 2906.
- [47] Z. S. Wang, N. Koumura, Y. Cui, M. Takahashi, H. Sekiguchi, A. Mori, T. Kubo, A. Furube, K. Hara, *Chem. Mater.* 2008, 20, 3993.
- [48] H. Tian, X. Jiang, Z. Yu, L. Kloo, A. Hagfeldt, L. Sun, Angew. Chem. 2010, 122, 7486; Angew. Chem. Int. Ed. 2010, 49, 7328.
- [49] E. M. J. Johansson, M. Hedlund, M. Odelius, H. Siegbahn, H. Rensmo, J. Chem. Phys. 2007, 126, 244303.
- [50] E. M. J. Johansson, T. Edvinsson, M. Odelius, D. P. Hagberg, L. H. Sun, A. Hagfeldt, H. Siegbahn, H. Rensmo, J. Phys. Chem. C 2007, 111, 8580.
- [51] E. M. J. Johansson, M. Hedlund, H. Siegbahn, H. Rensmo, J. Phys. Chem. B 2005, 109, 22256.
- [52] A. Shafir, S. L. Buchwald, J. Am. Chem. Soc. 2006, 128, 8742.

- [53] D. A. K. Vezzu, J. C. Deaton, M. Shayeghi, Y. Li, S. Huo, Org. Lett. 2009, 11, 4310.
- [54] A. Suzuki, J. Organomet. Chem. 1999, 576, 147.
- [55] S. Ito, M. K. Nazeeruddin, P. Liska, P. Comte, R. Charvet, P. Péchy, M. Jirousek, A. Kay, S. Zakeeruddin, M., M. Grätzel, *Prog. Photo-voltaics* 2006, 14, 589.
- [56] Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT 2004.
- [57] N. M. O'Boyle, A. L. Tenderholt, K. M. Langner, J. Comput. Chem. 2008, 29, 839.

Received: December 26, 2010 Revised: March 14, 2011 Published online: April 20, 2011