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New phosphorus podands labelled by a cyanine probe: synthesis and fluorescence enhancement with cation complexation

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Abstract

The reaction between a suitable cyanine and a bicyclophosphane gives in good yield new eight membered cyclic phosphonate podands. Their complexation with calcium and magnesium cations induces an enhancement of the fluorescence intensity. Thus, these labelled heterocycles are convenient sensors for the detection of divalent cations.

Keywords: Cyanines; Dioxazaphosphocanes; Cation complexation; UV-visible; Fluorescence; Chemosensors

1. Introduction

The detection and quantification of metal ions is of great importance in any kind of chemical, biological and environmental analysis. Thus the research of metal ions dissolved in liquid media (e.g. water or body fluids) is of major analytical interest. In numerous biological processes, cytosolic Ca^{2+} plays a crucial role as secondary messenger. For example, the increase of Ca^{2+} concentration in the muscular cells induces the contraction of the muscle [1]. The design of chemosensors which are specific for the detection of biologically relevant cations such as Na^{+}, K^{+}, Mg^{2+} and Ca^{2+} is a topic of considerable interest [2].

Cyanine dyes have been known for a long time and are used in a variety of applications, such as photosensitisers for colour photography, markers for flow cytometry, in studies and detection of nucleic acids and as phototherapy agents. Additionally, the absorption and fluorescence characteristics of these dyes are sensitive to environmental conditions, e.g. the fluorescence quantum yield of some cyanine dyes is drastically increased upon interaction with nucleic acids [3]. These dyes are widely used as fluorescent probes in investigations of biological materials. Such applications, in particular to DNA detection [4], rely on the substantial enhancement of the fluorescence intensity of dyes upon binding to biopolymers [5]. Armitage et al. have used compounds like cyanine $DisC_2$ to study the structure of DNA [6]. Gockel et al. [7] have prepared deep blue colored hemicyanines from *N*-phenyl-aza-15-crown-5 and 9-methylacridine and studied the complex formation of the crown ether derivatives with Na^{+} and K^{+} using ^1H NMR and UV/VIS spectroscopy.

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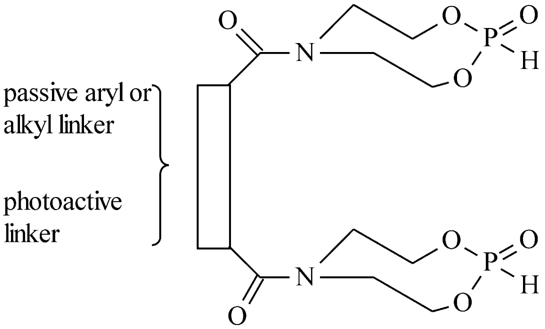
The complexes between crown ether styryl dyes and Ca^{2+} and Mg^{2+} are also described by Alfimov [8]. The syntheses and photophysical properties of cation-sensitive fluoroionophores carrying the tetraoxa monoaza 15-crown-5 receptor are described and discussed by Rurack [9]. In some cases cation-induced fluorescence enhancement or quenching is found.

For several years, we have been interested in the problem of calcium transport. The eight membered cyclic dioxazaphosphocanes bearing a lipophilic moiety have been studied for their phospholipid properties [10]. Their reactivity towards calcium dependent systems and the presence of amide and phosphoryl groups in the same molecule prompted us to study the complexing ability of these heterocycles [11]. Until now, the studied dioxazaphosphocanes do not bear a photoactive component. As the complexation equilibrium with metal cations can only be assessed by indirect ways, we aimed to introduce a fluorescent linker between the two phosphorus heterocycles. This could serve both as a rigid spacer and a probe for the complexation (Scheme 1).

In this paper, we describe the synthesis and the characterization of new phosphonate podands linked by a cyanine moiety. The main goal of the study reported herein is the synthesis and characterisation of these new podands and their complexing ability; furthermore we demonstrate that the complexation of divalent cations like calcium or magnesium involves an enhancement of fluorescence intensity.



Scheme 1.

2. Results and discussion

2.1. Synthesis and characterization

We prepared a series of cyanines **1** with a benzothiazole ring as terminal moiety. The nitrogen atoms of these cyanines are functionalised by a carboxylic group which permits the condensation with bicyclophosphanes. We thus obtain new podands in which two eight membered dioxazaphosphocane cycles are linked by a fluorescent spacer (Scheme 2).

2.2. Podand synthesis

The *N*,*N′*-dicarboxyalkylthiacarbocyanines **1** with carboxylic functions ($n=0$, 1, 3) were synthesised following Almeida et al. [12] In this paper we present only the results obtained with three carbon atoms in the methine chain between the benzothiazole rings but we have also synthesised the five carbons analogs to modulate their λ_{max} absorption area (work in progress).

The two-step process involved *N*-alkylation with a β-bromoacid followed by condensation with ethylorthoformate $CH(OEt)_3$ in dry pyridine. Scheme 3 presents the reaction pathway in the case of ethanoic acid ($n=1$). The resulting inner salts **c** were converted to compounds **d** by treatment with H_2SO_4 and then to the iodide **1** by further action of an aqueous 14% KI solution. Their structures were established by NMR, IR and UV spectroscopy.

The bicyclophosphanes **2** and **3** ($R=CH_3$ and $R=H$) were prepared according to a literature procedure of Houalla et al. [13] For the synthesis of the podands we added a stoechiometric quantity of the cyanine on the bicyclophosphane in DMF at room temperature and we obtained the podands in good yield. Monitoring the reaction by ^{31}P NMR indicates the formation of a single product with a chemical shift of −3.99 and 8.12 ppm and coupling constants $^1J_{PH}$ of 708.9 and 737.5 Hz for podands **4** and **5** respectively.

It is of value to notice that the α aminoacid derivative ($n=0$) did not react with the bicyclophosphane, presumably due to its zwitterionic configuration, this observation was already made in the reactivity of aminoacid on bicyclophosphane [14].

2.3. Absorption spectroscopy of cyanine **1** and of podand **5**

The absorption spectra of cyanine **1** and of podand **5** in various solvents are presented in Table 1. All spectra are recorded at room temperature and are normalized at the maximum of absorption.

The spectra of podand **5** present very few changes in comparison with the cyanine ones (only a shift of 1 or 2 nm between **1** and **5**). Thus, the photoactive center of the podand, the cyanine moiety, is weakly influenced by the presence of the phosphorus heterocycle. Nevertheless, the absorption spectra exhibit large solvent effects. We note a variation of $\Delta\lambda = 18$ nm for the cyanine and $\Delta\lambda = 15$ nm for the podand **5**. In solvents of high dielectric constant, the absorption is around 555 nm while in solvents of low ε, the $\lambda_{\text{abs max}}$ is enhanced to 570 nm. This hypsochromic shift of the UV/vis absorption band with increasing solvent polarity, is usually described as "negative solvatochromism" [15]. The anomalous value found in the case of THF may be due to the coordinative power of this solvent.

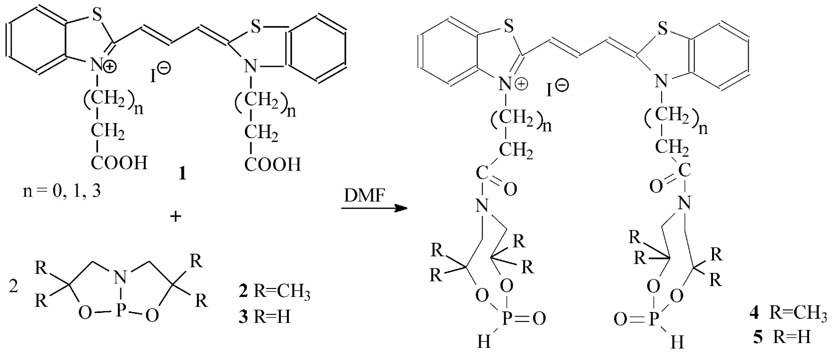
2.4. Calcium complexation

We tried to evaluated two main points:

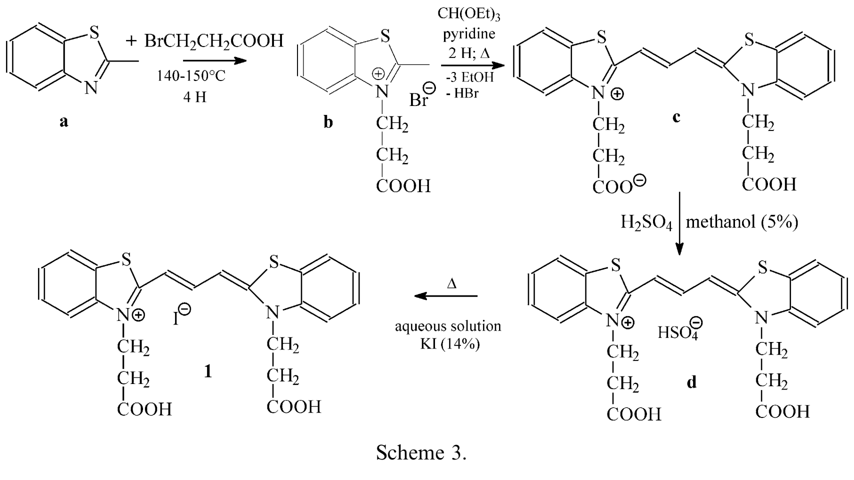
(1) The determination of the complexation sites by IR (solid state) and ^{31}P NMR (solution).
(2) The influence of the complexation on the UV absorption and fluorescence spectra of the podands.

2.4.1. Determination of complexation sites

We studied the infrared spectrum of the free podands **4** and **5** and their complexes with calcium



Scheme 2.



Scheme 3.

perchlorate in the solid state (KBr pellets). The ^{31}P NMR were run in CD_3CN with a small amount of DMSO-d_6 to increase the solubility of the product. The results are presented in Tables 2 and 3.

We observe a clear shift to lower frequencies of the carboxyl group (16–21 cm^{-1}). This fact can be explained by the decrease of the double character of the bond C÷O. This is the indication that the oxygen atoms are implicated in the complexation. In the ^{31}P NMR spectra of the complexes we observed a small deshielding ($\Delta\delta = 0.74$–1.60 ppm) for the complexes but mainly a large increase of the coupling constant $^1J_{PH}$ (30 Hz). This variation is due to a reinforcement of the bond P–H after the interaction of the oxygen atom of the phosphoryl group with the metal. A variation of the same magnitude has been observed for alkaline-earth complexes with linear amides by Simon [16], with macrocyclic polyether tetralactams by Tisnes [17] and with other dioxaphosphocane podands studied by Bellan [18].

The determination of the complexation sites made by IR and ^{31}P NMR corroborates the previously obtained results on podands with inactive spacers [19]. Thus, the oxygen atoms of the carboxyl and phosphoryl groups participate in the complexation of the cation.

Table 1
Solvent effects on compounds **1** and **5**

Solvents	Dielectric constant at 25 °C	λ abs max (nm) cyanine **1**	λ abs max (nm) podand **5**
Water	78.5	555	557
Acetonitrile	37.5	559	561
Ethanol	24.3	562	563
THF	7.4	564	565
Dichloromethane	8.9	568	570
Chloroform	4.7	573	572

Table 2
IR Spectroscopy of the free ligands and of their complexes with $Ca(ClO_4)_2$

		IR (cm^{-1}) KBr		
Podand	Vibrator	Ligand	Complex	Δν
4	ν C=O	1652	1636	16
5	ν C=O	1657	1636	21

2.4.2. *Influence of the complexation of alkaline earth cations on the photophysical properties of the podands*

To evaluate this influence, UV and fluorescence spectra in acetonitrile solutions were recorded for the free ligands and the complexes. The results are presented in Table 4.

We observe that the complexation induces only a very weak bathochromic shift (increase of the $\lambda_{max\ absorption}$ from 1 to 3 nm) in UV-visible spectra, and this result is in accordance with previous observations [20].

The most important observation is the great increase in fluorescence emission intensity by the formation of the complex with $Ca(ClO_4)_2$ (Fig. 1). Analogous results were obtained for complexes with $Mg(ClO_4)_2$ whereas no complexation is observed with $NaClO_4$ thus indicating a clear selectivity for the divalent metals.

As the carboxylic substituted cyanines may resemble to some extent the well known BAPTA calcium sensors [21], we also tried their direct complexation with $Ca(ClO_4)_2$ but in this case the

Table 3
^{31}P NMR results for compounds **4** and **5**

	^{31}P NMR δ (ppm) $^1J_{PH}$ (Hz)					
Podand	Ligand		Complex			
	δ^{31}P	$^1J_{PH}$	δ^{31}P	$^1J_{PH}$	Δδ^{31}P (ppm)	Δ$^1J_{PH}$ (Hz)
4	−3.99	708.9	−3.25	741.8	+0.74	+32.9
5	+8.12	737.5	+9.72	772.0	+1.60	+34.5

Table 4
Photophysical characteristics of the podands and their complexes with $Ca(ClO_4)_2$ in acetonitrile ($\rho = [Metal]/[L] > 10$)

Podands	**4**		**5**	
	Ligand	Complex	Ligand	Complex
λ_{max} abs (nm)	559	561	559	561
$\epsilon_{max} \cdot 10^{-3}$(l.mol^{-1}.cm^{-1})	94.6	106.9	50.6	47.9
λ_{em}(nm)	579	580	579	582
Fluorescence intensity (au)	689	936	532	968
Fluorescence area (au)	26531	36240	19782	38995

fluorescence enhancement is much weaker than with the phosphorus derivatives.

2.5. Stability constants

As the changes in absorbance or position in the UV-visible spectra are not significant, the stability constants of the podands/calcium or magnesium perchlorate complexes were determined in acetonitrile solutions by fluorescence spectrophotometry.

The emission spectrum of the ligands undergoes a small hypsochromic shifts (3 nm) in the presence of the cation perchlorate with a concomitant enhancement of the fluorescence intensity. For instance the emission maximum of the free ligand **5** is shifted from 579 to 582 nm upon complete complexation with Ca^{2+}.

Fluorescence quantum yield ($\Phi f = 0.135$ for **5**) is measured relative to the rhodamine B in ethanol ($\Phi f = 0.97$). This value is lower than the merocyanine 540 one [22] (0.25 in ethanol) which was used to correlate our results, but greater than the usual cyanine values (i.e. $\Phi f \leqslant 0.006$ for thiacyanines in ethanol) [23]

The complexation of a metal cation M by a ligand L in solution can be represented by the equilibrium:

$$M + L \rightleftharpoons ML$$

which is controlled by the stability constant

$$K_S = [ML]/[L][M]$$

expressing the degree of stability of the complex in a given solvent and temperature conditions.

The plot of the variations in fluorescence intensity as a function of cation concentration permit the determination of the stability constants. Fluorometric titrations were carried out at room temperature, by addition of known quantities of metal cations to a 3.66×10^{-5} M solution of free ligand in CH_3CN for Ca^{2+} and a 1.85×10^{-5} M solution for Mg^{2+}. The wavelengths of excitation and emission were chosen to 558 and 580 nm respectively for Ca^{2+} and 559 and 579 nm for Mg^{2+}.

When plotting fluorescence intensity I_F against metal concentration, we observed a linear dependence, thus indicating a constant 1:1 stoichiometry in the investigated range of concentration. See Fig. 1 for Ca^{2+}experiment.

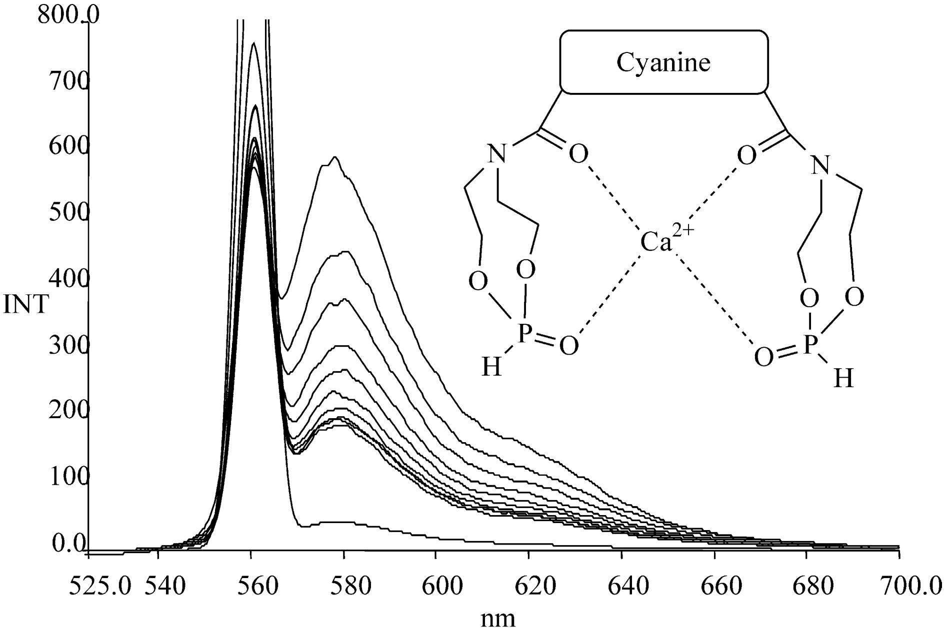


Fig. 1. Fluorescence intensity enhancement with successive addition of $Ca(ClO_4)_2$.

For the data analysis we used the methods described by Valeur et al. [24] to avoid the determination of I_F^{max}, which is not always possible to achieve with good accuracy. Following the relationship:

$$I_F^0/\left(I_F^0 - I_F\right) = \varepsilon_L\phi_L/(\varepsilon_L\phi_L - \varepsilon_{LM}\phi_{ML}) \\ \times (1/K_s[M]) + 1)$$

where ε_L and ε_{LM} are the molecular extinction coefficients of the ligand and the complex whereas ϕ_L and ϕ_{ML} are their respective quantum yields.

The quantity $I_F^0/(I_F - I_F^0)$ is plotted versus $[M]^{-1}$, and the stability constant is then given by the ratio intercept/slope. Linear least-squares analysis of the data leads to good correlation coefficients ($r = 0.998$ for Ca^{2+} and $r = 0.998$ for Mg^{2+}). We obtain $\log K_S = 4.82$ for Ca^{2+} and $\log K_S = 4.77$ for Mg^{2+}.

This method was also used by Ajayaghosh et al. [25] for the determination of stability constant in the case of a highly specific Ca^{2+} ion sensor.

We notice that the optical response of podand **5** for cation binding is only slightly more selective for Ca^{2+} than for Mg^{2+}. In the literature, numerous approaches to enhance the Mg^{2+}/Ca^{2+} selectivity have predominantly exploited differences in the size of these cations. Another criteria is the charge densities of the metal ions. In fact, the charge density of Ca^{2+} (0.24) is lower than for Mg^{2+} (0.75), and the magnesium cation has the highest charge density in a series of metal ions [26]. Thus in the future, we aim to modify our compounds to have a better fit for a chosen cation, by varying the cyanine chain length and also by varying the ω bromoacid. Moreover, our work with other divalent cations like Sr^{2+} and Ba^{2+} is in progress.

3. Conclusion

We have demonstrated that *N,N′*-dicarboxyalkylthiacarbocyanines can be easily anchored to bicyclophosphane to produce new podands with phosphonate heads, linked by a fluorescent probe. The spectroscopic analysis by IR and by ^{31}P NMR have shown that the complexation sites of the calcium cation are the functional groups C=O and P=O of the ligand.

The most noticeable result is the enhancement of the intensity of fluorescence when the podands interact with $Ca(ClO_4)_2$ and $Mg(ClO_4)_2$. It may be due to a metal binding induced conformational restriction in the same way as the chelation-enhanced fluorescence (CHEF) effect described for the complexation with Ca^{2+} by Kim [27].

Our work demonstrates that dioxazaphosphocanes linked by a cyanine are effective probes for the detection of divalent cations . In addition, the cyanine structure is suitable for further structural modifications. Further refinement of the sensing capabilities of this class of chemosensors is in progress.

4. Experimental

4.1. N,N′-*dicarboxyalkylthiacarbocyanines*

4.1.1. *Compound **1***

3-(2-Carboxyethyl)-2-[3-(3-(2-carboxyethyl)-1,3-benzothiazol-2-ylidene)-1-propenyl]-1,3-benzothiazol-3-iumiodide

The mixture of 2-methylbenzothiazole (3.0 g; 20.0 mmol) and 3-bromopropionic acid (3.2 g; 20.0 mmol) is heated at 140 °C during 4h. Then triethylorthoformate (7 ml; 40.0 mmol) and 60 ml of pyridine are added to the mixture. A change of colour is immediately observed (deep purple). The mixture is heated at reflux under magnetic stirring during 2 h to complete the reaction. After cooling to room temperature, 20 ml diethyl ether are added to the mixture which is refrigerated over a night. A purple precipitate is isolated by filtration. The solid is dissolved in the minimum amount of methanol (40ml). An aqueous solution of H_2SO_4 (5%, 100 ml) is then added to the solution. After evaporation of the solvent, a purple solid is filtrated (corresponding to the cyanine in its hydrogenosulfate form). The residue is dissolved in 25 ml methanol, then diluted in 125 ml of an aqueous 14% KI solution. The mixture is heated to ebullition, then cooled to room temperature and kept at

4 °C overnight . The cyanine **1** ($n=1$) is isolated by filtration (3.1 g; Yield: 55%). The product is crystallised in methanol.

^{1}H NMR (250 MHz, DMSO-d_6), $\delta_{ppm,}$ J_{Hz}: 7.98 (*d*, 2H, $J=7.9$; H_7); 7.84–7.71 (m, 3H, β-CH and H_4); 7.57 (t, 2H, $J=7.7$; H_5); 7.41 (t, 2H, $J=7.7$; H_6); 6.63 (*d*, 2H, $J=12.8$; α-CH); 4.55 (t, 4H, J = 7.2; CH_2); 2.81 (t, 4H, J = 7.2; CH_2COOH). ^{13}C NMR (63 MHz, DMSO-d_6), δ_{ppm}: 171.6 (COOH); 164.2 (C_2); 146.6 (β-CH); 140.9 (C_{3a}); 127.9 (CH_5); 125.1 (CH_6); 124.9 (C_{7a}); 122.9 (CH_7); 113.7 (CH_4); 99.1 (α-CH); 42.1 (N-CH_2); 31.5 (CH_2COOH). IR (KBr pellets) ν_{cm}^{-1}: 2964 (=CH); 1739 (C=O); 1548-1464 (C=CH arom.). UV/vis: $\lambda_{max}=562.5$ nm, $\varepsilon=9.30{\cdot}10^{4}$ cm^{-1} mol^{-1} dm^{3} (ethanol).

The bicyclophosphanes were prepared following the procedure of Houalla et al. [13]

4.2. Dioxazaphosphocane podands:

4.2.1. Podand 4

The cyanine **1** (318 mg; 0.55 mmol) in 4 ml of anhydrous DMF is added under argon to a 3 ml solution of the bicyclophosphane **2** (207 mg; 1.1 mmol) in the same solvent. The mixture is kept under agitation during 1 h. The DMF is then evaporated; we obtain 520 mg of podand**4** (bright violine), yield: 100%.

^{31}P NMR (81 MHz, DMF), $\delta_{ppm,}$ J_{Hz}:−3.99 ($^{1}J_{PH}=708.9$). ^{1}H NMR (250 MHz, $CDCl_3$), $\delta_{ppm,}$ J_{Hz}: 8.00 (d, 2H, J = 8.1; H_7); 7.78 (m, 3H, β-CH and H_4); 7.57 (t, 2H, J = 7.34; H_5); 7.43 (t, 2H, J = 7.6; H_6); 6.82 (d, 1H, $J_{PH}=710.7$; P–H); 6.63 (d, 2H, J = 13.1; α-CH); 4.54 (m, 4H, N–CH_2); 3.52–3.74 (m, 8H, N–CH_2 cycle); 3.03 (m, 2H, CH_2CON); 2.80 (m, 2H, CH_2CON); 1.09–1.42 (m,24H, CH_3). ^{13}C NMR (63 MHz, DMSO-d_6), δ_{ppm}: 171.5 (CON); 163.6 (C_2); 150.5 (β-CH); 141.0 (C_{3a}); 128.0 (CH_5); 125.1 (CH_6); 124.8 (C_{7a}); 122.9 (CH_7); 113.7 (CH_4); 99.0 (α-CH); 84.2 (COP); 58.6 (CON cycle); 42.2 (N–CH_2); 31.0 (CH_2CON); 27.1 (CH_3). IR (KBr pellets) ν_{cm}^{-1}: 2991 (=CH); 2433 (P–H); 1652 (N–C=O); 1555–1462 (C=CH arom); 1262 (P=O). UV/vis: $\lambda_{max}=562.1$ nm, $\varepsilon=8.40{\cdot}10^{4}$cm^{-1} mol^{-1} dm^{3} (ethanol); $\lambda_{max}=559.2$ nm, $\varepsilon=1.695{\cdot}10^{5}$ cm^{-1} mol^{-1} dm^{3} (acetonitrile). SM (FAB, DMF, positive mode) m/z = 831[M+] (23.4%); 642 (46.1%); 453 (22.3%); 335 (32.3%).

4.3. Podand 5

To a mixture of bicyclophosphane **3** (205 mg; 1.5 mmol) in 4 ml of anhydrous DMF is added under argon the cyanine **1** (454 mg; 0.77 mmol) dissolved in 5 ml of DMF. The mixture is kept under agitation during one hour. The DMF is then evaporated; we obtain 650 mg of podand **5** (violine), yield: 100%.

^{31}P NMR (81 MHz, DMF), $\delta_{ppm,}$ J_{Hz}: 8.12 ($^{1}J_{PH}=737.5$). ^{1}H NMR (250 MHz, $CDCl_3$), $\delta_{ppm,}$ J_{Hz}: 8.00 (d, 2H, J = 9.1; H_7); 7.80 (m, 3H, β-CH and H_4); 7.57 (t, 2H, J = 7.39; H_5); 7.42 (t, 2H, J = 7.7; H_6); 6.84 (d, 1H, $J_{PH}=733.7$; P-H); 6.65 (d, 2H, J = 12.7; α-CH); 4.52 (m, 4H, N–CH_2); 3.18–4.49 (m, 16H, N–CH_2 and O–CH_2 cycle); 2.89 (m, 2H, CH_2CON); 2.74 (m, 2H, CH_2CON). ^{13}C NMR (63 MHz, DMSO-d_6), δ_{ppm}: 172.5 (CON); 165.6 (C_2); 147.6 (β-CH); 141.9 (C_{3a}); 128.9 (CH_5); 126.1 (CH_6); 125.8 (C_{7a}); 123.9 (CH_7); 114.9 (CH_4); 100.2 (α-CH); 65.4 (CH2–O cycle); 50.0 (N–CH_2 cycle); 43.1 (N–CH_2); 31.7 (CH_2CON). IR (KBr pellets) ν_{cm}^{-1}: 2961 (=CH); 1657 (N–C=O); 1559–1466 (C=CH arom); 1261 (P=O). UV/vis: $\lambda_{max}=562.2$ nm, $\varepsilon=7.0{\cdot}10^{4}$cm^{-1} mol^{-1} dm^{3} (ethanol); $\lambda_{max}=559.0$ nm, $\varepsilon=6.2{\cdot}10^{4}$ cm^{-1} mol^{-1} dm^{3} (acetonitrile). SM (ES, methanol, positive mode): *m/z* = 719 [M+]; 586; 453; 355.

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