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Novel Chromogenic Pyridinium Derivatives of Calix[4]arenes,II[1]

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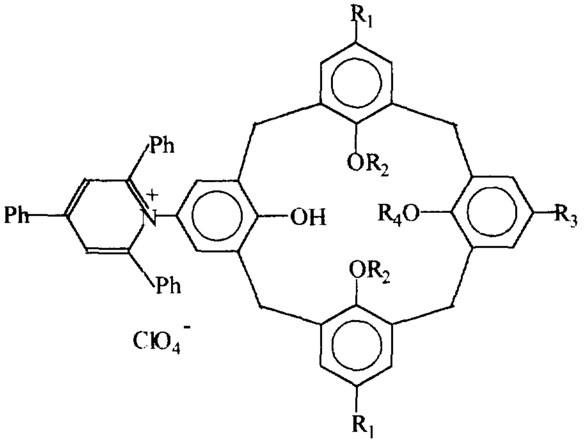
Abstract: Chromoionophoric calix[4]arenes (**8,9**) containing dissociable OH and quaternary pyridinium indicator groups have been synthesized. Optical measurements of the target molecules performed in various solvents in the presence of weak base and alkali cations revealed Li^+, Na^+ and Ca^{2+} recognition depending on the binding sites. Solvato- and halochromism of betaines **10,11** formed *in situ* upon complexation were also observed. © 1997 Elsevier Science Ltd.

INTRODUCTION

Chromogenic calixarenes with different coordination spheres attached to the calixarene skeleton have attracted much attention in the past years.[2,3] The absorption spectra of these ligands change upon the binding of metal ions and the coloration process thus serves as a transducer of the chemical signal to the optical one.This phenomenon plays an important role in the operation of *optrodes* (optical sensors) which have increasingly been applied in the determination of physiologically important cations.

In the previous paper[1] of this series we reported the synthesis and optical properties of some new calixarene chromoionophores containing dissociable phenolic OH group(s) on the lower rim and 2,4,6-triphenyl-1-pyridinium group(s) in *para* position to the OH on the upper rim (Fig.1). Deprotonation of compounds **1** and **2** was attempted in order that the pyridinium N-phenoxide betaine chromophore system (known as Reichardt dye) could be formed. However, we failed to obtain stable betaines: weak organic bases were not effective whilst on the exposure to strong bases intensive coloration indicated the formation of betaines but we did not succeed in isolating them. Notwithstanding, compounds **1** and **2** behaved as real chromoionophores in non-aqueous solvents upon simultaneous addition of alkali metal salts and weak base (e.g.Et_3N). Dissociation of the free OH induced by the metal ion and facilitated even by weak base caused significant bathochromic shifts (200-330 nm) in the UV/VIS spectra of **1,2**. The new bands appearing at 510-650 nm could be assigned to the CT bands of betaines formed during complexation. Moreover some selectivities in respect of the cations (**1** was selective toward Li^+ while **2** showed interaction with Li^+, Na^+ and K^+) and halochromism (the shift of CT band was dependent on the cation added) could be observed.



R^1,R^3= Bu^t, R^2,R^4= Et (**1a**), Bu (**1b**); R^1= Bu^t, R^2= CH_2CO_2Et, R^3= 2,4,6-$(Ph)_3$-1-pyridinium ClO_4^-, R^4=H(**2**)

Figure 1.

Continuing our efforts to develop more selective chromoionophores, we planned to change the coordination sphere on the calixarene framework, meanwhile keeping the 2,4,6-triphenyl-1-pyridinium indicator group introduced previously in compounds **1** and **2** was also an aim. It was clear that enhanced complexing ability could be achieved if the binding site consists of at least three good donor groups e.g. carboxyl, ester, amide etc. Unfortunately, the synthesis of such ligands supplied with the chromophore depicted in Fig.1 resulted in the formation of a mixture of conformers which could not be separated. Therefore, partly changing our original aim, we tried to find other indicator groups containing also pyridinium moiety in the hope of successful preparation of conformationally pure ligands.

A recent report[4] on the solvato- and halochromic properties of the imino dyes **4** (Fig.2) resembling merocyanine dyes aroused our attention. The betaines **4** obtained *in situ* from quaternary salts **3** by deprotonation prior to the optical measurements exhibited solvatochromic reversal and proved to be a good model to study how the isomeric substitution of the pyridinium ring might affect the optical properties. In one respect the structural features of compounds **3** (phenolic OH in conjugation with a pyridinium group through an azomethin unit) are similar to those of our earlier chromoionophores **1**,**2**, but the pyridinium group is not attached directly to the aromatic ring of the calix. In order to study the optical properties of the new N-methylpyridinium(methylidene)imino chromophore system, for comparison it was introduced first into the 25,26,27-trialkoxycalix[4]arene skeleton (**8a,b,c**), then in another attempt the trialkoxy binding site was replaced with better ligating functions (ethoxycarbonylmethoxy groups) to obtain compounds **9a,c**. Beside the advantage of applying similar synthesis as described for compounds **3**, the new chromophore also provided structural variability concerning the position of the attached pyridinium ring..

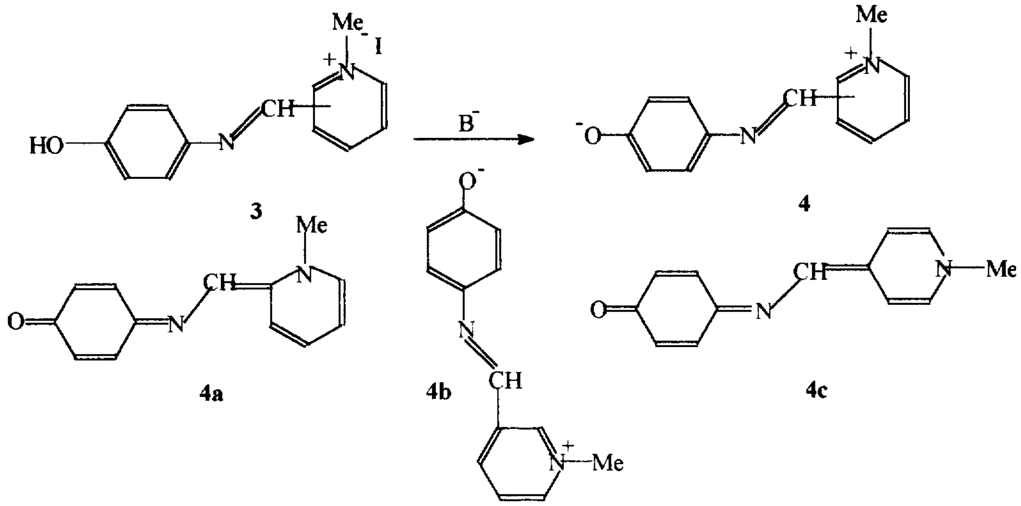


Figure 2.

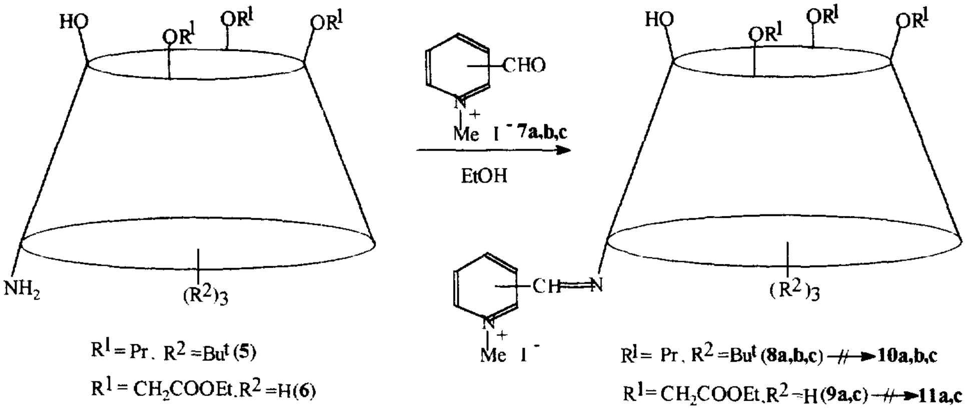
RESULTS AND DISCUSSION

*Synthesis of ligands **8a,b,c** and **9a,c***

The synthetic approach was based on the reaction of the appropriate aminocalixarenes **5** and **6** with **7a,b,c** pyridinium carbaldehydes (Scheme 1). Starting compounds **5,6** were prepared from 11,17,23,29-tetra-tert-butyl-25,26,27-tripropoxy-28-hydroxycalix[4]arene[5] and 25,26,27-triethoxycarbonyl(methoxy)-28-hydroxycalix[4]arene[6], respectively, by selective nitration[7] followed by catalytic hydrogenation as described earlier[1]. The amino derivative **6** proved to be sensitive to air, therefore, the ethanol solution was used in the next step after the Pd-C catalyst had been removed.

The condensations of **5** and **6** aminocalixarenes with **7** pyridinium-2(**a**), -3(**b**) and- 4(**c**)-carbaldehyde methoiodide salts were carried out in boiling ethanol and **8,9** quaternary salts were precipitated from the solution in pure form. The cone conformation of products was unambigously proved by ^{1}H NMR measurements.

We failed again to obtain **10,11** betaines in stable form by deprotonation of **8** and **9** since strong bases (NaH, KOBu^t, Me$_4$N$^+$OH$^-$) in various solvents caused decomposition. On the exposure to bases intensive coloration occured due to the formation of betaines but it faded in a relatively short time indicating the deterioration of the chromophoric system (nucleophilic ring opening and/or solvolysis of the pyridinium moiety might occur). Nevertheless, the spectroscopic investigations of **8** and **9** salts revealed that the metal ion recognition associated with the coloration process was similar to that observed for **1** and **2**.



$R^1 = Pr, R^2 = Bu^t$ (5)
$R^1 = CH_2COOEt, R^2 = H$ (6)

$R^1 = Pr, R^2 = Bu^t$ (**8a,b,c**) ⇸ **10a,b,c**
$R^1 = CH_2COOEt, R^2 = H$ (**9a,c**) ⇸ **11a,c**

Scheme 1.

*Spectroscopic studies of ligands **8a,b,c***

The UV/VIS spectra of the ligands ($c=5\times10^{-5}$mol.dm^{-3}) were recorded in eight solvents: MeOH, EtOH, BuOH, MeCN, DMF, acetone, CH_2Cl_2 and $CHCl_3$. The longest wavelength absorption maxima of the iodide salts fell in the range of 413-466 nm. The addition of Et_3N ($c=5\times10^{-3}$mol.dm^{-3}) or alkali metal bromides ($c=5\times10^{-3}$mol.dm^{-3} or saturated solution obtained by shaking the salt with the ligand solution in the case of $CHCl_3$ and CH_2Cl_2) in great excess, separately, did not lead to observable changes, providing evidence that neither the formation of **10a,b,c** betaines could be achieved with a weak base nor metal ion induced dissociation took place due to the weak cation-ligand interaction. When LiBr, NaBr or KBr and Et_3N were added simultaneously, a new band at longer wavelength emerged in the spectra measured in five solvents. The new bands are attributed to complex formation, whereas the absorptions at shorter wavelength belong to the uncomplexed form . Figure 3. shows a set of spectra of ligand **8a** ($c=5\times10^{-5}$ mol.dm^{-3}) recorded at different Li^+ concentrations in acetone in the presence of Et_3N ($c=9\times10^{-5}$mol.dm^{-3}). An isobestic point is clearly seen suggesting a simple equilibrium between the ligand and a single complex form. The spectral changes in the five solvents are summarized in Table 1.

In protic solvents (MeOH, EtOH, BuOH) the spectra did not show any change in the presence of cations, indicating that no complexes were formed (these data are not recorded in the table). Due to the weak complexing ability of the PrO groups in the coordination sphere which are not sufficient to strongly bind the cation localised in the vicinity of phenoxide moiety, the strong solvation power of alcohols suppresses the complex formation.

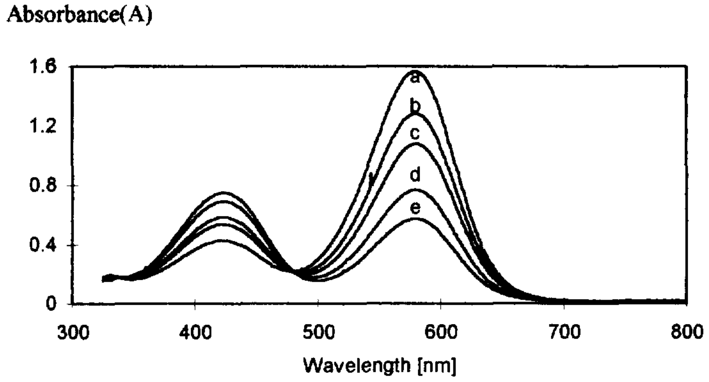


Figure 3. Spectra of ligand **8a** measured in the presence of Et_3N and LiBr
$[Li^+]$: a) $5x10^{-3}$mol.dm^{-3} b) $1x10^{-3}$mol.dm^{-3} c) $5x10^{-4}$mol.dm^{-3} d) $2x10^{-4}$mol.dm^{-3} e) $1x10^{-4}$mol.dm^{-3}

solvent	λ_{max}(nm. A)						
	8a			**8b**	**8c**		
	Li^+	Na^+	K^+	Li^+	Li^+	Na^+	K^+
MeCN	588(1.216)	602(0.301) 422(0.259)	588(1.154)	516(0.504)	609(1.280)	629(0.110) 429(0.341)	429(0.370)
DMF	597(0.220) 421(0.283)	609(0.091) 420(0.325)	420(0.339)	385(0.271)	620(0.044) 429(0.337)	429(0.366)	426(0.373)
acetone	596(0.747) 425(0.168)	610(0.054) 424(0.398)	426(0.393)	387(0.296)	620(0.127) 449(0.235)	434(0.446)	433(0.537)
CH_2Cl_2	619(1.770)	456(0.315)	455(0.390)	411(0.293)	662(1.619) 456(1.908)	463(0.446)	462(0.463)
$CHCl_3$	590(0.914)	455(0.401)	456(0.454)	503(0.260)	596(0.680)	464(0.476)	464(0.387)

Table 1. Absorption maxima and absorbance values of **8a,b,c** in the presence of LiBr, NaBr, KBr and Et_3N
[Ligand] =$5x10^{-3}$mol.dm^{-3}, [MBr] =10^{-2}mol.dm^{-3} (or saturated solution in the case of CH_2Cl_2 and $CHCl_3$) ,
$[Et_3N]$ =$5x10^{-3}$mol.dm^{-3}

Three interesting features can be recognised from the spectral data:

1. Selectivity and relative stability of the complexes decrease in the order Li^+>Na^+>>K^+ and **8a**>**8c**>>**8b**. Actually KBr does not influence the spectra except in the case of **8a** (MeCN). Ligand **8b** has no response to alkali metal ions except for Li^+ (MeCN,$CHCl_3$). The selectivities can be interpreted if the different coordination properties of the alkali cations are considered. The simple complexing environment represented by ligands **8** fits

Li^+ (coordination number 4) and to a less extent Na^+ but it is not appropriate for K^+ (coordination number 8). The stability of complexes is influenced by the solvent polarity in the case of all ions and ligands. The Li^+ ion is completely complexed by **8a** in MeCN, CH_2Cl_2 and $CHCl_3$, by **8c** in MeCN, $CHCl_3$ and partially complexed in DMF and acetone with both ligands. The Na^+ ion is partially complexed by **8a** in MeCN, DMF and acetone, by **8c** in MeCN and no complexation was detected in CH_2Cl_2 or $CHCl_3$ with both ligands. As expected, the solvation of alkali cations in DMF and acetone competes with complexation (a quantitative treatment of the complex formation with a simplified equilibrium model was described for this system[8]).

2. Solvatochromism can be studied with betaine dyes such as **4** which were reported to exhibit reverse (negative) solvatochromism[4] i.e. a hypsochromic shift of the longest wavelength absorption band (λ_{CT}) with increasing solvent polarity. Since we have no pure betaines but complexes resembling the betaine structure modified by the interaction with cations, we could observe combined effects of halochromism and solvatochromism. The measure of halochromism is the shift of the CT band which is influenced by the effective ionic charge (n/r: $Li^+ > Na^+ > K^+$) and the solvent polarity [9]. Increasing the positive charge density enhances the hypsochromic shift. Without going into speculation it is worth noting that $\lambda_{CTLi+} < \lambda_{CTNa-}$ by 12-20 nm which is characteristic of ligands **8a,c** in each solvent. The relative order of the absorption maxima in various solvents, however, cannot be explained in terms of the solvent polarity scale ($E_T(30)$: MeCN > DMF> acetone > CH_2Cl_2 > $CHCl_3$) since the pure phenolate-cation interaction is disturbed by the complex formation. Nevertheless, the negative solvatochromism characteristic of the chromophore system can be recognised in certain cases, e.g. **8a**-Li^+, λ_{CT}: 588 (MeCN) < 596 (acetone) ~ 597 (DMF) < 619 (CH_2Cl_2).

3. Although ligands **8a,b,c** possess the same coordination sphere there are significant differences in their spectroscopic behavior. Ligands **8a,c** exhibit stronger chromoionophoric properties to alkali cations than **8b**. This phenomenon can be explained if the zwitterionic character of **10a,b,c** betaines derived from **8a,b,c** quaternary salts are compared. Quantum chemical calculations on the analogous molecules[4] **4** suggest that the $S_0 \rightarrow S_1$ transition in such zwitterionic dyes is of a complex nature. The π-electron charge densities of the phenolate and the pyridinium moieties vary much more in the chromophore system of **4b** in the course of the transition than those in **4a,c**. In this respect the latter are close to the model of *charge resonance* dyes, whereas the former is nearly a *charge transfer* dye[10]. The betaine form of **4a,c** would have a quinonoid mesomeric structure which might be dominant in apolar solvents where the above transition cannot be observed.

Summarizing our results we can conclude that ligand **8a** in the presence of Et_3N exhibits selective recognition toward Li^+ which is the most pronounced in CH_2Cl_2 (λ_{max}= 619nm).

Spectroscopic studies of ligands 9a,c

In order to achieve stronger effects during the complexation, a more effective coordination sphere was constructed by replacing the Pr groups in hosts **8** with ethylesters of good donor property. Due to the negative results observed with **8b** the analogous **9b** was omitted from the series. The spectra were recorded in EtOH, MeCN, acetone in a similar manner as described above but Ca^{2+} and Mg^{2+}were also used (Table 2, 3).

Two striking differences can be recognised when comparing the spectra of **9a,c** taken in the separate presence of base or cations, with those of **8a,b,c** under the same conditions (Table 2).

1. In contrast to **8a,b,c** partial deprotonation of the OH group took place with ligands **9a,c** when Et_3N was added. The new band at 595-647 nm might be attributed to the formation of betaines **11a,c** which are actually the dominant species in MeCN (the shorter wavelength bands belong to **9a,c**). In the case of **9c** the spectral changes measured in various solvents are in accordance with the expected negative solvatochromism observed for the betaine dyes **4**. It means that the wavelength of the CT bands increases in the order of EtOH(623) < MeCN(630) < acetone(647). Ligand **9a**, however, behaves anomalously, λ_{CT}: MeCN(595)< acetone (601) <EtOH(612). Deeper conclusions cannot be drawn from the spectral data, especially if we assume that triethylammonium ion formed during the deprotonation can be complexed (calixarene esters are described to form complexes with various ammonium ions[11] therefore it would have been difficult to find any organic base for the deprotonation where this phenomenon can unambiguously be excluded). If this process is also taken into consideration (not knowing the complex stabilities in the different solvents) then the spectral changes cannot be attributed merely to the formation of betaines **11a,c** but rather to the result of an equilibrium between **11** and the respective ammonium complex

solvent	λ_{max}(nm, A)					
		9a		**9c**		
	Et_3N	Li^+	Ca^{2+}	Et_3N	Li^+	Ca^{2+}
EtOH	612(0.395) 437(0.660)	436(0.789)	555(0.662) 435(0.551)	623(0.144) 442(0.847)	442(0.886)	566(0.465)
MeCN	595(1.015) 422(0.507)	422(0.723)	538(1.347)	630(2.602) 430(0.290)	431(0.834)	553(1.729)
acetone	601(0.361) 428(0.811)	583(1.132) 428(0.459)	559(1.228) 433(0.344)	647(0.211) 434(0.833)	600(1.345) 433(0.441)	563(0.687) 434(0.607)

Table 2. Spectral changes of ligands **9a,c** in the presence of base and alkali cations, separately

2. Complexation of Li^+ in aprotic and Ca^{2+} in each solvent was achieved by both ligands in the *absence* of Et_3N (Na^+, $K^+$and Mg^{2+} gave no responses) (Table 2). It means that the complex formation with these cations itself can effect dissociation of the free OH group taking part in the coordination by enhancing its acidity. Earlier a host molecule similar to **9** but supplied with 2,4-dinitrophenylazo chromophore was prepared in our laboratory[12] and found to give analogous optical changes with Li^+,Ca^{2+} and to a less extent with Na^+. On the contrary, when it was incorporated into PVC membrane and used in potentiometric and optical transduction as

well, Na^+ selectivity was observed in aqueous solutions[12](similar measurements with **9a,c** are in progress). Consequently, the host-guest interactions in organic solvents and liquid PVC membranes are influenced by different factors (medium, counter ion effect, etc.) resulting sometimes reversal in the order of selectivities.

Experiments carried out with Et_3N and cations simultaneously revealed that the complexation of Li^+, Na^+ and Ca^{2+} was stronger than that of K^- and Mg^{2-} (by both ligands in each solvent, see Table 3).

solvent	λ_{max} (nm A)									
	9a					**9c**				
	Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
EtOH	575(1.049) 438(0.345)	612(1.974) 437(0.230)	611(0.935) 436(0.539)	565(1.546)	422(1.503)	571(1.384)	629(2.273)	618(0.195) 441(0.827)	576(1.764)	440(0.917)
MeCN	574(2.217)	606(2.800)	588(1.962)	603(2.059) 427(0.281)	633(0.876) 430(0.656)	592(2.369)	631(3.106)	635(1.143) 431(0.581)	573(1.724)	633(0.876) 429(0.656)
acetone	582(2.430)	614(2.337) 433(0.225)	610(0.583) 428(0.806)	576(1.926)	426(0.822)	602(2.676)	645(2.757) 439(0.214)	645(0.790) 435(0.697)	564(1.921)	581(0.363) 434(0.738)

Table 3. Spectral changes of ligands **9a,c** in the presence of alkali cations and base

K^- and Mg^{2+} also gave responses but they showed weaker binding than the other alkali ions. If the effect of the solvents upon complexation is considered, it can be concluded that MeCN is superior to acetone and EtOH for binding Li^+, Na^+, K^+ regardless of the ligands (the bands of the uncomplexed species are missing from the spectra or their absorptions are much smaller than those of the complexed form). Of the cations Ca^{2+} shows the strongest binding to the ligands since it is almost completely complexed in each solvent.

As to the halochromic behavior of ligands **9a,c** a straightforward relationship between the cations, solvents and the λ_{CT} shifts cannot be recognised but $Ca^{2+}$and Li^+ possessing the highest positive charge densities gave rise to significant hypsochromic shifts, $\lambda_{CT\ betaine}-\lambda_{CT\ Ca^{2+},Li^-} = 20\text{-}80$nm, in each solvent. It is the consequence of strong cation-phenolate interaction in these cases keeping the cation in the proximity of the lower rim of the calix and stabilizing mostly by the aryl ether oxygens. However, some information on the possible structure of Na^+ complexes can also be obtained. Practically no shift of the $\lambda_{CT\ betaine}$ bands in the spectra of **9c** is found in the presence of sodium salt indicating that Na^+ is situated below the calix surrounded by the ester carbonyl groups and thus being relatively far from the phenolate anion. The three ester moieties with the etheric oxygen atoms suit the coordination requirement of Na^+ quite well but not sufficient for $K^+$and Mg^{2+} (partially complexed). It remained unclear why ligand **9a** having the same complexing enviroment as **9c** exhibits bathochromic shift (about 10 nm) in aprotic solvents when Na^+ is added. This phenomenon might be answered if the solvent polarity were varied in a wider range.

In conclusion, by introducing ester donor groups into the lower rim of the calix, **9a,c** chromoionophoric molecules were synthesized which exhibited enhanced metal ion binding ability compared to our prior publication[1] with the preference of Ca^{2+}, Na^{+} and Li^{+}.

EXPERIMENTAL

Melting points are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ at 500 MHz on a Bruker DRX 500 spectrometer. All δ values are reported in ppm, TMS was used as internal standard. UV/VIS spectra were taken on PYE UNICAM SP8-500 UV/VIS spectrophotometer. Precoated silica gel plates (Merck 60 F_{254}) were used for analytycal TLC. All chemicals were reagent grade and used without further purification. Compounds **5** and **6** were prepared analogously as described in our previous paper[1] and **7a,b,c** were obtained according to the literature[13].

*General procedure for the synthesis of ligands **8a,b,c** and **9a,c***

A solution of **7a,b,c** (0.28g, 1.1mmol) and **5** (0.73g, 1mmol) or **6** (1mmol, without isolating from the reduction mixture) from EtOH (15 ml) was refluxed for 2h. After cooling a precipitated yellow product was collected and recrystallized in EtOH (the analytical samples were dried at 80°C in 10^{-1} Torr).

8a: 0.55g (58%), mp 186-188°C ^{1}H NMR δ: 8.89(1H,N=CH), 8.89s(2H,PyH), 8.48d(1H,PyH), 8.47d (1H,PyH), 7.35s(2H,ArH), 7.11s(2H,ArH), 6.96s(1H,OH), 6.64s(2H,ArH), 6.62s(2H,ArH), 4.37d and 3.20d (2+2H,J=12.5Hz,$ArCH_2Ar$), 4.30d and 3.38d(2+2H,J=13.5Hz,$ArCH_2Ar$), 4.11s(3H,$^+NCH_3$), 3.84m and 3.79m (2+4H,OCH_2), 2.20m and 1.88m (2+4H,CH_2), 1.26s and 0.88s(9+18H,Bu^t), 1.23t and 0.99t (6+3H, CH_3), Anal. calcd. for $C_{56}H_{73}N_2O_4I$ (965.11): C 69.69, H 7.62, N 2.90, Found: C 69.53, H 7.59, N 2.84

8b: 0.70g (74%), mp: 273-274°C ^{1}H NMR δ: 9.51s(1H,PyH), 8.99d(1H,PyH), 8.98d(1H,PyH), 8.91s (1H,CH=N), 8.08t(1H,PyH) 7.31s(2H,ArH), 7.14s(2H,ArH), 6.64s(2H,ArH), 6.63s(1H,OH), 4.43s(3H, $^+NCH_3$), 4.41d and 3.23d(2+2H,J=12.6Hz,$ArCH_2Ar$) 4.36d and 3.40d(2+2H,J=13.6Hz,$ArCH_2Ar$), 3.85 and 3.79m(2+4H,OCH_2), 2.33m and 1.95m(2+4H,CH_2), 1.35s and 0.87s(9+18H,Bu^t), 1.13t and 0.99t(6+3H, CH_3), Anal. calcd. for $C_{56}H_{73}N_2O_4I$ (965.11): C 69.69, H 7.62, N 2.90, Found: C 69.70, H 7.60, N 2.87

8c: 0.80g (85%), mp 194-196°C ^{1}H NMR δ: 8.91d(2H, J=6.6Hz, o-PyH), 8.91s(1H, CH=N), 8.51d(2H, J=6.5Hz, m-PyH), 7.38s(2H, ArH), 7.16s(2H, ArH), 6.89s(1H, OH), 6.65d, 6.61d(2+2H, ArH), 4.39d and 3.22d, 4.34d and 3.41d (4x2H, J=12.5Hz, $ArCH_2Ar$), 4.30s(3H, $^+NCH_3$), 3.84t and 3.76t(6H, OCH_2), 2.30m and 1.95m(6H, CH_2), 1.32s and 0.89s(9+18H, Bu^t), 1.16t and 0.99t(6+3H, CH_3), Anal. calcd. for $C_{56}H_{73}N_2O_4I$ (965.11): C 69.69, H 7.62, N 2.90, Found: C 69.41, H 7.58, N 2.86

9a: 0.36g (39%), mp 196-198°C ^{1}H NMR δ: 9,06s(1H, N=CH), 8.20s(1H, OH), 8.20d(1H, PyH), 7.49s (2H, ArH), 7.14d(2H, ArH), 7.03d(2H, ArH), 6.80d(2H, ArH), 6.73m(1H, ArH), 6.69d(1H, PyH), 6.62m (2+1H, ArH, PyH), 5.41t(1H, PyH), 4.97s(2H, OCH_2CO), 4.93d and 4.55d(2+2H, J=15.8Hz, OCH_2CO), 4.96d and 3.38d(2+2H, J=13.1Hz, $ArCH_2Ar$), 4.41d and 3.57d (2+2H, J=13.4Hz, $ArCH_2Ar$), 4.37s(3H, $^+NCH_3$), 4.30m and 4.20m (4+2H, OCH_2), 1.35t and 1.29t(6+3H, CH_3), Anal. calcd. for $C_{47}H_{49}N_2O_{10}I$ (928.82): C 60.87, H 5.32, N 3.02, Found: C 60.95, H 5.28, N 3.08

9c: 0.40g (43%), mp 187-189°C ^{1}H NMR δ: 8.97s(1H, N=CH), 8.29d(2H, PyH), 7.93d(2H, PyH), 7.27s(2H, ArH), 7.06m(4H, ArH), 6.79m(5H, ArH), 7.53s(1H, OH), 5.01d and 4.57d(2+2H, J=15.8Hz, OCH_2CO), 4.89s(2H, OCH_2CO), 4.90d and 3.38d(2+2H, J=13.2Hz, $ArCH_2Ar$), 4.44d and 3.48d(2+2H, J=13.5Hz, $ArCH_2Ar$), 4.34m and 4.20m(4+2H, OCH_2), 2.85s(3H, N^+CH_3), 1.37t and 1.30t(6+3H, CH_3), Anal.calcd.for $C_{47}H_{49}N_2O_{10}I$ (928.82): C 60.87, H 5.32, N 3.02, Found: C 60.79, H 5.36, N 2.98

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