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Synthesis and characterization of *salen*-type ligands functionalized with pyrrole derivative pendant arms

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ABSTRACT: Several *salen*-type ligands functionalized with two pyrrole derivative pendant arms were prepared. These Schiff base ligands, which differ in the imine bridge, were prepared by a multi-step procedure that includes (i) synthesis of 3-pyrrol-1-ylpropanoic acid, (ii) transformation of the latter compound into the mixed carboxylic–carbonic anhydride (MCCA) intermediate followed by reaction with 2,3-dihydroxybenzaldehyde to give (3-formyl-2-hydroxyphenyl) 3-(pyrrol-1-yl)propanoate and finally (iii) Schiff condensation of the different 1,2-diamines with (3-formyl-2-hydroxyphenyl) 3-(pyrrol-1-yl)propanoate. The key step in the Schiff base ligand preparation is the functionalization of the 2,3-dihydroxybenzaldehyde at the C-3 hydroxyl group without protection of the C-2 hydroxyl group, by a regiospecific acylation of the *ortho*-hydroxyl group via esterification with the mixed carboxylic–carbonic anhydride of 3-pyrrol-1-ylpropanoic acid. The compounds were characterized by elemental analyses, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and FTIR and UV–visible spectrophotometry. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: *Salen*-type ligands; regiospecific acylation; functionalized ligands; pyrrole derivatives; salicylaldehyde

INTRODUCTION

The design of functionalized receptors for the development of potential molecular chemosensors is a field of active research; the sensing function is generally achieved by coupling selective binding sites and signalling subunits.[1–3] *Salen*-type ligands constitute one of the most promising building blocks for the preparation of multifunctional ligands as they are easy to functionalize with receptor groups (crown ethers, calixarenes and cryptands)[4–6] and can coordinate a great variety of transition metal cations which can act as signalling units. Owing to the intrinsic spectroscopic and redox properties of transition metal cations, these functionalized *salen*-type complexes can act as molecular sensors for charged and neutral guests.

We have been interested in the preparation of *salen*-type ligands and N_2O/N_2O_2 Schiff base ligands functionalized with crown ether groups (dibenzo-18-crown-6 and benzo-15-crown-5), which, after transition metal coordination, have acted as hosts for alkali and alkaline earth metal and lanthanide ions in solution[7–9] or as polymeric films deposited on Pt and ITO electrodes.[10] We are now pursuing our work on the design of molecular sensors based on *salen*-type ligands to receptors with mixed O,N coordinating atoms, to extend their recognition properties to softer cations (Cd, Zn and Hg) and to allow for anion interactions. Although crown ethers and other macrocycles are known for their ability to act as efficient and selective hosts for representative cations,[4–7] the homologous open-chain derivatives containing donor atoms can also be extremely effective in this respect.[8,9]

In this paper, we report the preparation of new *salen*-type ligands functionalized at the C-3 of the aldehyde moieties with pendant arms derived from pyrrole. These ligands have two mixed N,O-type coordination sites: one that comprises the N_2(imine)O_2 coordination sphere that is well suited for coordination of transition metal cations, and the other that is composed by the coordinating atoms within the pyrrole derivative pendant arms, which can potentially act as a receptor site for representative cations, lanthanides and also anions. To follow on our work on the design of molecular receptors based on *salen* complexes, these ligands will be used to complex transition metals and the resulting compounds will be screened as molecular receptors for cations and anions.

The pyrrole-based *salen* ligands were prepared using a multi-step procedure that involves a key step, the functionalization of the 2,3-dihydroxybenzaldehyde at C-3 via a regiospecific acylation using a pyrrole-based mixed carboxylic–carbonic anhydride (MCCA) intermediate; within this synthetic approach the C-3 hydroxyl group of 2,3-dihydroxybenzaldehyde could be functionalized without protection of the C-2 hydroxyl group.

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The preparation of MCCA intermediates from the corresponding carboxylic acids and alkyl haloformates is a common method in peptide synthesis[11] and in the preparation of alcohols by reduction using soft conditions.[12] MCCA are useful mediators in soft esterification leading to high product yields, as for example in the preparation of esters of *N*-protected α-amino acids without loss of optical activity.[13] In this work, we prepared the MCCA intermediate from 3-pyrrol-1-ylpropionic acid and reacted it with 2,3-dihydroxybenzaldehyde to obtain a mono-*O*-acylated ester.

In previous work, functionalization of 2,3-dihydroxybenzaldehyde at the C-3 hydroxyl group was performed with protection of the C-2 hydroxyl group by regioselective mono-*O*-alkylation to prevent multi-substitutions;[14] this procedure used 1 equiv. of NaH and allyl bromide and depended on the experimental conditions, such as pH (alkaline), solvent and alkylating agent.[14,15] In the present work, the C-3 functionalization of the same salicylaldehyde was effected under mild conditions, using a straightforward methodology, with no need for C-2 hydroxyl protection, by using regiospecific mono-*O*-acylation via an MCCA pyrrole based intermediate.

RESULTS AND DISCUSSION

Salen-type ligands with two $OC(O)CH_2CH_2NC_4H_4$ pendant arms were prepared in a multi-step procedure as depicted in Scheme 1. In the first step, the pyrrole precursor derivative 3-pyrrol-1-ylpropanoic acid (**I**), was prepared by reaction of 3-pyrrol-1-ylpropionitrile with sulfuric acid in presence of sodium hydroxide. This compound was converted into the corresponding MCCA intermediate by treatment with triethylamine and ethyl chloroformate following the methodology described by Kim *et al.*;[13] the MCCA intermediate, which was not isolated, was reacted directly with 2,3-dihydroxybenzaldehyde, giving (3-formyl-2-hydroxyphenyl) 3-(pyrrol-1-yl)propanoate in 60% yield.[16,17] No protection of the C-2 hydroxyl group was needed to prevent its functionalization, as the MCCA intermediate induces the regiospecific acylation of the C-3 hydroxyl group; moreover, the predicted keto–enol tautomerism involved in 2,3-dihydroxybenzaldehyde also contributed to a more effective functionalization at C-3 due to the higher nucleophilic character of this hydroxyl group compared with the more hindered C-2 hydroxyl group.

Schiff condensation of (3-formyl-2-hydroxyphenyl) 3-(pyrrol-1-yl)propanoate with the diamines *meso*-1,2-diphenylethylenediamine, 4,5-dimethyl-1,2-phenylenediamine and 4,5-dichloro-1,2-phenylenediamine gives the corresponding ligands H_2-[1,2-diphenylethylenebis(3-oxyethylpyrrole)salicylideneimine] (**III**), H_2-[1,2-(4,5-dimethyl)phenylenebis(3-oxyethylpyrrole)salicylideneimine] (**IV**) and H_2-[1,2-(4,5-dichloro)phenylenebis(3-oxyethylpyrrole)salicylideneimine] (**V**).

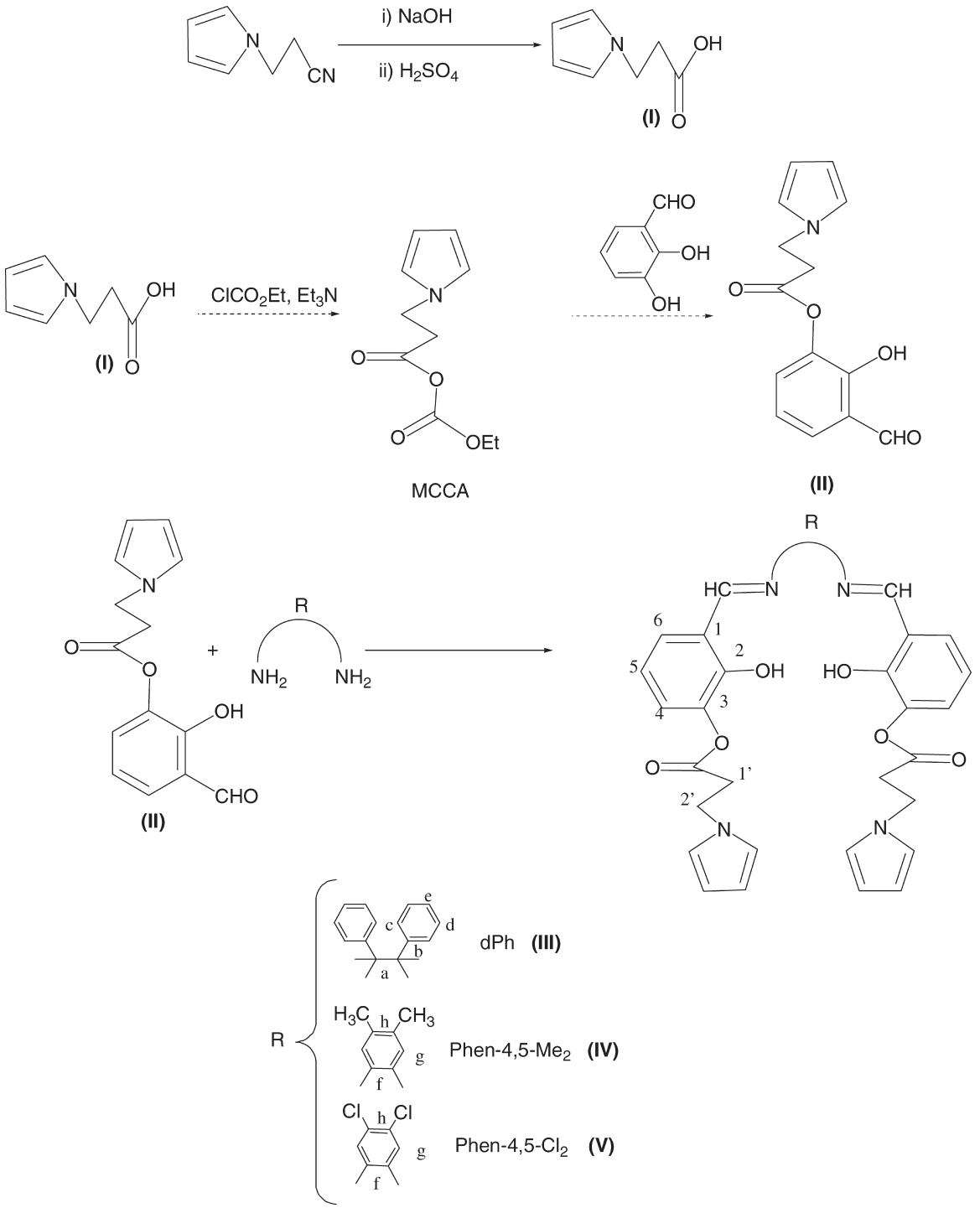
The precursor compound **I** was characterized by ^{1}H NMR spectroscopy to confirm its structure and the functionalized salicylaldehyde **II** was characterized by ^{1}H NMR and mass spectrometry (EI). The new pyrrole-based *salen* ligands **III–V** were characterized by elemental analyses, ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry [fast atom bombardment (FAB)] and FTIR and UV–visible spectrophotometry. All data are summarised in the Experimental section.

The mass spectrum [electron ionization (EI)] of (3-formyl-2-hydroxyphenyl) 3-(pyrrol-1-yl)propanoate (**II**) reveals the presence of an intense peak corresponding to the molecular ion M^+, whereas for those of Schiff base ligands (**III–V**) (FAB) a peak due to $[M+H]^+$ was observed. The mass spectra of **II** and those of **III–V** reveal similar fragmentation profiles: the spectrum of **II** evidences a peak at *m/z* 122 due to the $C_4H_4NCH_2CH_2CO$ fragment and the spectra of **III–V** show peaks corresponding to $[M - C_4H_4NCH_2CH_2CO + H]^+$ and $[M - 2C_4H_4NCH_2CH_2CO + H]^+$. The high-resolution mass spectra of the Schiff base ligands confirm the proposed structures.

The presence of a resolved singlet with δ between 8.67 and 8.10 ppm assigned to the two C(H)═N protons in the ^{1}H NMR spectra of **III–V** confirms the Schiff condensation reaction between the diamines and the aldehyde group of (3-formyl-2-hydroxyphenyl) 3-(pyrrol-1-yl)propanoate (**II**). For **III–V**, a singlet due to the C-2 OH proton is observed in the range 13.57–12.87 ppm; it is worth noting that the OH chemical shift is strongly increased in these compounds compared with **II**, suggesting the presence of hydrogen bonding with the oxygen atoms of the pendant arms.

For all compounds the pyrrole aromatic protons constitute an AA′XX′ system and therefore δ values were measured at the middle of each multiplet.[18] The protons in the $\alpha\alpha'$ position with respect to N (δ in the range 6.67–6.74 ppm) are more deshielded than those in the $\beta\beta'$ position (δ in the range 6.14–6.22 ppm); **III** shows the highest δ value and **V** the lowest. The CH_2CH_2 group in each pendant arm gives two triplets, with the group in the $\alpha\alpha'$ position with respect to N being more deshielded (δ in the range 4.40–4.26 ppm) than that in $\beta\beta'$ position (δ in the range 3.14–3.00 ppm); as observed before, **III** shows the highest δ value and **V** the lowest.

As regards the phenyl group substituted in at position 1 by CH═O or CH═N (**II** and **III–V**, respectively), at position 2 by OH and at position 3 by an OCO pendant group, H-5 behaves as a real triplet and is the more shielded, H-6 [*ortho* to CH═O (**II**) or to CH═N (**III–V**) is the more deshielded and H-4 (*ortho* to the OCO pendant group) is at an intermediate position;[18] both H-4 and H-6 give a doublet of doublets. Compound **II** when compared with **III–V** shows all the δ at higher values, indicating that the Schiff condensation with the diamines has introduced some electron density within the phenyl



Scheme 1. Multi-step procedure used in the preparation of *salen*-type ligands functionalized with pyrrole derivative pendant arms

moieties. On comparing the Schiff bases, **III** shows the more shielded H-4–H-6 protons.

For the aromatic protons in the imine bridge, a singlet is expected for **IV** and **V** at 7.06 and 7.33 ppm, respectively; the two different values are a consequence of the electron-donating properties of the methyl groups (lower δ) in opposition to the withdrawing properties of the chloride atoms (higher δ). In **III**, *ortho* and *meta* protons of the phenyl imine bridge appear at 7.30, *para* protons at 7.00 ppm and the methine protons at 4.70 ppm.

The ^{13}C NMR spectra of the Schiff base ligands (**III**–**V**) also confirm the structure of the synthesized compounds. From the comparison of the three spectra it is possible to make some peak assignments, especially for the resonances at the two limits of the spectra: those which are in the most deshielded region and those ^{13}C

which are more shielded, which in these compounds correspond to aromatic carbon atoms linked to electronegative atoms (O and N) and aliphatic carbons, respectively.[18] In this context we propose the following peak assignments for **III–V**:—^{13}C═O resonance δ at 169.0–169.1 ppm, δ N═^{13}CH in the range 165.5–162.6 ppm, δ^{13}C2–OH at 152.7–153.1 ppm, $^{13}C\beta\beta'$ pyrrole at 108.4–108.5 ppm, in the CH_2CH_2 group of the pendent arm the ^{13}C in the $\alpha\alpha'$ position with respect to N is more deshielded (δ in the range 44.9–44.8) than that in the $\beta\beta'$ position (δ in the range 36.3–36.5). For **III** the ^{13}CH—^{13}CH group in the imine bridge has a resonance peak at 79.8 ppm and **IV** has a resonance peak at 19.6 ppm that can be assigned to $^{13}CH_3$ in the phenyl group of the imine bridge.

In pursuing the assignments of aromatic carbons near electronegative atoms, the peak that appear in **IV** and **V** at the same value, δ 138.7 ppm, and 138.8 ppm for **III**, can be tentatively assigned to ^{13}C3—O—C═O, as the ^{13}C is far from the direct influence of the imine bridge, leading to similar values for all three compounds. The next resonance peaks in the range 139.1–141.2 for **IV** and **V** can be tentatively assigned to ^{13}Cf in the aromatic imine bridge and the peak at 138.4 ppm for **III** can be tentatively assigned to ^{13}Cb in the phenyl ring of the imine bridge.

One more tentative assignment can be made considering the relative intensity of some peaks. In fact, in all three compounds the pyrrole carbons that are $\beta\beta'$ with respect to N are unambiguously assigned at 108.5, 108.4 and 108.5 ppm; four equivalent carbons contribute to these signals. However, in **IV** and **V** there is only one other signal originating from four equivalent carbons, which corresponds to the pyrrole carbons that are $\alpha\alpha'$ with respect to N and its intensity must be very similar to those of the 108.4 and 108.5 ppm signals and, therefore, higher than all other signals of these compounds, which originate from two equivalent carbons. In this context, the peaks with the highest intensity, that match that of $^{13}C\beta\beta'$-pyrrole, appear at exactly the same value for both compounds, 120.6 ppm, and can be tentatively assigned to $^{13}C\alpha\alpha'$-pyrrole. Once these assignments have been made, the corresponding signal in **III** can be assigned since it will appear at a very similar position: 120.7 ppm. Finally, the other peaks that appear in the range 135–105 ppm can not be unambiguously assigned separately and include all the others aromatic carbons.

The IR spectra of **III–V** show the C═O (pendant arm) and C═N(imine) bond stretching vibrations in the regions 1762–1756 and 1628–1614 cm^{-1} respectively;[19] the latter values are similar to those observed for other *salen*-type ligands with similar imine bridges.[7–9] It is also possible to observe one band due the C–H out-of-plane bending of pyrrole in the range 730–723 cm^{-1}.[19] No bands due to NH_2 stretching vibrations are present, thus confirming that Schiff condensation took place between the diamines and functionalized salicylaldehyde.

There is a decrease in the frequency of C═N(imine) bond stretching vibration on going from **III** to **V**; this variation suggests a decrease in the electronic density of the C═N(imine) bond, induced by the electronic properties of the different imine bridges.

Electronic spectra of the functionalized Schiff base ligands (**III–V**) show high-intensity bands in the range $\lambda = 260–370$ ($\varepsilon = 29\,000–8000\ dm^3\ mol^{-1}\ cm^{-1}$) and a medium-intensity shoulder at $\lambda = 410–460$ nm ($\varepsilon = 340–350\ dm^3 mol^{-1} cm^{-1}$), which are assigned to $\pi^* \rightarrow n$ and to $\pi^* \rightarrow \pi$ transitions within the aromatic moieties.[20] As observed in the IR spectra, there is a small shift of all bands towards lower energies on going from **III** to **V**, a consequence of the electronic effects of the different imine bridge substituents.

CONCLUSIONS

Three new *salen*-type ligands functionalized with pyrrole derivative arms, which differ in the imine bridge, were prepared using a new and facile methodology that involves the C-3 hydroxyl functionalization of 2,3-dihydroxybenzaldehyde with pyrrole derivatives without any protection step for the C-2 hydroxyl group of the same aldehyde moiety.

The spectroscopic characterization of the ligands has shown that the different imine bridges, which have different electronic properties, have an effect on the electronic density distribution within the ligand. This aspect is of great importance for the ultimate goal of these compounds, which is to act as hosts for representative cations, lanthanides and anions, after their complexation by transition metal ions. Their electronic/structural properties will be enhanced by coordination of transition metal complexes and will determine the extent of interaction between the target species and the host, thus determining their efficiency and selectivity as molecular chemosensors. We are now preparing and characterizing their respective transition metal complexes.

EXPERIMENTAL

All solvents were obtained from Merck and all other reagents from Aldrich; all were used as received. Elemental analyses (C, H, N) were performed at the Micro Analytical Laboratory, Department of Chemistry, University of Manchester (UK), and EI and FAB mass spectra were measured at the Facultad de Química, Universidad de Santiago de Compostela (Spain), using 3-nitrobenzylalcohol (NBA) as matrix (FAB). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with a Bruker DRX-300 instrument at the Departamento de Química, Universidade de Aveiro (Portugal); chemical shifts are reported in ppm referred to TMS as internal standard. IR spectra in the 400–4000 cm^{-1} region were recorded on a

Biorad FTS 155 instrument using KBr pellets or Nujol mulls. UV–visible spectra were recorded with a Unicam UV-2 instrument in the range 250–600 nm, using quartz cells with a 1 cm optical path; acetonitrile solutions of the Schiff base ligands with concentration between 1.00×10^{-3} and 4.00×10^{-5} mol dm^{-3} were used.

Syntheses

3-Pyrrol-1-yl-propanoic acid (**I**): 3-pyrrol-1-ylpropionitrile (11.83 g; 0.098 mol) and a solution of NaOH (5 mol dm^{-3}) in water (79 cm^3) were stirred for 8 h, at room temperature, under an argon atmosphere. Concentrated sulfuric acid was added to the mixture until pH3. The mixture was extracted with diethyl ether and the extract dried over $MgSO_4$. The resulting solution was concentrated and *n*-hexane was added. After cooling, 3-pyrrol-1-ylpropionic acid (**I**) was obtained as yellow crystals, which were washed with *n*-hexane and dried under vacuum. Yield 10.92 g (80.1%). ^{1}H NMR ($CDCl_3$): δ 6.68 (m; 2H; $\alpha\alpha'$-pyrrole), 6.16 (m; 2H; $\beta\beta'$-pyrrole), 4.22 (t; 2H; C2′H_2), 2.84 (t; 2H; C1′H_2).

(3-Formyl-2-hydroxyphenyl) 3-(pyrrol-1-yl)propanoate (**II**): under an argon atmosphere, triethylamine (8.0 cm^3, 0.057 mol) was added to 3-pyrrol-1-ylpropanoic acid (**I**) (8.79 g; 0.063 mol) in dried CH_2Cl_2 at −17 °C. Ethyl chloroformate (5.4 cm^3; 0.056 mol) in dried CH_2Cl_2 was added slowly to the solution, under an argon atmosphere, with stirring, at −17 °C during 30 min; then a solution of 2,3-dihydroxybenzaldehyde (7.15 g; 0.052 mol) in dried CH_2Cl_2 was added. The mixture was kept between −17 and −13 °C for 1 h, at −3 °C during 1.5 hours and finally at room temperature, with stirring, for 20 h under an argon atmosphere. The mixture was extracted with water and the organic layer was washed with a saturated aqueous solution of $NaHCO_3$. The organic layer was dried with $MgSO_4$, the solvent was evaporated and the solid (3-formyl-2-hydroxyphenyl) 3-(pyrrol-1-yl)propanoate (**II**) was obtained. Recrystallization from acetone afforded the expected white solid. Yield 6.72 g (50.0%). MS (EI) *m*/*z* (%): 259 (M^+, 50%). ^{1}H NMR ($CDCl_3$): δ 11.13 (s; 2H; *H*O), 9.93 (s; 2H; C*H*O), 7.49 (m, 2H, C6-*H*), 7.25 (m; 2H; C4-*H*), 7.02 (t, 2H, C5-*H*), 6.74 (m; 2H; $\alpha\alpha'$-pyrrole), 6.18 (m; 2H; $\beta\beta'$-pyrrole), 4.35 (t; 2H; C2′H_2), 3.09 (t; 2H; C1′H_2).

H_2-[1,2-diphenylethylenebis(3-oxyethylpyrrole)salicylideneimine] (**III**): to a solution of *meso*-1,2-diphenylethylenediamine (1.38 g; 0.0065 mol) in methanol was added a solution of (3-formyl-2-hydroxyphenyl) 3-(pyrrol-1-yl)propanoate (**II**) (3.37 g; 0.013 mol) in $CHCl_3$. The resulting yellow solution was refluxed for 1.5 h to afford a yellow solid, which was filtered under reduce pressure, recrystallized from acetone and dried under vacuum. Yield 3.98 (88.1%). Anal. Calcd for $C_{42}H_{38}N_4O_6$: C, 72.60; H, 5.51; N, 8.07. Found: C, 71.90; H, 5.65; N, 7.88% MS (FAB) *m*/*z* (%): 695 (M^+, 20%); high resolution: 695, $C_{41}{}^{13}CH_{38}N_4O_6$, found 695.283506; calc. 695.282490. ^{1}H NMR ($CDCl_3$, ppm): δ 13.54 (s; 2H; *H*O), 8.10 (s; 2H; N═C*H*), 7.30 (m, 2H, C6-*H*), 7.04 (m; 2H; C4-*H*), 7.30 (m, 8H, Cc,d-*H*), 7.00 (m, 2H, Ce-*H*), 6.83 (t, 2H, C5-*H*), 6.79 (m; 4H; $\alpha\alpha'$-pyrrole), 6.22 (m; 4H; $\beta\beta'$-pyrrole), 4.75 (s, 2H, Ca-*H*), 4.40 (t; 4H; C2′H_2), 3.14 (t; 4H; C1′H_2). ^{13}C NMR ($CDCl_3$, ppm): δ 169.1 (s; ^{13}C═O), 165.5 (s; N═^{13}CH), 152.7 (s; arom ^{13}C2-OH), 138.8 (s, arom ^{13}C3-OCO), 138.4 (s, arom ^{13}Cb), 129.2 (s, arom ^{13}C), 128.7 (s, arom ^{13}C), 128.1 (s, arom ^{13}C), 128.0 (s, arom ^{13}C), 125.7 (s, arom ^{13}C), 120.7 (s, $^{13}C\alpha\alpha'$-pyrrole), 119.8 (s, arom ^{13}C), 118.2 (s, arom ^{13}C), 108.5 (s, $^{13}C\beta\beta'$-pyrrole), 79.8 (s, ^{13}Ca), 44.9 (s, $^{13}C2'H_2$), 36.4 (s, $^{13}C1'H_2$). IR (KBr) ν (cm^{-1}): 3463 (br), 3135, 3103, 3055, 3025, 2930, 2895, 1754, 1628, 1586, 1498, 1463, 1422, 1365, 1343, 1283, 1269, 1234, 1200, 1149, 1092, 1073, 1034, 982, 928, 876, 854, 823, 787, 769, 750, 727, 705, 606, 577, 551, 530, 506, 434. UV–visible (CH_3CN) λ_{max} (nm) (ε (dm^3 mol^{-1} cm^{-1})): 260 (28 220), 320 (8050), 414 sh (340).

H_2-[1,2-(4,5-dimethyl)phenylenebis(3-oxyethylpyrrole)salicylideneimine] (**IV**): this compound was prepared using the procedure described for **III**, but using a methanolic solution of 4,5-dimethyl-1,2-phenylenediamine (0.44 g; 0.0033 mol) and a solution of (3-formyl-2-hydroxyphenyl) 3-(pyrrol-1-yl)propanoate (**II**) (1.69 g; 0.0065 mol) in $CHCl_3$. The resulting light-orange solid was collected by filtration, recrystallized from methanol, washed with diethyl ether and dried under vacuum. Yield 0.81 g (40.0%). Anal. Calcd for $C_{36}H_{34}N_4O_6$: C, 69.89; H, 5.54; N, 9.06. Found: C, 69.68; H, 5.75; N, 8.86%. MS (FAB) *m*/*z* (%): 619 ($[M+H]^+$, 100%); high resolution: 619, $C_{36}H_{35}N_4O_6$, found 619.257389; calc. 619.255660. ^{1}H NMR ($CDCl_3$): δ 13.57 (s; 2H; O*H*), 8.67 (s; 2H; N═C*H*), 7.32 (m, 2H, C6-H), 7.11 (m; 2H; C4-*H*), 7.06 (s, 2H, Cg-*H*), 6.92 (t, 2H, C5-*H*), 6.75 (m; 4H; $\alpha\alpha'$-pyrrole), 6.18 (m; 4H; $\beta\beta'$-pyrrole), 4.31 (t; 4H; C2′H_2), 3.05 (t; 4H; C1′H_2), 2.36 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 169.0 (s; ^{13}C═O), 162.6 (s; N═^{13}CH), 153.1 (s; arom ^{13}C2-OH), 139.1 (s, arom ^{13}Cf), 138.7 (s, arom ^{13}C3-OCO), 136.8 (s, arom ^{13}C), 129.9 (s, arom ^{13}C), 126.1 (s, arom ^{13}C), 121.1 (s, arom ^{13}C), 120.6 (s, $^{13}C\alpha\alpha'$-pyrrole), 120.5 (s, arom ^{13}C), 118.4 (s, arom ^{13}C) 108.4 (s, $^{13}C\beta\beta'$-pyrrole), 44.8 (s, $^{13}C2'H_2$), 36.3 (s, $^{13}C1'H_2$), 19.6 (s, $^{13}CH_3$). IR (KBr) ν (cm^{-1}): 3453 (br), 3096, 2919, 1762, 1746, 1617, 1574, 1496, 1450, 1410, 1382, 1363, 1283, 1230, 1187, 1144, 1088, 1068, 1043, 1015, 978, 925, 879, 853, 831, 777, 750, 735, 723, 701, 614, 564, 482, 425. UV–visible (CH_3CN) λ_{max} (nm) (ε (dm^3 mol^{-1} cm^{-1}): 268 (17 015), 332 (14 530), 368 (9635), 455 sh (345).

H_2-[1,2-(4,5-dichloro)phenylenebis(3-oxyethylpyrrole) salicylideneimine] (**V**): this compound was synthesized following the procedure described for **III**, but using a methanolic solution of 4,5-dichloro-1,2-phenylenediamine (0.73 g; 0.0041 mol) and a solution of (3-formyl-

2-hydroxyphenyl) 3-(pyrrol-1-yl)propanoate (**II**) (2.14 g; 0.0082 mol) in $CHCl_3$. The resulting brown solid was collected by filtration, recrystallized from acetonitrile and dried under vacuum. Yield 0.93 g (34.2%). Anal. Calcd for $C_{34}H_{28}N_4O_6Cl_2$: C, 61.92; H, 4.28; N, 8.49. Found: C, 61.31; H, 4.22; N, 8.46% MS (FAB) *m/z* (%): 659 ($[M+H]^+$, 45%); high resolution: 659, $C_{34}H_{29}N_4O_6Cl_2$, found 659.146714; calc. 659.146415. ^{1}H NMR ($CDCl_3$): δ 12.87 (s; 2H; O*H*), 8.60 (s; 2H; N═C*H*), 7.33 (s, 2H, Cg-*H*), 7.30 (m, 2H, C6-*H*), 7.11 (m; 2H; C4-*H*), 6.91 (t, 2H, C5-*H*), 6.70 (m; 4H; $\alpha\alpha'$-pyrrole), 6.14 (m; 4H; $\beta\beta'$-pyrrole), 4.26 (t; 4H; C2′H_2), 3.00 (t; 4H; 1′1′, C1′H_2). ^{13}C NMR ($CDCl_3$, ppm): δ 169.0 (s; ^{13}C═O), 164.5 (s; N═^{13}CH), 153.0 (s; arom ^{13}C2-OH), 141.2 (s, arom ^{13}Cf), 138.7 (s, arom ^{13}C3-OCO), 131.3 (s, arom ^{13}C), 130.3 (s, arom ^{13}C), 127.5 (s, arom ^{13}C), 121.5 (s, arom ^{13}C), 120.6 (s, $^{13}C\alpha\alpha'$-pyrrole), 120.0 (s, arom ^{13}C), 118.9 (s, arom ^{13}C), 108.5 (s, $^{13}C\beta\beta'$-pyrrole), 44.8 (s, $^{13}C2'H_2$), 36.3 (s, $^{13}C1'H_2$). IR (KBr) ν (cm^{-1}): 3133, 3094, 2949, 2869, 1762, 1748, 1614, 1583, 1566, 1550, 1499, 1462, 1399, 1362, 1283, 1244, 1214, 1197, 1147, 1092, 1069, 1012, 985, 972, 955, 924, 887, 874, 851, 785, 763, 738, 730, 716, 679, 616, 557, 535, 424. UV–visible (CH_3CN) λ_{max} (nm) (ε ($dm^3\,mol^{-1}\,cm^{-1}$)): 274 (32 870), 338 (23 220).

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