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Cu(I) and Zn(II) chelations on polymer beads modified by attachment of a bipyridyl-calixarene-based chelate

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ABSTRACT

A new chelating calix[4]arene derivative incorporating two bipyridyl groups and one primary amino attachment function at the lower rim has been synthesised and coupled to Wang benzaldehyde resin. The new material effectively displayed complexation abilities towards Cu(I) and Zn(II) transition metal cations. The grafting efficiency was evaluated and quantified by complexation experiments, using UV/visible spectrophotometry, and ionic chromatography.

Copper and zinc are common metals widely employed in house roofs and rain collectors, prone to atmospheric aggression, dissolution by rain and introduction as salts in local watersheds.[1] Collecting these ions before dilution in waterways can be of high environmental concern. This may involve solid phase extraction, notably with polymeric materials designed as metal sequestering agents. Some recent works deal, for example, with chitosan grafted with 8-hydroxyquinolein groups,[2] polystyrene grafted with 6-mercaptopurinylazo[3] or aminosulfonyl[4] groups, amidoxime-, amidrazone- or oxazoline-derivatives of polyacrylonitrile,[5] Merrifield or poly(glycidylmethacrylate) resins grafted with various pyridyl derivatives[6] or silica-gel coated with terpyridine-norbornene block-copolymers.[7] Polymers supporting pre-organised complexing units have also been studied. For example, glycidyl(polymethacrylates incorporating carboxymethylated pentaethylene hexamine,[8] or various polyaza/thia/oxa-crown ethers[9] have been recently described. Aza-crowns were also attached to silica-gel for similar purpose.[10]

Due to the possibilities they offer in terms of structural and functional modifications, the calixarene platforms are subjected to intense investigations in particular for the building of highly organised metal chelators, with objectives of separation, purification, waste depollution and evaluation/use of various metal-centred properties.[11] Some of these contributions are devoted to polymerised or polymer-grafted calixarene derivatives. For the latter, recent examples deal with covalent attachment of various calix[4]arene podands for preconcentration/separation of various metal ions: including copper and zinc, on chitosan;[12] including copper but not zinc, on Merrifield resin derivatives,[13] polystyrene,[14] chitosan,[15] cellulose,[16] dextran[17] and silica-gel.[18]

It has been shown that calixarene derivatives integrating two 2,2′-bipyridine chelating units in alternate positions of the lower rim gave tetrahedral mononuclear complexes with Cu(I) salts and zinc triflate, and a dinuclear species with zinc chloride.[19] With the objective of developing extracting polymers incorporating such calixarene-bipyridyl units, we describe in the present report (i) the synthesis of a new bifunctional calix[4]arene species, aimed at complex ions with tetrahedral coordination geometry and incorporating for this purpose two 6-methylene-[6′-methyl-2,2′-bipyridine]yl arms in alternate position of the lower rim, and a *p*-aminoethyl-phenoxypropyl attachment group on one of the two residual phenol units; (ii) the grafting of this compound on Wang-benzaldehyde resin; and (iii) the simultaneous evaluation of grafting efficiency and some complexation properties towards copper(I) and zinc(II) species of the new materials, using UV/visible spectrophotometry and ionic chromatography.

The bis-bipyridyl calix[4]arene **1**, prepared according to the literature,[20] was reacted with (*p*-boc-aminoethyl)phenyl-(3-bromopropyl)ether[21] in dry DMF and NaH, to give the podand **2** with a yield of 80%. The Boc-protective group was removed by treatment

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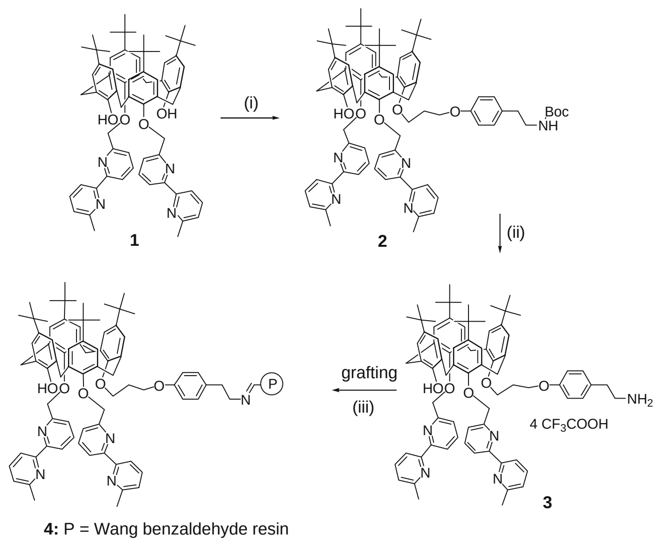
of **2** with TFA in CH_2Cl_2, to give the salt **3** with a yield of 90% (Scheme 1).

The two new intermediates **2** and **3** gave satisfactory analyses, in accordance with the proposed formulas. ^1H and ^{13}C NMR showed that they are in the cone conformation, the necessary condition for exhibiting the expected complexation properties.[22] The functional polymer **4** was prepared by stirring the Wang benzaldehyde resin, the amine salt **3** and NEt_3 in toluene at 50 °C under argon, during 48 h. The time of reaction was evaluated by the observation of colouration of an aliquot of resin after treatment by a Cu(I) salt.

The grafting yield was first appreciated by elemental analysis. Taking into account the concentration of CHO groups available in commercial Wang benzaldehyde resin (3.0×10^{-3} mol g^{-1}), its general formula was evaluated to be $C_{69.8}H_{66.2}O_6$, resulting in calculated proportions of 83.70% C, 6.60% H and 0.00% N. The combustional analysis afforded approaching values, with 83.20% C, 6.65% H and 0.00% N. The polymer **4** gave in this case 80.71% C, 6.36% H and 0.58% N. The grafting was confirmed by the presence of N, the proportion of which corresponds at least to 41.4×10^{-3} mol of N, or to 8.3×10^{-3} mol (5 available N atoms), that is, 9.8 g of calixarene subunit (free base of **3**, MW = 1189.7) in 100.0 g of **4**. The mass of corresponding starting polymer was thus evaluated at 90.2 g. Relating the number of calixarene subunits to the number of initially available CHO sites gave a grafting yield of 3.1%.

A mass gain of 0.073 g was observed with a 0.5 g Wang resin sample. The latter, treated in similar conditions but without **3** and NEt_3, lost 0.021 g of the substance. Considering this loss to be recurrent, the mass of grafted calixarene in polymer **4** was evaluated to be 0.094 g, corresponding to a grafting yield of 5.5%.

Before extraction experiments, the complexation abilities of the calixarene subunit were evaluated in solution by UV/visible spectroscopy with the organosoluble derivative **2**, expecting a similar behaviour in polymer **4**. By analogy with similar ligands,[19] **2** should give tetrahedral mononuclear complexes with Cu(I) salts and zinc triflate, and a dinuclear species with zinc chloride. As shown in Figure 1, the addition of $Cu(MeCN)_4PF_6$ to a solution of **2** in CH_2Cl_2 resulted in the bathochromic shift of the bipyridyl transitions from 290 nm to 302 nm, with an isosbestic point at 296 nm, and the appearance of the expected MLCT (Metal-to-Ligand Charge Transfer) band at ca. 445 nm; the evolution of the spectrum was completed at 1 equiv of metal salt, confirming the expected ML stoichiometry.



Scheme 1. Reagents and conditions: (i) NaH, (*p*-boc-aminoethyl)phenyl-(3-bromopropyl)ether, DMF, 80%; (ii) TFA, CH_2Cl_2, 90%; (iii) Wang benzaldehyde resin, NEt_3, toluene, 50 °C.

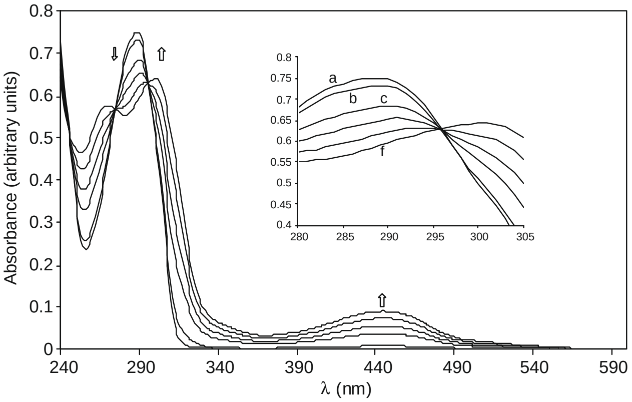


Figure 1. UV/vis titration of **2** by $Cu(MeCN)_4PF_6$ in CH_2Cl_2. [**2**] = 1.6×10^{-5} M, [Cu(I)] = 3.85×10^{-4} M, $V_{aliquot}$ = 12.4 µL. (a) Free **2**; (b) **2** + 0.1 equiv Cu(I); (c) to (f)): **2** + 0.4–1.0 equiv Cu(I).

The addition of $ZnCl_2$ to a solution of **2** in CH_2Cl_2 resulted in the bathochromic shift of the bipyridyl transitions from 291 nm to 309 and 320 nm, with two isosbestic points at 299 nm then at 301 nm; the evolution of the spectrum was completed at 2 equiv of metal salt, resulting in the expected M_2L stoichiometry (Fig. 2).[19]

Finally, and as shown in Figure 3, the addition of $Zn(OTf)_2$ to a solution of **2** in CH_2Cl_2 showed a similar bathochromic shift from 291 nm to 308 nm, with one isosbestic point at 302 nm; the evolution of the spectrum was completed at 1 equiv of metal salt, resulting as expected in an ML stoichiometry.[19]

Taking into account that these stoichiometries should be conserved with polymer **4**, the extraction experiments were carried out against CH_2Cl_2 solutions of $Cu(MeCN)_4PF_6$, $Zn(CF_3SO_3)_2$ and $ZnCl_2$ salts. The evaluation of the grafting yield, ion extraction capacity and extraction kinetic was performed by direct metal-extraction method, followed by quantification of residual metal salt. This was done by UV/visible-monitored complexation by 6,6′-dimethyl-2,2′-bipyridine (dmbp) for Cu(I) and Zn(II), and by ionic chromatography for Zn(II). In these conditions, no uptake of copper or zinc salts was observed with the commercial Wang resin. The typical experiment and calculation mode are presented hereafter.

UV/visible titration by 6′6′-dimethyl-2,2′-bipyridine (dmbp): A fixed volume of a CH_2Cl_2 salt solution, at a defined concentration, was mixed to a known mass of polymer **4**, and shaken in a gas-tight vial. A fixed volume of supernatant (0.3 mL for Cu(I) and 0.1 mL for

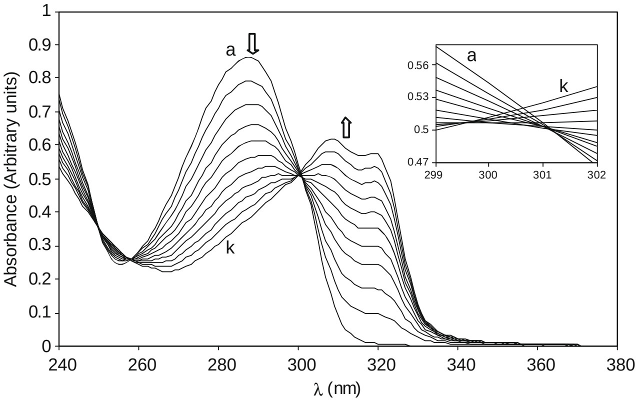


Figure 2. UV/vis titration of **2** by $ZnCl_2$ in CH_2Cl_2. [**2**] = 1.76×10^{-5} M, [Zn(II)] = 4.8×10^{-4} M, $V_{aliquot}$ = 11 µL. (a) Free **2**; (b) to (k) **2** + 0.2–2 equiv $ZnCl_2$.

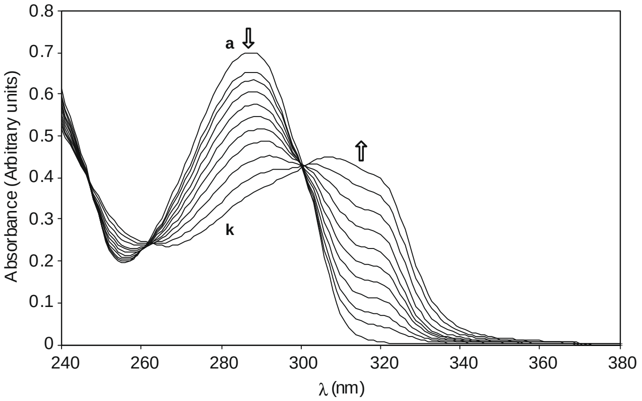


Figure 3. UV/vis titration of **2** by Zn(OTf)$_2$ in CH$_2$Cl$_2$. [**2**] = 1.6 × 10^{-5} M, [Zn(II)] = 3.85 × 10^{-4} M, V_{aliquot} = 12.4 μL. (a) Free **2**; (b) to (k) **2** + 0.1–1 equiv Zn(TfO)$_2$.

Zn(II)) was collected at regular times, and was diluted by addition of CH$_2$Cl$_2$ (2.0 mL) before UV/visible data collection. The final metal concentration in the UV cell was about 5.0 × 10^{-5} M for Cu(I), and about 2.8 × 10^{-5} M for Zn(II), in order to respect the Beer–Lambert law (absorbance <1) at the selected wavelength (455 nm for Cu(I) and 320 nm for Zn(II)). The concentration of residual metal salt was evaluated by titration with a 4.95 × 10^{-4} M solution of dmbp, on the assumption of the formation of an M:(dmbp)$_2$ complex with CuPF$_6$ (survey at 455 nm, MLCT, = ca. 5800 mol^{-1} L cm^{-1})[23,24] and Zn(TfO)$_2$ (survey at 320 nm) and an MCl$_2$:dmbp complex with ZnCl$_2$ (survey at 320 nm).[25] This titration was done for each sampling, until stabilisation of the residual metal concentration occurred (ca. 100–240 min).

The amount of fixed metal ion was thus deduced, giving, on the assumption of ML and M$_2$L stoichiometries extrapolated from Figures 1–3, the amount of grafted calixarene ligand. From this step, the calculation mode of grafting yield was similar to the one employed with the elemental analysis. The results obtained for the three salts of the study are given in Table 1. The UV/visible kinetics of extraction of CuPF$_6$, Zn(CF$_3$SO$_3$)$_2$ and ZnCl$_2$ extractions are illustrated in Figures 4 and 6.

Ion chromatography titration was performed with indirect spectrophotometric detection (λ = 220 nm) on a Zorbax 300 SCX column (5 μm, 250 × 4.6 mm), using a 2.0 mM CuSO$_4$ water solution at 3.0 mL/min as mobile phase. A 100 μL injection loop was used and calibration was performed on aqueous solutions of Zn(TfO)$_2$ or ZnCl$_2$ ranging from 1.0 to 6.0 × 10^{-4} M (r^2 >0.99). The Zn(II) ion was detected in these conditions with a retention time of 4.1 min. The working solutions were the same as those used for Zn(II) UV/visible titration experiments. A fixed volume of supernatant (0.2 mL) was collected at regular times, and was evaporated to dryness. The residue was dissolved in water (0.2 mL) before injection. A typical chromatogram for ZnCl$_2$ is given in Figure 5A, showing the water and chloride void volume peak

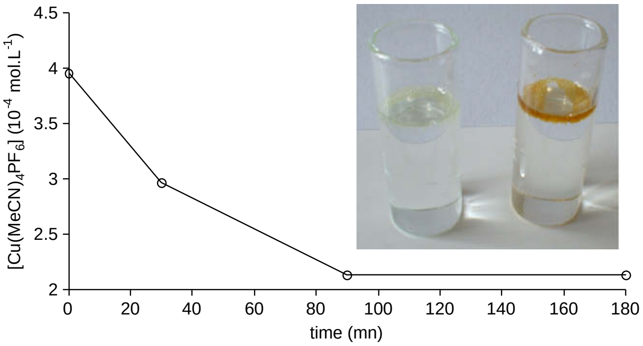


Figure 4. Complexation kinetics of Cu(I) on polymer **4**. Titration of residual Cu(MeCN)$_4$PF$_6$ by UV/vis spectroscopy (dmbp 4.95 × 10^{-4} mol L^{-1} in CH$_2$Cl$_2$,455 nm). Image: polymer 4 before addition of Cu(I) salt (left) and at the end of extraction (right).

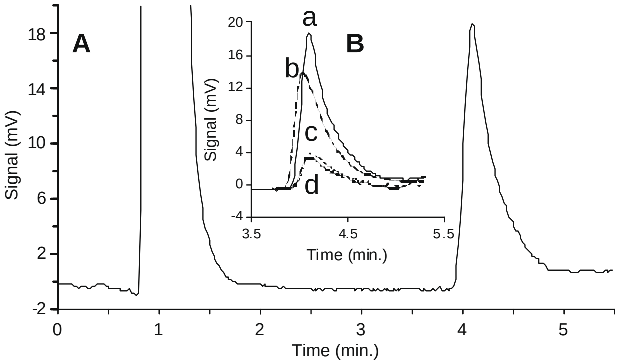


Figure 5. (A) Typical ionic chromatogram obtained with a ZnCl$_2$ solution (5.7 × 10^{-4} M), and (B) decrease of the Zn(II) peak as a function of the contact time with polymer **4** (a, b, c and d: 0, 15, 30 and 240 min).

Table 1

Data collection for the evaluation of the grafting yield in resin **4**, and determination of its extraction capabilities towards Cu(I) and Zn(II) salts

Titration method	UV/visible			Ionic chromatography	
Metal salt	CuPF$_6$	Zn(TfO)$_2$	ZnCl$_2$	Zn(TfO)$_2$	ZnCl$_2$
Figures	4	6	6	6	6
[M]$_0$ (10^{-4} mol L^{-1})	3.96	6.20	5.80	5.70	5.70
Volume (10^{-3} L)	10.0	10.0	20.0	10.0	20.0
[M]$_{\text{final}}$ (10^{-4} mol L^{-1})	2.14	4.70	3.50	4.30	3.48
Time (min)	180	240	240	240	240
Number of fixed metal ions (10^{-6} mol)	1.82	1.50	4.60	1.40	4.44
Number of fixed ligand units (10^{-6} mol)	1.82	1.50	2.30	1.40	2.22
Mass of fixed ligand (10^{-3} g)[a]	2.16	1.79	2.73	1.67	2.64
Mass of polymer **4** (10^{-3} g)	10.40	9.60	15.60	9.60	15.60
Mass ratio—loading amount (%)	20.8	18.6	17.5	17.5	16.9
Mass of original polymer (10^{-3} g)	8.24	7.81	12.87	7.93	12.96
Initial number of CHO groups (10^{-5} mol)	2.47	2.34	3.86	2.38	3.89
Grafting yield (%)	7.4	6.4	6.0	6.9	5.7
Mass (g) of metal/kg polymer **4**	11.0	10.2	19.3	9.5	18.6
Mass (g) of salt/kg polymer **4**	36.4	56.7	40.2	53.0	38.9
Moles of salt/kg polymer **4**	0.174	0.156	0.295	0.146	0.285

[a] Molecular weight of **3**, free base form: 1189.7.

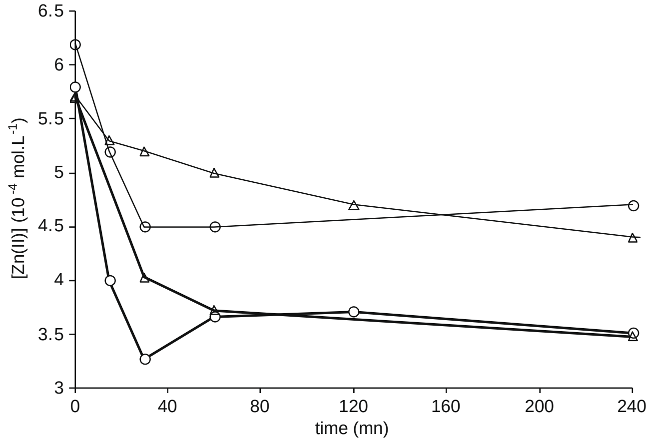


Figure 6. Complexation kinetics of $ZnCl_2$ (broad line) and $Zn(OTf)_2$ (thin line) on functionalised Wang resin **4**. Titration of residual $ZnCl_2$ and $Zn(OTf)_2$ by ionic chromatography (Δ) and UV/vis spectroscopy (dmbp 4.95×10^{-4} mol L^{-1} in CH_2Cl_2, at 320 nm (O)).

at 1.0 min and the expected Zn(II) peak at 4.1 min. The decrease of the residual Zn(II) peak after contact with the grafted polymer **4** is illustrated in Figure 5B from 0 to 240 min (curves a–d).

The concentration of residual Zn(II) ion was directly evaluated from the corresponding peak surface. The calculations were similar to UV/visible titration experiments (Table 1). The ion chromatography kinetics of extraction of $Zn(CF_3SO_3)_2$ and $ZnCl_2$ extractions are illustrated in Figure 6.

One can observe that the amount of complexed $ZnCl_2$ is approximately the double of $Zn(OTf)_2$, in accordance with the expected M_2L and ML stoichiometries. This corresponds, depending on the ligand behaviour of counter-anion (Cl^-: coordinating; TfO^-: non-coordinating), to an extraction capacity of 0.29–0.15 mmol by gram (or 20 to ca. 10 g of pure metal ion by kilogram) for 4. The latter appears thus less efficient than the *N*-sulfonylpolyamine resins described by Jeragh et al. (0.85 mmol g^{-1})[4] or than the 6-mercaptopurinylazo resin of Mondal et al. (0.52 mmol g^{-1}),[3] but equivalent to or better than poly-(*O*-,*S*-)glycidylmethacrylate resins incorporating N,O,S- (0.05–0.13 mmol g^{-1}),[9a] N,O- (0.05 mmol g^{-1})[9b] or N,S-crown ethers (0.10–0.15 mmol g^{-1})[9c] described by Driessen and coll.

As shown in Figure 6, the complexation of zinc salts by resin 4 is achieved between 40 min and 1 h of contact, close to the 14 min described for a 50% uptake by 6-mercaptopurinylazo resin,[3] or 20 min for a 100% uptake by the *N*-sulfonylpolyamine resins mentioned above.[4] No kinetic data were available for the above mentioned crown ether-derived polymers, except a contact time of 48 h.

Even if copper(I) is much less abundant than copper(II), we found interesting to compare, in the limits of their different coordination chemistry, the copper capacities of 4 and other complexing polymers, involving here, *a contrario* to Zn, polymers appended calixarene derivatives. We found that polymer 4 displays a copper capacity of 0.17 mmol g^{-1} (i.e., 11 g of pure metal by kilogram), far from the 6-mercaptopurinylazo resin of Mondal et al. (1.48 mmol g^{-1}),[3] from the *N*-sulfonylpolyamine resins described by Jeragh et al. (1.00 mmol g^{-1}),[4] or from a chitosan-appended nitrilocalixarene described by Tabakci et al. (1.00 mmol g^{-1}),[15b] but close to the poly-(*O*-,*S*-)glycidylmethacrylate resins incorporating N,O,S- (0.13–0.36 mmol g^{-1}),[9a] N,O- (0.00–0.36 mmol g^{-1})[9b] or N,S-crown ethers (0.24–0.36 mmol g^{-1}).[9c]

Finally, we observe that the grafting yield values obtained from extraction experiments are similar, whatever the metal ion or the titration method be, approaching 6.5%. This average value is close to 5.5% calculated from mass gain evaluation, but is the double of the one obtained by elemental analysis (3.1%); taking into account the low amount of nitrogen measured here (0.58%) and the precision of the combustional method (±0.2% by element), we have to consider that the elemental analysis is not pertinent enough for polymer 4.

We have prepared a new polymer including a bis-bipyridyl-calixarene chelating agent aimed at complex metal ions with a tetrahedral coordination geometry. Its demonstrated chelating properties are currently explored in separation studies involving various metal ions of economical or environmental interest.

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22. *Compound* **2**: A mixture of bis-bipyridyl calix[4]arene **1** (0.85 g, 0.84×10^{-3} mol) and NaH (0.034 g at 60% in oil, 0.84×10^{-3} mol) in dry DMF (20 mL) was stirred at rt under Ar during 15 min. The *p*-(bromopropyl)-(*N*-Boc)-tyramine (0.288 g, 0.84×10^{-3} mol) was then added, and stirring was continued during 24 h. The solvent was evaporated to dryness under high vacuum, and the resulting solid was dissolved in CH_2Cl_2 (50 mL); the solution was washed with H_2O (25 mL), dried over Na_2SO_4 and concentrated for

chromatography (Al_2O_3, hexane/CH_2Cl_2 1/1). Compound **2** (0.94 g; 87%). White powder. Mp: 103–104 °C. IR: 1717.9 (COO), 1575.9 (C=N). UV/vis (CH_2Cl_2): 289 (46910). ^{1}H NMR (400 MHz; $CDCl_3$): 0.81 (s, 18H, Me_3C b); 1.29 (s, 9H, Me_3C a or c); 1.30 (s, 9H, Me_3C c or a); 1.39 (s, 9H, Me_3CO); 2.25 (quint, *J* = 7.6 Hz, 2H, $CH_2\mathit{CH}_2CH_2$); 2.58 (s, 6H, *Me*bpy); 2.60 (m, 2H, $C\mathit{H}_2CH_2N$); 3.28 (m, 4H, $CH_2C\mathit{H}_2N + CH_2CH_2C\mathit{H}_2O$-Ar d); 3.85 (t, *J* = 7.8 Hz, 2H, $CH_2CH_2C\mathit{H}_2O$-Ar c); 3.09–4.33 (‘q’, AB, J_{AB} = 13.2 Hz, 4H, Ar-$C\mathit{H}_2$-Ar); 3.24–4.48 (‘q’, AB, J_{AB} = 13.2 Hz, 4H, Ar-$C\mathit{H}_2$-Ar); 4.99 (‘q’, AB, J_{AB} = 12.4 Hz, 4H, $OC\mathit{H}_2$bpy); 5.87 (s, 1H, OH); 6.42 (d, *J* = 8.4 Hz, 2H, Ar*H* d); 6.53 (*br* d, 4H, Ar*H* b); 6.84 (d, *J* = 8.4 Hz, 2H, Ar*H* d); 7.10–7.19 (d + s + s, 6H, H(5’)bpy + Ar*H* a + Ar*H* c); 7.53 (t, *J* = 8.0 Hz, 2H, H(4′)bpy); 7.62 (t, *J* = 7.6 Hz, 2H, H(4)bpy), 7.67 (d, 2H, H(5)bpy); 8.13 (d, *J* = 8.0 Hz, 2H, H(3′)bpy); 8.26 (d, *J* = 7.6 Hz, 2H, H(3)bpy). ^{13}C NMR ($CDCl_3$): 24.63 (*Me*bpy); 28.42 (OC*Me*$_3$); 29.61 (CH_2–CH_2–CH_2); 31.01 (Me_3C Ar b); 31.19 (Ar-$\mathit{C}H_2$-Ar); 31.66, 31.75 (Me_3C Ar a and c); 33.70 ($Me_3\mathit{C}$ Ar b) 33.86, 34.12 ($Me_3\mathit{C}$ Ar c and a); 35.13 ($\mathit{C}H_2CH_2NH$); 41.89 (CH_2CH_2NH); 65.44 ($\mathit{C}H_2OAr$ d); 71.99 ($\mathit{C}H_2OAr$ c); 78.78 ($O\mathit{C}H_2$bpy and $Me_3\mathit{C}O$); 114.35 (C_o Ar d); 118.33 (C(3′)bpy); 120.02 (C(3)bpy); 122.70 (C(5)bpy); 123.19 (C(5′)bpy); 124.87 (C_m Ar a or c); 125.08 (C_m Ar b); 125.59 (C_m Ar a or c); 129.30, 128.32 (C_o Ar a and C_m Ar d); 129.45 (C_p Ar d); 131.82 (C_o Ar b); 132.48, 135.85 (C_o Ar b and C_o Ar c); 137.06 (C(4′)); 137.08 (C(4)); 137.35 (C(4)); 141.59, 145.72 (C_p Ar a and c); 145.60 (C_p Ar b); 150.82 (C_i Ar a); 151.15 (C_i Ar b); 154.02 (C_i Ar c); 155.46, 157.69 (C(2′), C(6′)); 155.84, 156.58 (C(2), C(6)); 157.65 (*C*OO); 157.72 (C_i Ar d). Anal. Calcd for $C_{85}H_{103}N_5O_7$, 0.5 H_2O (1314.79): C, 77.59; H, 7.97; N, 5.32. Found: C, 77.53; H, 7.60; N, 5.44. ES-MS (negative mode): 1288.7 $[M{-}H]^-$; (positive mode): 1290.7 $[M+H]^+$, 1312.7 $[M+Na]^+$, 1328.7 $[M+K]^+$, 645.8 $[M+2\ H]^{2+/2}$, 656.8 $[M+H+Na]^{2+/2}$. *Compound* **3**: The calixarene **2** (0.5 g, 3.8 × 10^{-4} mol) was dissolved in anhydrous CH_2Cl_2 (50 mL) and TFA (1.6 mL) was then added. The resulting yellow mixture was stirred at rt under Ar during 4 h (TLC monitoring, SiO_2, CH_2Cl_2/MeOH:95/5+1 drop NH_4OH) and the solvent was evaporated to give an oily residue. The latter was dissolved in H_2O (40 mL), and the solution was evaporated again to remove excess of TFA. The resulting yellow powder was repeatedly dissolved in CH_2Cl_2 (20 mL) and evaporated, until neutral pH was obtained. Compound **3** (0.41 g; 64%). Light yellow powder. Mp: 145–146 °C. IR: 1513.03 (C=N), 1677.8 (COO). UV/vis (CH_2Cl_2): 290 (44500). ^{1}H NMR (400 MHz; $CDCl_3$): 0.81 (s, 18H, Me_3C b); 1.28 (s, 9H, Me_3C a or c); 1.29 (s, 9H, Me_3C c or a); 2.19 (quint, *J* = 7.3 Hz, $CH_2C\mathit{H}_2CH_2$); 2.58 (s, 6H, *Me*bpy); 2.82 (t, *J* = 7.3 Hz, 2H, $C\mathit{H}_2CH_2N$); 3.07 (t, *J* = 6.8 Hz, 2H, $CH_2C\mathit{H}_2N$); 3.10–3.14 (m, 4H, $CH_2CH_2C\mathit{H}_2O$-Ar d + Ar-$C\mathit{H}_2$-Ar); 3.25,4.49 (‘q’, AB, J_{AB} = 13.2 Hz, 4H, Ar-$C\mathit{H}_2$-Ar); 3.77 (t, *J* = 7.6 Hz, 2H, $CH_2CH_2C\mathit{H}_2O$-Ar c); 3.85 (br s, 3H, $NH_3{}^+$); 4.97 (q, *J* = 11.4 Hz, 4H, $OC\mathit{H}_2$bpy); 6.29 (d, *J* = 8.4 Hz, 2H, Ar*H* d); 6.53 (s, 4H, Ar*H* b); 6.86 (d, *J* = 8.4 Hz, 2H, Ar*H* d); 7.05 (s, 2H, Ar*H* a or c); 7.09 (s, 2H, Ar*H* c or a); 7.13 (d, *J* = 7.6 Hz, 2H, H(5) of bpy); 7.62–7.65 (m, 6H, H(4), H(4′) and H(5′) of bpy); 8.16–8.20 (m, 7H, H(3), H(3′) of bpy and 3H pyridinium). ^{13}C NMR ($CDCl_3$): 23.54 (*Me*bpy); 29.44 (CH_2–$\mathit{C}H_2$–CH_2); 31.00 (Me_3C Ar b); 31.14 (Ar b-$\mathit{C}H_2$-Ar c); 31.43 (Ar a-$\mathit{C}H_2$-Ar b); 31.64, 31.73 (Me_3C Ar a and Ar c); 32.62 ($\mathit{C}H_2CH_2N$); 33.71 ($Me_3\mathit{C}$ Ar b); 33.86 ($Me_3\mathit{C}$ Ar a); 34.12 ($Me_3\mathit{C}$ Ar c); 41.11 (CH_2CH_2N); 65.10 ($\mathit{C}H_2OAr$ d); 71.64 ($\mathit{C}H_2OAr$ c); 78.60 ($O\mathit{C}H_2$bpy); 114.40 (C_o Ar d); 119.33, 120.60, 123.29, 137.68, 138.73 (C(3), C(4), C(5), C(3′), C(4′)); 124.02 (C(5′)); 125.08 (C_m Ar b); 125.14 (C_m Ar a); 125.63 (C_m Ar c); 127.67 (C_p Ar d); 129.41 (C_m Ar d); 131.82 (C_o Ar b); 132.41, 135.72 (C_o Ar a and c); 141.67 (C_p Ar a or c); 145.75 (C_p Ar b); 145.84 (C_p Ar a or c); 150.62 (C_i Ar a); 151.07 (C_i Ar b); 154.04 (C_i Ar c and (C(6) or C(6′)); 154.28 (C(6′) or C(6)); 156.66, 157.19 (C(2), C(2′)); 157.83 (C_i Ar d). Anal. Calcd for $C_{79}H_{91}N_5O_5$, 4 CF_3COOH, $2H_2O$ (1682.72): C, 62.10; H, 5.93; N, 4.16. Found: C, 62.26; H, 5.70; N, 4.48. ES-MS (positive mode): 1212.7 $[M+Na]^+$, 1190.7 $[M+H]^+$, 606.85 $[M+H+Na]^{2+/2}$, 595.9 $[M+2H]^{2+/2}$. *Free base of* **3**: ^{1}H NMR (400 MHz; $CDCl_3$): 0.77 (s, 18H, Me_3C b); 1. 16 (br s, 2H, NH_2)1.27 (s, 9H, Me_3C a or c); 1.28 (s, 9H, Me_3C c or a); 2.22 (quint, *J* = 7.1 Hz, $CH_2C\mathit{H}_2CH_2$); 2.52 (s, 6H, *Me*bpy); 2.74 (t, *J* = 7.1 Hz, 2H, $C\mathit{H}_2CH_2N$); 2.99 (t, *J* = 6.8 Hz, 2H, $CH_2C\mathit{H}_2N$); 3.10,4.32 (‘q’, AB, J_{AB} = 12.6 Hz, 4 H, Ar-$C\mathit{H}_2$-Ar); 3.21–3.24 (m, 4 H, $CH_2CH_2C\mathit{H}_2O$-Ar d + Ar–$C\mathit{H}_2$-Ar); 3.81 (t, *J* = 7.1 Hz, 2 H, $CH_2CH_2C\mathit{H}_2O$-Ar c); 4.46 (d, 2H, Ar-CH_2-Ar); 4.95 (q, *J* = 11.3 Hz, 4 H, $OC\mathit{H}_2$bpy); 5.86 (s, 1H, Ar-O*H*); 6.35 (d, *J* = 8.4 Hz, 2H, Ar*H* d); 6.51 (s, 4 H, Ar*H* b); 6.79 (d, *J* = 8.4 Hz, 2H, Ar*H* d); 7.03 (s, 2H, Ar*H* a or c); 7.05 (s, 2H, Ar*H* c or a); 7.08 (d, *J* = 7.3 Hz, 2H, H(5) of bpy); 7.51 (t, *J* = 7.3 Hz, 2H, H(4) of bpy); 7.56–7,64 (m, 4H, H(4′) and H(5′) of bpy); 8.10 (d, *J* = 7.3 Hz, 2H, H(3) of bpy); 8.18 (d, *J* = 7.3 Hz, 2H, H(3′) of bpy). *Polymer* **4**: The Wang benzaldehyde resin (3.0 × 10^{-3} mol g^{-1}; 50 mg, 1.5 × 10^{-4} mol of CHO) was added to a solution of calixarene **3** (10 mg, 5.9 × 10^{-6} mol) in toluene (10 mL). Triethylamine (0.1 mL, 1.5 mol) was then added and the resulting mixture was heated at 50 °C during 48 h. After cooling to rt, the resin was recovered by filtration, rinsed with CH_2Cl_2 (2 × 10 mL) and MeOH (2 × 10 mL) and finally dried under vacuum. Anal. Calcd for: C, 80.71; H, 6.36; N, 0.58. For the commercial Wang resin: Anal. Calcd for ($C_{69.8}H_{66.2}O_6$): C, 83.70; H, 6.60; N, 0.0. Found: C, 83.20; H, 6.65; N, 0.0.

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