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Binding ability of first and second generation / carbazolylphenyl dendrimers with Zn(II) tetraphenylporphyrin core towards small heterocyclic substrates


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A study of complex formation of Zn(II) tetraarylporphyrin dendrimers with carbazolylphenyl branches towards 1,4-diazabicyclo[2.2.2]octane, pyridine, imidazole, N-methylimidazole and 1,2,3-triazole was carried out by spectrophotometric and 1H NMR titration methods. It has been shown that the binding ability of the porphyrin receptors towards mono and bidentate N-containing substrates depends on the nature, number and generation of the branches. Bulky substituents are able either to significantly reduce the binding ability of the tetrapyrrolic cores due to the shielding of the porphyrin reaction centres, or to significantly increase it by forming intramolecular cavities for complementary binding of substrates. It has been determined that due to a good geometric match of the ligand's size to the size of the intramolecular cavities of the porphyrin receptors, and by the existence of additional hydrogen bonding and/or π-π interactions between the ligand and the triazole fragments of the porphyrin the Zn-tetraarylporphyrins with eight 4-carbazolylphenyl-1,2,3-triazole end groups of the first and the second generations could be used as an effective receptors for imidazole, N-methylimidazole and 1,2,3-triazole.

Taking into account the fact that binding is accompanied by a clear and easily identifiable response in the UV-Vis spectra of the reaction mixture, this metalloporphyrins could be considered as a molecular optical sensing device for small heterocyclic substrates.

Introduction

Dendrimers are monodisperse macromolecules with highly branched three-dimensional structure. Given the fact that the size of dendrimeric macromolecules can be predicted and controlled with a high accuracy they are often called a new generation of polymers and have a great future as polyfunctional materials. The presence of channels and pores allows them to encapsulate and/or activate small guest molecules, including physiologically active ones.

According with the literature, porphyrin-based dendrimers are of great interest.1-8 It was found that Fe(II) porphyrins containing polyethyleneglycol branches have a much higher (1500 times) constant of reversible binding of O2 compared with human hemoglobin in which the iron porphyrin (heme) is surrounded by a globular protein (globin).9,10 In both cases, the fixation of oxygen occurs as a result of its coordination at the iron atom. It is assumed that a causal factor responsible for the affinity of O2 to dendrimer porphyrins is the formation of hydrogen bonds between oxygen molecules and the amide groups of the branches' first generation. The design and properties of “patched dendrimers” has been described,11 in which different types of oligopeptide dendrons are asymmetrically introduced on the Zn(II) porphyrin core. The “patch” gives the porphyrin dendrimer an additional interface to bind with another molecule or macromolecule. “Patched dendrimers” with porphyrin cores show molecular recognition phenomena at the nanoscale, which provides good insight into the biological molecular recognition performed by proteins and enzymes.

Porphyrin-based dendrimers are often used as photofunctional artificial receptors, in which the strong photoabsorption and intense fluorescence signals of the porphyrin can respond sensitively to substrate binding.12-17

This paper investigates the binding ability of Zn-tetraarylporphyrins with different number [two (ZnD1-G1, ZnD4-G1, ZnD7-G2), four (ZnD2-G1, ZnD5-G1, ZnD8-G2) and eight (ZnD3-G1, ZnD6-G1, ZnD9-G2)] and generation [the first (ZnD1-G1, ZnD2-G1, ZnD3-G1, ZnD4-G1, ZnD5-G1, ZnD6-G1) and the second (ZnD7-G2, ZnD8-G2, ZnD9-G2)] of carbazolylphenyl branches towards 1,4-diazabicyclo[2.2.2]octane (L1), pyridine (L2), imidazole (L3), N-methylimidazole (L4) and 1,2,3-triazole (L5) in toluene. The dendrimers also differ by the nature of bridging spacers [oxoxygen (ZnD1-G1, ZnD2-G1, ZnD3-G1) and 1,2,3-triazole (ZnD4-G1, ZnD5-G1, ZnD6-G1, ZnD7-G2, ZnD8-G2, ZnD9-G2)] connecting the tetraarylporphyrin core and carbazolylphenyl fragments. Zn(II) tetraphenylporphin (ZnTPP) was taken as the...
object of comparison. The compounds ZnD4-G1, ZnD5-G1, ZnD6-G1, ZnD7-G2, ZnD8-G2, ZnD9-G2 were previously synthesized\textsuperscript{18} as new fluorescent switches and photoactive devices for detection of substrates of different nature.

5 Result and discussion

Synthesis

The synthesis of dendrimers H\textsubscript{2}D1-G1, H\textsubscript{2}D2-G1 and H\textsubscript{2}D3-G1 was based on Lindsey method starting from 5-mesityldipyromethane\textsuperscript{19} or pyrrole and carbazole-based aldehydes.

\begin{equation}
\text{Mes} + \text{Py} \rightarrow \text{ZnD1-G1, ZnD2-G1, ZnD3-G1}
\end{equation}

The nucleophilic substitution reaction of 4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenol (1)\textsuperscript{20} and 4-bromomethylbenzaldehyde (2)\textsuperscript{21} in DMF resulted in the formation of 4-[(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenoxy)methyl]benzaldehyde (3) (Scheme 1). Similarly, the mixture of arylaldehydes consisting of 3,5-bis(bromomethyl)-2,4,6-trimethylbenzaldehyde (4) and 3-bromomethyl-5-chloromethyl-2,4,6-trimethylbenzaldehyde (5)\textsuperscript{18} was reacted with (1) and 3,5-bis[(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenoxy)methyl]-2,4,6-trimethylbenzaldehyde (6) was obtained (Scheme 1) in pure form after column chromatography purification.

\begin{equation}
\text{Scheme 1. Synthesis of carbazole-based aldehydes}
\end{equation}

The condensation between arylaldehyde (3) and 5-mesityldipyromethane\textsuperscript{19} was carried out in dry CH\textsubscript{2}Cl\textsubscript{2} and the presence of a Lewis acid catalyst BF\textsubscript{3}.OEt\textsubscript{2} at room temperature. Then p-chloranil was used as oxidant and the reaction mixture was refluxed for 1 hour. The starting materials’ concentration was optimized at 10 mM in CH\textsubscript{2}Cl\textsubscript{2}, the yield of 5,15-bis(2,4,6-trimethylphenyl)-10,20-bis(4-(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenoxy)methylphenyl) porphyrin (7) (Scheme 2) reached 34% with 0.3 equivalent of BF\textsubscript{3}.OEt\textsubscript{2}. Similarly, 5,10,15,20-tetrakis(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenoxy)methylphenyl porphyrin (8) was obtained in 15% when arylaldehyde (3) was reacted with pyrrole under the same conditions that were used to make dendrimer (7). The synthesis of 5,10,15,20-tetrakis(3,5-bis(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenoxy)methyl)-2,4,6-trimethylphenyl porphyrin (9) was unsuccessful when using the procedure that applied for making dendrimer (7). In the presence of 0.75% absolute ethanol in dry CH\textsubscript{2}Cl\textsubscript{2}, the tetrasubstituted porphyrin (9) was obtained in 5%. The increase in the amount of Lewis acid catalyst from 0.3 to 0.8 equivalent as well as the condensation time between (6) and pyrrole did not lead to any change in the yield of dendrimer (9). The low yield of making dendrimer (9) was due to the sterically hindered methyl groups at 2 and 6 positions and bulky groups at 3 and 5 positions of compound (6). Dendrimers (7), (8) and (9) were then metallated in CHCl\textsubscript{3} to obtain ZnD1-G1, ZnD2-G1 and ZnD3-G1 in quantitative yield.

Dendrimers ZnD4-G1, ZnD5-G1, ZnD6-G1, ZnD7-G2, ZnD8-G2, ZnD9-G2 (Scheme 3) were synthesized via the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC reaction or click reaction) in THF solvent under [Cu(NCCH\textsubscript{3})\textsubscript{4}][PF\textsubscript{6}] catalysis.\textsuperscript{18}

\begin{equation}
\text{Scheme 3. Structures of dendrimers ZnD4-G1, ZnD5-G1, ZnD6-G1, ZnD7-G2, ZnD8-G2, ZnD9-G2}
\end{equation}

Binding ability

The strength of axial binding of electron donating ligands (L) on Zn(II) porphyrins (ZnP) depends on the degree of aromaticity of the tetrapyrrolic macrocycle.\textsuperscript{22,23} The aromaticity of the tetrapyrrolic macrocycle is higher, the more strongly a zinc cation is connected with the macrocycle nitrogen atoms. The reasons of
decreasing of the tetrapyrrolic macrocycle aromaticity can be both the electronic influence of the substituents, and a spatial factor causing distortion of the planar structure of the tetrapyrrolic macrocycle, especially due to unsymmetrical substitution with bulky substituents.

Next to distortion of the planar structure of the tetrapyrrolic macrocycle, bulky substituents can also create steric hindrance to the ligands axial coordination due to shielding of the metalloporphyrin reaction center from both sides or a single side of the molecule. On the other hand, highly branched bulky substituents may form intramolecular binding cavities for effective binding of guest molecules.

Axial coordination of **L1-L5** (Scheme 4) to ZnP is accompanied by a characteristic red shift of the absorption bands in the UV-Vis spectra of the system ZnP-L and a high field shift of the ligand protons signals in the $^1$H NMR spectra of the corresponding complexes. It should be noted that upon complexation of ZnP with monodentate ligands L2-L5, over a wide concentration range of the ligands ($C_L = 1 \times 10^{-7}$ to $8 \times 10^{-2}$ M), changes in the UV-Vis spectra of the reaction mixture occur with the formation of one family of spectral curves with one set of isosbestic points. The titration curve has one step, which indicates the formation of a single type of complexes in a ratio of 1:1. The details of the spectrophotometric and $^1$H NMR titration are described in the preliminary communication.$^{24}$ The changes in the UV-Vis spectra of the system ZnD3-G1 - L3 and the corresponding binding isotherms are depicted on Figure 1S as an example (supplementary information).

It was found that *para*-substitution of the tetrapyrrolic core phenyl groups by two (ZnD1-G1) or four (ZnD2-G1) 4-(4-(3,6-bis(t-butyl)carbazol-9-ylphenyl)-oxy) fragments and by two (ZnD7-G2) or four (ZnD8-G2) 4-(4-(3,6-bis(t-butyl)carbazol-9-ylphenyl)-1,2,3-triazole branches of the second generation leads to an increase in the stability constants of the 1:1 complexes between the dendrimers and the monodentate ligands L2-L5 as compared with the similar complexes of ZnTPP and *para*-substituted dendrimers ZnD1-G1, ZnD2-G1, ZnD3-G1, ZnD4-G1, ZnD5-G1, ZnD7-G2, ZnD8-G2.$^{24}$ As could be seen from Table 1, among the complexes of ZnD6-G1 with L2-L5,$^{24}$ the complex between ZnD6-G1 and L4 has the highest stability constant. This could be explained by a good geometric match of the ligand size to the size of the intramolecular cavities of the porphyrinic receptor. The decrease in the value of the binding constant of the complexes between ZnD9-G2 and L4 in comparison with the similar complexes of the dendrimer with L3 testifies that beside a good geometric match between host-guest molecules the formation of additional hydrogen bonding interactions between the L3 and the triazole fragments of ZnD9-G2 may be possible.

The dendrimers ZnD6-G1, ZnD9-G2 can be seen as a "picket-fence" porphyrins with intramolecular cavities formed by the 4-carbazolophenyl-1,2,3-triazole end groups emanating from both sides of the porphyrin core (Figure 4S) (supplementary information).$^{24}$

On the other hand, the meta-octasubstituted dendrimer ZnD3-G1 can not form similar intramolecular cavities for the ligand due to the lack of 1,2,3-triazole bridging fragments between tetrapyrrolic core and carbazolophenyl branches. This is the reason why the binding ability of ZnD3-G1 towards L2-L5 is much less in comparison with ZnD6-G1,$^{24}$ ZnD9-G2 and it is comparable while significantly higher than the corresponding values for ZnD1-G1, ZnD2-G1 (Table 1). The dependence of the stability constants of octa-substituted dendrimers ZnD3-G1, ZnD6-G1, ZnD9-G2 with L2-L5 on the nature of small N-containing organic molecules is summarized in Figure 1.
In line with our interests in the supramolecular chemistry of porphyrins, we also investigated the binding ability of ZnD1-G1, ZnD2-G1, ZnD3-G1, ZnD4-G1, ZnD5-G1, ZnD6-G1, ZnD7-G2, ZnD8-G2, ZnD9-G2 towards the bidentate ligand L1. It is well known that upon interaction of ZnP with bifunctional nitrogen containing ligands formation of the complexes in a ratio of either 1:1 or 2:1 is possible. Spatially distorted porphyrins or porphyrins with bulky substituents do not form complexes with L1 in a ratio of 2:1.

The study of complex formation of dendrimers with two (ZnD1-G1, ZnD4-G1, ZnD7-G2) and four (ZnD2-G1, ZnD5-G1, ZnD8-G2) branches and the octa-substituted dendrimer ZnD3-G1 without 1,2,3-triazole bridging groups between the tetrapyrrolic core and the carbazolophenyl fragments with L1, using the method of spectrophotometric titration, showed that these processes, similarly to the system ZnP-L1, proceed in two stages. The changes in the UV-Vis spectra of the system ZnD3-G1 - L1 in toluene are depicted in Figure 2 as an example.

Figure 2. The changes in the UV-Vis spectra of the system ZnD3-G1-L1 in toluene at 20°C, C_{ZnD3-G1} = 1.0×10^{-4} M.

There are two families of spectral curves with two sets of isosbestic points in the UV-Vis spectra of the system. Each of them is characterized by its own step in the corresponding titration curve (Figure 5S and Figure 6S) (supplementary information). Existence of two steps in the complexation also is confirmed by the graphical dependence of lg[(A_i-A_s)/(A_i-A_p)] from lgC_L for the system. The splitting of the ligand non-equivalent proton signal in the \(^1\)H NMR spectrum of the complex formed at the high concentrations of the ligand according with the literature indicates the formation of a 1:1 complex. One signal of the ligand equivalent protons in the spectrum of the complex at lower concentrations of the ligand reveals the formation of the 2:1 complex between ZnD3-G1 and L1.

<table>
<thead>
<tr>
<th>2:1 complexes, (K_{assoc,2}) (M^{-1})</th>
<th>1:1 complexes, (K_{assoc,1}) (M^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnTPP</td>
<td>5.0×10^{7}</td>
</tr>
<tr>
<td>ZnD1-G1</td>
<td>1.9×10^{7}</td>
</tr>
<tr>
<td>ZnD2-G1</td>
<td>6.0×10^{8}</td>
</tr>
<tr>
<td>ZnD3-G1</td>
<td>2.1×10^{3}</td>
</tr>
<tr>
<td>ZnD4-G1</td>
<td>4.0×10^{10}</td>
</tr>
<tr>
<td>ZnD5-G1</td>
<td>7.0×10^{9}</td>
</tr>
<tr>
<td>ZnD6-G1</td>
<td>1.3×10^{9}</td>
</tr>
<tr>
<td>ZnD7-G2</td>
<td>2.3×10^{4}</td>
</tr>
<tr>
<td>ZnD8-G2</td>
<td>8.9×10^{4}</td>
</tr>
<tr>
<td>ZnD9-G2</td>
<td>1.5×10^{6}</td>
</tr>
</tbody>
</table>

The error in determining the stability constants was 5% - 7% (for 1:1 complexes) and 10% (for 2:1 complexes).

Conclusions

Thus, the study of complex formation of Zn(II) tetrapyrrolyporphyrins with carbazolophenyl branches by spectrophotometric and \(^1\)H NMR titration methods showed that their binding ability towards mono and bidentate N-containing organic molecules depends on the nature, number and generation of the branches. Bulky substituents are able either to significantly reduce the binding ability of the tetrapyrrolic cores due to the shielding of the porphyrin reaction centers, or significantly increase it by forming of intramolecular cavities for complementary binding of substrates. By varying the number of the branches and the number of their generation, it is possible to develop intramolecular cavities of different shapes for selective binding of guest molecules by a good geometric match of the ligand size to the size of the cavities, and by a existence of additional \(\pi-\pi\) and/or hydrogen bonding interactions between the ligand and the triazole fragments of the porphyrin. These metalloporphyrins could be considered as a molecular optical sensing device for small heterocyclic substrates due to a clear and easily identifiable response in the UV-Vis spectra of the reaction mixture.

Experimental

General experimental methods: NMR spectra were acquired on commercial instruments (Bruker Avance 300 MHz, Bruker AMX 400 MHz or Bruker Avance II 600 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (TMS) or the internal (NMR) solvent signals. Mass spectra were run using a HP5989A apparatus (Cl and El, 70 eV ionisation energy) with Apollo 300 data system or a Thermo Finnigan LCQ Advantage apparatus (ESI). Exact mass measurements were acquired on a Kratos MS50TC instrument (performed in the El mode at a resolution of 10000). Melting
Spectroscopic methods and instrumentation: 1,4-Diazabicyclo-[2.2.2]octane (L1), pyridine (L2), imidazole (L3), N-methylimidazole (L4) and 1,2,3-triazole (L5) from Sigma-Aldrich were used without further purification. MALDI-TOF mass spectrometry was carried out on Bruker Daltonics – ultraflex II & ultraflex II TOF/TOF using the matrix 2,5-dihydroxybenzoic acid for all samples.

The stability constants of the metalloporphyrin complexes with the ligands in ratio of 1:1 (Kassoc.1) and 2:1 (Kassoc.2) were calculated accordingly with the literature (17) based on spectrophotometric data at two wavelengths (decreasing and increasing) using the following relationships:

\[ K_{assoc.1} = \frac{[A-B]}{[A][B]} = \frac{\Delta \lambda_1}{\Delta \lambda_2} \]

\[ K_{assoc.2} = \frac{[A-B]}{[A]^2[B]} = \frac{\Delta \lambda_1}{\Delta \lambda_2} \]

where, \( \lambda_1 \) is the decreasing wavelength, \( \lambda_2 \) is the increasing wavelength, \([A]\) is the Zn-porphyrin concentration, \([B]\) is the ligand concentration, \( \Delta \lambda_1 \) is the maximal change of the optical density at the given wavelength, and \( \Delta \lambda_2 \) is the change of the optical density of the solution at a given wavelength at a given concentration.

Synthesis of 4-[(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenoxy)methyl]benzaldehyde (3): 4-bromomethylbenzaldehyde (2) (200 mg, 1.1 mmol, 1 eqv) and 4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenol (1) were stirred in DMF (10 ml) for a few minutes. Then K2CO3 was added and the reaction was conducted at 80°C overnight under N2 atmosphere. Crude product was purified by column chromatography (silica, eluent CHCl3/heptane 2:1) to obtain (3) (366 mg, 73%) as a white solid. M.p. 190-192°C. 1H NMR (300 MHz, CDCl3, 25°C, TMS): \( \delta = 10.05 \) (s, 1 H, CHO), 8.63 (s, 2 H, H-carbazole), 7.95 (d, \( J_{HH} = 7.92 \), 2 H, H-Ar), 7.66 (d, \( J_{HH} = 7.98 \), 2 H, H-Ar), 7.44 (d, \( J_{HH} = 8.67 \), 4 H, H-Ar), 7.25 (d, \( J_{HH} = 8.49 \), 2 H, H-Ar), 7.14 (d, \( J_{HH} = 8.64 \), 2 H, H-Ar), 1.45 ppm (s, 18 H, tert-butyl). 13C NMR (75 MHz, CDCl3, 25°C, TMS): \( \delta = 191.86 \), 130.14, 128.34, 127.58, 123.53, 116.21, 115.88, 109.03 (CHO), 157.25, 143.69, 142.60, 139.63, 136.09, 131.48, 123.08 ppm (C-Ar), 69.57 (CH3), 34.71 (C, tert-butyl), 32.02 ppm (CH3, tert-butyl). HRMS (EI): m/z calcd. for C36H36NO2: 549.27 [M+]: found 549.26 [M+].

Synthesis of 3,5-bis[(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenoxy)methyl]-2,4,6-trimethylbenzaldehyde (6): the mixture of aroylaldheydes (180 mg), consisting of 3,5-bis(bromomethyl)-2,4,6-trimethylbenzaldehyde (4) and 3-bromomethyl-5-chloromethyl-2,4,6-trimethylbenzaldehyde (5), and carbazole-based phenol (1) were dissolved in DMF (10 ml) and the mixture was stirred at room temperature for a few minutes. Subsequently, K2CO3 (148 mg, 1.08 mmol) and a catalytic amount of 18-crown-6 (26.4 mg, 0.1 mmol) were added and the reaction was carried out at 80°C overnight under N2 atmosphere. Purification was conducted via a silica column (CH2Cl2/heptane:1:5) to obtain (6) (390 mg) as a white solid. M.p. 268-270°C. 1H NMR (300 MHz, CDCl3, 25°C, TMS): \( \delta = 10.72 \) (s, 1 H, CHO), 8.14 (s, 4 H, H-carbazole), 7.48 (m, 8 H, H-carbazole), 7.29 (d, \( J_{HH} = 8.64 \), 4 H, H-Ar), 7.21 (d, \( J_{HH} = 8.67 \), 4 H, H-Ar), 5.22 (s, 4 H, CH2), 2.66 (s, 6 H, 2×CH3), 2.62 (s, 3 H, CH3), 1.46 ppm (s, 36 H, tert-butyl). 13C NMR (75 MHz, CDCl3, 25°C, TMS): \( \delta = 195.33 \) (CHO), 128.34, 123.51, 116.21, 115.64, 109.05 (CH-Ar), 157.76, 143.63, 142.60, 140.26, 139.68, 134.01, 132.51, 131.42, 123.09 (C-Ar), 64.48 (CH3), 34.72 (C, tert-butyl), 32.04 (CH3, tert-butyl), 16.58 (CH3), 15.89 ppm (CH3). MALDI-TOF: m/z calcd. for C69H62N2O2: 914.54 [M+]; found 914.53 [M+].

Synthesis of 5,15-bis(2,4,6-trimethylphenyl)-10,20-bis[(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenoxy)methyl]porphyrin (7): arylaldehyde (3) (100 mg, 0.20 mmol, 1 eqv) and 5-mesityldipyrromethane (54 mg, 0.20 mmol, 1 eqv) were dissolved in dry CH2Cl2 (20 ml) and the solution was purged with N2 for a few minutes. Then BF3·OEt2 (7.5 μL, 0.06 mmol, 0.3 eqv), in dry CH2Cl2 (1 ml), was added dropwise and the resulting solution was stirred at room temperature for 1 hour under N2 atmosphere. Subsequently, p-chloranil (100 mg, 0.41 mmol, 2 eqv) was added in powder form and the mixture was heated at reflux for 1 hour. The solvent was evaporated and then purification was carried out with column chromatography. The first flash column (silica, eluent CH2Cl2) was to remove dark pigments and the second one (silicagel, CH2Cl2/heptane 1:1.5) was to separate the different porphyrin fractions. Pure product (51 mg, 54%) was obtained as a purple solid. 1H NMR (300 MHz, CDCl3, 25°C, TMS): \( \delta = 8.84 \) (d, \( J_{HH} = 4.5 \), 4 H, H-pyrole), 8.71 (d, \( J_{HH} = 7.71 \), 4 H, H-Ar), 8.17 (s, 4 H, H-carbazole), 7.87 (d, \( J_{HH} = 7.74 \), 4 H, H-Ar), 7.56 (d, \( J_{HH} = 8.46 \), 4 H, H-Ar), 7.49 (d, \( J_{HH} = 8.64 \), 4 H, H-Ar), 7.36 (m, 8 H, H-Ar), 7.29 (s, 4 H, H-mesityl), 5.50 (s, 4 H, 2×CH2), 2.63 (s, 6 H, 2×CH3), 1.85 (s, 12 H, 4×CH3), 1.48 (s, 36 H, tert-butyl), -2.59 ppm (s, 2 H, 2×NH). 13C NMR (75 MHz, CDCl3, 25°C, TMS): \( \delta = 134.77 \), 128.40, 127.78, 125.94, 123.54, 116.20, 116.04, 109.12 (CH-Ar), 157.88, 142.56, 141.88, 139.75, 139.39, 138.40, 137.76, 136.16, 131.31, 123.10, 118.86, 118.42 (C-Ar), 70.50 (CH2), 34.74 (C, tert-butyl), 32.06 (CH3, tert-butyl), 21.65 (CH3), 21.48 ppm (CH3). MALDI-TOF: m/z calcd. for C104H84N4O4: 1465.94 [M+]; found 1465.84 [M+].
dendrimer D1 (7). Crude product was purified by column chromatography (silica, CHCl₃:heptane 1:1) to get pure compound (15%) as a purple solid. 

1H NMR (300 MHz, CDCl₃, 25°C, TMS): δ = 8.92 (s, 8 H, H-pyrrrole), 8.28 (d, JₜH₂H = 7.71 Hz, 8 H, H-π), 8.17 (s, 8 H, H-carbazole), 7.86 (d, JₜH₂H = 7.71 Hz, 8 H, H-π), 7.55 (d, JₜH₂H = 8.46 Hz, 8 H, H-π), 7.49 (d, JₜH₂H = 8.67 Hz, 8 H, H-π), 7.35 (d, JₜH₂H = 8.64 Hz, 16 H, H-π), 5.45 (s, 8 H, CH₂), 1.48 (s, 72 H, tert-butyll), 2.70 ppm (s, 2 H, 2°-NH). 

13C NMR (75 MHz, CDCl₃, 25°C, TMS): δ = 134.83, 128.38, 125.98, 135.11, 126.21, 126.00, 109.12 (CH-Ar), 157.86, 142.57, 141.97, 139.73, 136.27, 131.31, 123.10, 119.82 (C-Ar), 70.42 (CH₂), 34.73 (C, tert-butyll), 32.05 (CH₂, tert-butyll). MALDI-TOF: m/z calcd. for C₁₃₅H₂₅₁₂NO₂Zn: 2148.84 [M⁺]; found 2148.30 [M⁺].

Synthesis of 5,10,15,20-tetraakis[(3,3'-di-tert-butyll-9H-carbazol-9-yl)phenoxymethyl]-2,4,6,8,10,12,14,16,18,20-decaketetrabutylylporphyrin \( \text{(9): 3,5-bis[4-(3,3'-di-tert-butyll-9H-porphyrinoxymethyl)]-2,4,6,8,10,12,14,16,18,20-decaketetrabutylylporphyrin} \)

General procedure for synthesis of zinc (II) porphyrin: porphyrin (15 mg, 1 equiv) and Zn(OAc)₂·H₂O (4 equiv) were added to a flask of 25 mL containing CHCl₃ (10 ml) and the solution was heated at reflux for 4 hours. The resulting mixture was washed three times with distilled water. The organic layer was dried over MgSO₄ and the solvent was evaporated under vacuum to obtain Zn (II) porphyrin in pure form in quantitative yield.

**Dendrimer ZnD2-G1:** 

1H NMR (300 MHz, CDCl₃, 25°C, TMS): δ = 9.03 (s, 8 H, H-pyrrrole), 8.30 (d, JₜH₂H = 7.71 Hz, 8 H, H-π), 8.17 (d, JₜH₂H = 1.29 Hz, 4 H, H-carbazole), 7.88 (d, JₜH₂H = 7.92 Hz, 4 H, H-Ar), 7.56 (d, JₜH₂H = 8.67 Hz, 8 H, H-π), 7.49 (dd, JₜH₂H = 6.74 Hz, JₜH₂H = 1.68 Hz, 8 H, H-Ar), 7.35 (dd, JₜH₂H = 8.64 Hz, JₜH₂H = 2.46 Hz, 16 H, H-Ar), 5.48 (s, 8 H, CH₂), 1.48 (s, 72 H, tert-butyll). 

13C NMR (75 MHz, CDCl₃, 25°C, TMS): δ = 134.70, 132.13, 128.38, 125.87, 125.54, 116.21, 110.03, 109.12 (CH-Ar), 157.89, 150.24, 142.65, 145.27, 139.75, 136.02, 131.31, 123.10, 120.80 (C-Ar), 70.54 (CH₂), 34.73 (C, tert-butyll), 32.05 (CH₂, tert-butyll). MALDI-TOF: m/z calcd. for C₁₅₁H₃₄₂NO₂Zn: 2210.06 [M⁺]; found 2210.28 [M⁺].

**Dendrimer ZnD3-G1:** 

1H NMR (600 MHz, CDCl₃, 25°C, TMS): δ = 8.88 (s, 8 H, H-pyrrrole), 8.12 (s, 16 H, H-π), 7.50 (d, JₜH₂H = 8.11 Hz, 16 H, H-π), 7.40 (d, JₜH₂H = 8.82 Hz, 16 H, H-π), 7.32 (s, 16 H, H-Ar), 7.27 (d, JₜH₂H = 8.82 Hz, 16 H, H-Ar), 5.48 (s, 16 H, CH₂), 2.95 (s, 12 H, CH₂), 2.05 (s, 24 H, CH₃), 1.43 ppm (s, 144 H, tert-butyll). 

13C NMR (100 MHz, CDCl₃, 25°C, TMS): δ = 131.84, 129.47, 127.03, 115.77, 109.08 (C, CH-Ar), 65.86 (CH₂), 34.68 (C, tert-butyll), 32.00 (CH₂, tert-butyll), 19.32 (CH₃), 16.33 ppm (CH₂).

**Notes and references**

Synthesis and complexation of Zn(II)-tetraarylporphyrin dendrimers with carbazolylphenyl branches towards organic ligands was carried out by spectrophotometric and $^1$H NMR titration methods.