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PAPER

New molecular architectures by aggregation of tailored zinc(II) Schiff-base complexes†

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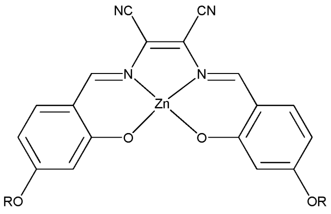
This contribution reports the synthesis, characterization, ^{1}H NMR, optical absorption and fluorescence properties of a bis(salicylaldiminato)Zinc(II) Schiff base complex, **1**, having dipodal, alkyl ammonium bromide derivatized side chains in the salicylidene rings. The comparison of ^{1}H NMR and optical spectroscopic properties of **1** with those of the closely related amphiphilic alkyl derivative allowed getting insights into the nature of species in solutions. Present data suggest the existence of Zn···Br interactions, thus avoiding intermolecular Zn···O interactions, as usually occur in the absence of other coordinating species. SEM images of samples obtained by drop-casting from dichloromethane solutions of **1** reveal the existence of branched nanostructures, consistent with intermolecular Zn···Br interactions. The present approach thus suggests a new method to unique supramolecular architectures for coordination metal complexes.

Introduction

Tetracoordinated Zn^{II} complexes, in particular Schiff-base derivatives, are Lewis acidic species[1] which saturate their coordination sphere by coordinating a large variety of neutral substrates such as alcohols, carbonyls, and nitrogen based donors Lewis bases,[1–3] including various anions,[4] or in their absence, can be stabilized through intermolecular Zn···O axial coordination involving the phenolic oxygen atoms of the ligand framework.[5] Thus, a variety of molecular architectures,[6] supramolecular assemblies,[7] columnar mesomorphic,[8] and nanostructures,[9] have been found. Schiff-base Zn^{II} complexes have recently been investigated also for their variegated fluorescent features, related to the structure of the salen template[10] and the axial coordination,[2–4,10,11] and second-order nonlinear optical properties.[12]

The demand for the axial binding to the Zn^{II} ion to saturate its coordination sphere in these complexes allows for the design of new molecular architectures, for example, using interconnecting ditopic Lewis donor[7c] or anionic[7a] species. Alternatively, the appropriate design of ligands possessing flexible Lewis donor atoms as side substituents, suitable to axially coordinate the Zn^{II} atom of another molecular unit, offers the advantage to achieve new tailored Zn^{II} supramolecular architectures.

With these ideas in mind, we have synthesized a Zn^{II} Schiff base complex, **1**, having dipodal alkyl side chains in the salicylidene rings, bearing an alkyl ammonium bromide (Chart 1), and studied its ^{1}H NMR and optical spectroscopy properties in solution. Actually, the bromide ion is expected to be a suitable Lewis base to coordinate the Zn^{II} ion, competing with the phenolic oxygen donor atoms of salicylaldehyde. Thus, a focus of the present study will be to investigate the aggregation properties of this derivatized alkyl-ammonium bromide complex in comparison to our previous studies on the analogous simpler amphiphilic species, **2**.[2]



R = $(CH_2)_{12}N^+(CH_3)_3Br^-$ **1**
R = $(CH_2)_9CH{=}CH_2$ **2**

Chart 1

Results and discussion

We have recently demonstrated that the closely related amphiphilic 4-(undec-10-enyloxy)-derivatized Zn^{II} Schiff base complex, **2**, forms aggregates in solutions of non-coordinating solvents, *e.g.*, dichloromethane (DCM). The switching to the monomer can be driven by addition of a coordinating species and involves substantial optical variations and a dramatic enhancement of the fluorescence emission. As this process occurs because of the axial coordination to the Zn^{II} ion, it has been found that it is selective and sensitive depending upon

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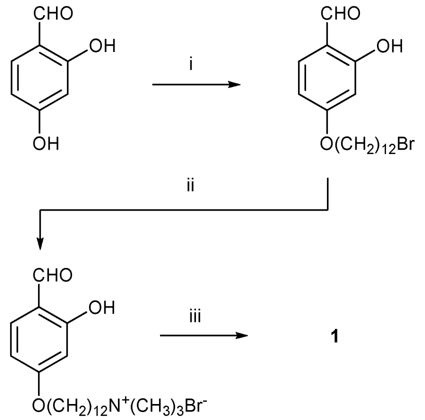


Scheme 1 *Reagents and conditions*: (i) $Br(CH_2)_{12}Br$, K_2CO_3, CH_3CN, reflux; (ii) $N(CH_3)_3$, EtOH, 50 °C; (iii) diaminomaleonitrile, $Zn(OAc)_2{\cdot}2H_2O$, EtOH, reflux.

the Lewis basicity of the coordinating species. On the other hand, ^1H NMR and optical spectroscopy properties of **2** in a solution of coordinating solvents suggest the existence of monomeric species having the solvent axially coordinated. These properties are superimposable to those achieved in non-coordinating solvents upon axial coordination with a Lewis base.[2]

The synthesis of the dipodal alkyl ammonium-derivatized complex **1** was accomplished in a three step approach (Scheme 1).

^1H NMR spectra of **1** in a solution of DMSO-d_6 show the presence of sharp signals with the expected multiplicity, according to its molecular structure and consistent with the existence of monomeric species, having the axially coordinated solvent. In fact, ^1H NMR signals related to the aromatic, OCH_2– and CH═N hydrogens are identical to those found in DMSO-d_6 solutions of **2** (Fig. S1, ESI†).[2]

With the exception of DMSO and DMF, compound **1** is very low soluble in most common coordinating (*e.g.*, acetonitrile, THF, methanol) or low-polarity non-coordinating (*e.g.*, DCM) solvents, while is almost insoluble in non-polar solvents. The substantial higher solubility in DMSO and DMF indicates the existence of monomeric species of **1** in these solvent media, as suggested by ^1H NMR analysis (*vide supra*).

Surprisingly, in strict contrast to our previous studies on **2**,[2] optical absorption spectral features of **1** are independent from the nature of the solvent. In fact, either in coordinating (THF, DMSO) or non-coordinating (DCM) solvents optical spectra are identical to each other, except for a red-shift of the longer wavelength band in the case of the more polar DMSO solvent (Fig. 1). The optical absorption features of **1** resemble those of the parent complex **2** in coordinating solvents or in DCM upon axial coordination of a Lewis base.[2] In other words, optical absorption properties of **1** in solution, independently of the presence or not of a Lewis base, indicate the existence of an axially coordinated species to the Zn^{II} ion. Moreover, complex **1** exhibits a moderate fluorescence emission ($\Phi \approx 0.08$), with the presence of an unstructured band, λ_{max} between 602 and 620 nm, independent from the excitation wavelength.

Therefore, present data suggest the existence of Zn···Br interactions in **1** in a solution of DCM, thus satisfying the coordination sphere of the Zn^{II} ion and avoiding intermolecular Zn···O interactions, as usually occur in the absence of other coordinating species.[5]

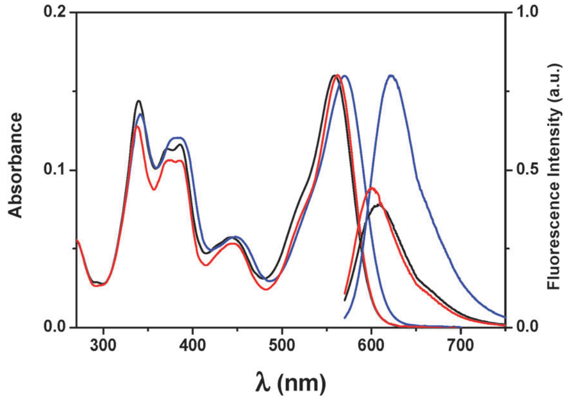


Fig. 1 UV/vis absorption and fluorescence (λ_{exc} = 564 nm) spectra of **1** in DMSO (5.0×10^{-6} M) (—), DCM (—) and THF (—). Absorption spectra in DCM and THF were recorded with an absorbance of the longer wavelength band equal to that recorded in DMSO.

To verify this hypothesis, we performed a series of experiments using DCM solutions of **2**, as reference species, by adding DCM solutions of a bromide, and compared the results with those achieved for the complex **1**.

As previously found for treatment of DCM solutions of **2** with neutral Lewis bases,[2] the addition of a stoichiometric amount of tetrabutylammonium (TBA) bromide to a DCM-d_2 solution of **2** results in a sizable down-field shift of aromatic H_3 and the OCH_2– signals, in agreement with the deaggregation process and formation of the **2**·BrTBA adduct (Fig. 2). Moreover, the resulting ^1H NMR spectrum is similar to that found for the **2**·pyridine adduct in DCM-d_2 solutions (Fig. S2, ESI†), thus suggesting an analogous axially coordination mode of the bromide to the Zn^{II} ion.

The ^1H NMR spectrum of **1** in DCM-d_2 solution is almost identical, in terms of chemical shift and multiplicity of the

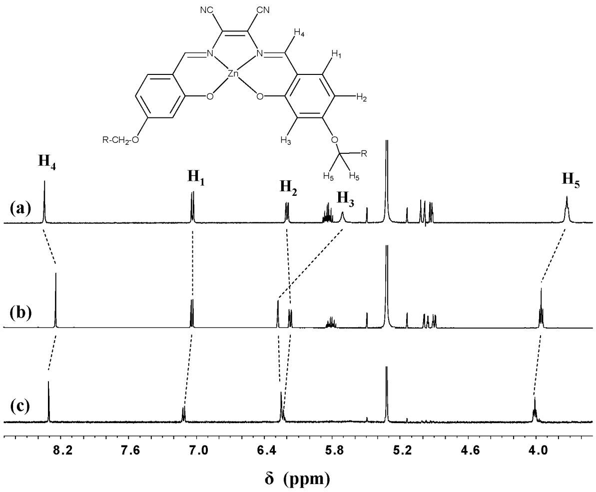


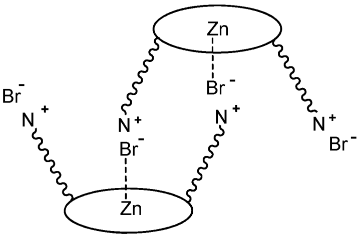
Fig. 2 ^1H NMR spectra in DCM-d_2 of **2** (a) and **2**·BrTBA adduct (obtained upon addition of an equimolar amount of TBA bromide to a DCM-d_2 solution of **2**) (b). The ^1H NMR spectrum of **1** in DCM-d_2 is reported for comparison (c).

signals, to that found for the above **2**·BrTBA adduct (Fig. 2, Table S1, ESI†). Moreover, the evidence of a single signal for H_1–H_5 protons of the two salicylidene moieties indicates that in both species a local C_2 axis passing through the central Zn^{II} ion and perpendicular to the chelate ring is present. These data suggest in both cases an analogous coordination mode of the alkyl-ammonium bromide to the Zn^{II} ion, ruling-out the existence of intramolecular Zn···Br interactions in **1**.

In order to study the optical properties of the **2**·BrTBA adduct, spectrophotometric and spectrofluorimetric titrations of 10 μM DCM solutions of **2** were performed using DCM solutions of TBA bromide as titrant (Fig. S3, ESI†). The resulting optical absorption spectra of the **2**·BrTBA adduct upon reaching the saturation point, except for a slightly red-shift (~6 nm) of the longer wavelength band, are equivalent to those of **1** in DCM (Fig. 3). Moreover, Job's plot analysis[13] clearly indicates the formation of 1 : 1 adducts (Fig. S4, ESI†).

Analogously, a comparison of fluorescence spectra for the **2**·BrTBA adduct and **1** indicates an identical emission, in terms of intensity and fluorescence maxima. Note however that, while optical absorption spectra of the **2**·BrTBA adduct do not significantly differ from those obtained for 1 : 1 adducts with neutral Lewis bases,[2] the fluorescence enhancement upon formation of the **2**·BrTBA adduct is lower. Actually, starting from DCM solutions of **2**, the formation of 1 : 1 adducts with neutral Lewis bases, *e.g.*, pyridine, involves a fluorescence enhancement of almost one order of magnitude.[2] Conversely, in the case of the **2**·BrTBA adduct, about a two-fold increase of the fluorescence intensity is observed (Fig. S3, ESI†). This lower fluorescence enhancement for the **2**·BrTBA adduct can be related to a quenching effect due to the heavy bromide ion.[14] As expected, analogous titrations of DCM solutions of **1** with TBA bromide or using non-coordinating anion species, *e.g.*, TBA hexafluorophosphate, do not involve appreciable optical absorption or fluorescence variations.

In summary, the comparison of optical absorption and fluorescent properties of **1** in DCM solution with those for the **2**·BrTBA adduct, analogously to ^{1}H NMR studies, indicates the existence of Zn···Br interactions. Although on statistical ground both intra- or intermolecular Zn···Br interactions or a combination of them are possible, however, spectroscopic data and the very low solubility of **1** in DCM in comparison to that of the **2**·BrTBA adduct[15] suggest the occurrence of intermolecular Zn···Br interactions and, hence, aggregate structures, *e.g.*, dimeric (Scheme 2) or oligomeric species, in solution.[16,17]



Scheme 2 A possible aggregation mode of **1** in DCM solution.

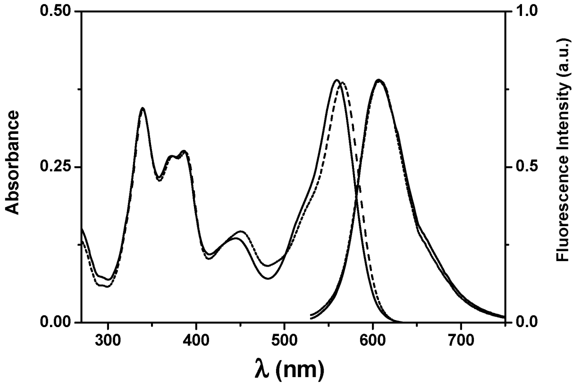


Fig. 3 UV/vis absorption and fluorescence (λ_{exc} = 501 nm) spectra in DCM of **1** (—) and the **2**·BrTBA adduct (– –) (1.0 × 10^{-5} M). The absorption spectrum of **1** was recorded with an absorbance of the longer wavelength band equal to that recorded for the **2**·BrTBA adduct.

These species are very stable in DCM and do not exhibit bromide displacement even with the addition of stoichiometric amounts of strong Lewis bases, *e.g.*, pyridine. To observe an appreciable **1**·pyridine adduct formation it needs adding 2000-fold mole excess of pyridine, as can be monitored by a significant increase of the fluorescence intensity. A complete bromide displacement is achieved by addition of *ca.* 10^5-fold mole excess of pyridine (Fig. S5, ESI†). Conversely, the addition of *ca.* 10^3-fold mole excess of pyridine is required for a complete bromide displacement in the case of the **2**·BrTBA adduct, in agreement with its simpler monomer nature.

Scanning electron microscopy (SEM) images of samples obtained by drop-casting from dilute DCM solutions of **1** indicate the existence of coral-like nanostructures (Fig. 4) whose structural motif may be related to an aggregate structure

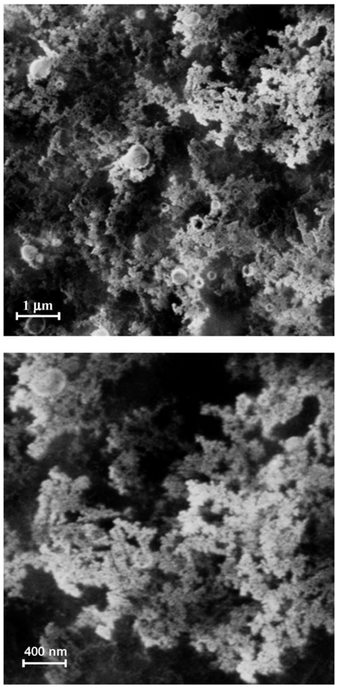
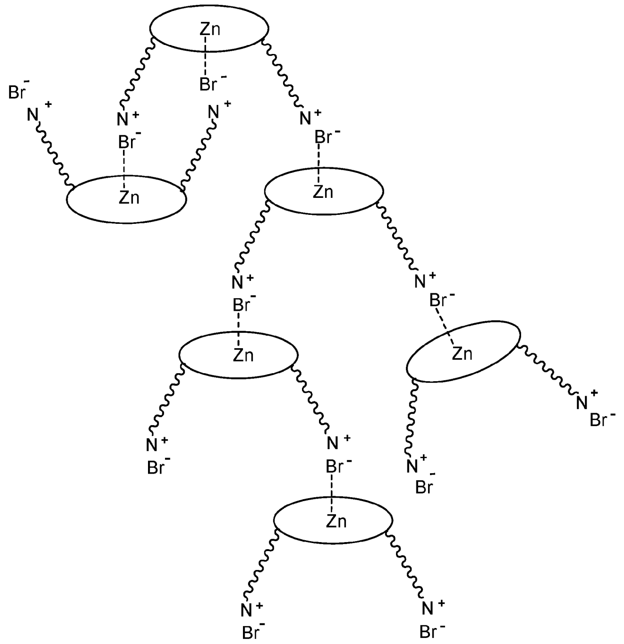


Fig. 4 Low (top) and high (bottom) magnification SEM images of **1** deposited by casting from a dilute DCM solution.



Scheme 3 A potential aggregation motif of **1** in the coral-like nanostructures.

as sketched in Scheme 3. In fact, considering intermolecular Zn···Br interactions and given the presence of the flexible side alkyl chains, a branched nanostructure can be envisaged. Although branched nanostructures are rather common among inorganic materials,[18] there are only a few molecular materials showing such a structure.[19] In this view, the present investigation represents a unique example of a metal–organic coordination complex exhibiting a branched nanostructure. On the other hand, SEM images of samples achieved by drop-casting from dilute DMSO solutions of **1** (Fig. S6, ESI†) indicate a very different, nanorod structure, in which **1** is presumably axially coordinated to the DMSO, thus avoiding any intermolecular branched aggregation.

Conclusions

The comparison of ^{1}H NMR and optical spectroscopic properties of the tailored bis(salicylaldiminato)Zinc(II) Schiff base complex, **1**, having dipodal, alkyl ammonium bromide derivatized chains in the salicylidene rings, with those of the reference complex **2**, through the study of the 1 : 1 **2**·BrTBA adduct, allowed getting insights into the nature of species in solutions.

In strict contrast to our previous studies on **2**, ^{1}H NMR and optical absorption spectral features of **1** are independent from the coordinating or non-coordinating nature of the solvent. With the exception of DMSO and DMF, in which 1 : 1 adducts with the solvent are likely to occur, present data suggest the existence of Zn···Br interactions in **1** in solution, thus satisfying its coordination sphere. This avoids intermolecular Zn···O interactions, as usually occur in the absence of other coordinating species.

SEM analysis of samples obtained by drop-casting from DCM solutions of **1** reveals the existence of branched nanostructures, whose structural motif is consistent with the existence of intermolecular Zn···Br interactions. These results represent an unprecedented example of a coordination complex exhibiting a branched nanostructure.

Experimental section

Materials and general procedures

Zinc acetate dihydrate, 2,4-dihydroxybenzaldehyde, 1,12-dibromododecane, trimethylamine, and TBA bromide (Aldrich) were used without purification. Diaminomaleonitrile (Aldrich) was purified by recrystallization from an ethanol solution. Dichloromethane (Aldrich) stabilized with amylene was used. DCM-d_2 was dried over anhydrous sodium sulfate and calcinated with zinc oxide overnight before using.

Measurements

Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. Solution NMR experiments were carried out on a Varian Unity Inova 500 (499.88 MHz for ^{1}H) spectrometer using an inverse detection tunable triple resonance pfg 5 mm ^{1}H^{13}C{X} probe capable of generating 60 G cm^{-1} field strengths. Optical absorption spectra were recorded at room temperature with a Varian Cary 500 UV-Vis-NIR spectrophotometer. Fluorescence spectra were recorded at room temperature with a Fluorolog-3 (Jobin Yvon Horiba) spectrofluorimeter. The fluorescence quantum yield was obtained using fluorescein (Φ_F = 0.925) in 0.1 M NaOH as standard. The absorbance value of the samples at and above the excitation wavelength was lower than 0.1 for 1 cm pathlength cuvettes. ESI mass spectra were recorded with a Finnigan LCQ-Duo ion trap electrospray mass spectrometer (Thermo). MALDI TOF mass spectra were recorded in linear mode with a Voyager-DE PRO (Perseptive Biosystem) mass spectrometer instrument, equipped with a nitrogen laser emitting at 337 nm, with a 3 ns pulse width and working in positive ion mode. The sample dissolved in DCM solvent was mixed with malononitrile/DMF, used as a matrix. The film surface morphology was examined by field emission scanning electron microscopy (FE-SEM) using a ZEISS SUPRA VP 55 microscope. Samples for SEM analysis were obtained by drop-casting dilute DMSO or DCM solutions ($\sim 1 \times 10^{-5}$ M) onto cleaned Si(100) substrates. Samples were sputtered with gold to avoid charging effects.

Syntheses

4-(12-Bromododecyloxy)-2-hydroxybenzaldehyde. A solution of 2,4 dihydroxybenzaldehyde (0.691 g, 5.00 mmol), 1,12-dibromododecane (1.641 g, 5.00 mmol) and potassium carbonate (0.346 g, 2.50 mmol) in acetonitrile (200 mL) was heated at reflux with stirring for 4 h under a nitrogen atmosphere. The reaction was followed by TLC (silica gel; eluent: cyclohexane/ethyl acetate 90 : 10 (v/v)). The solution was concentrated and the product was purified by column chromatography (silica gel; eluent: cyclohexane/ethyl acetate from 98 : 2 to 95 : 5 (v/v)) to obtain a white solid product (0.756 g, 39%). ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ = 1.26–1.39 (m, 16H; CH_2), 1.69–1.80 (m, 4H; CH_2), 3.51 (t, $^3J_{HH}$ = 6.5 Hz, 2H; CH_2–Br), 4.01 (t, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 2H; OCH_2), 6.46 (d, $^4J_{\mathrm{HH}}$ = 2.0 Hz, 1H; ArH), 6.55 (dd, $^3J_{\mathrm{HH}}$ = 8.5 Hz, $^4J_{\mathrm{HH}}$ = 2.0 Hz, 1H; ArH), 7.61 (d, $^3J_{\mathrm{HH}}$ = 8.5 Hz, 1H; ArH), 9.99 (s, 1H; CHO).

12-(4-Formyl-3-hydroxyphenoxy)-*N*,*N*,*N*-trimethyldodecan-1-ammonium bromide. In a two necked-flask, closed by a $\mathrm{CaCl_2}$ tube, a solution of 4-(12-bromododecyloxy)-2-hydroxybenzaldehyde (0.475 g, 1.23 mmol) in ethanol (40.0 mL) was saturated with trimethylamine. The yellow-brine solution was heated at 50 °C with stirring for 12 h and then concentrated to obtain a yellow solid product (0.542 g, quantitative yield). ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ = 1.39–1.42 (m, 16H; CH_2), 1.64–1.72 (m, 4H; CH_2), 3.03 (s, 9H; N(CH_3)$_3{}^+$), 3.03–3.27 (m, 2H; CH_2–N(CH$_3$)$_3{}^+$), 4.02 (t, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 2H; OCH_2), 6.46 (d, $^4J_{\mathrm{HH}}$ = 2.0 Hz, 1H; ArH), 6.54 (dd, $^3J_{\mathrm{HH}}$ = 8.5 Hz, $^4J_{\mathrm{HH}}$ = 2.0 Hz, 1H; ArH), 7.61 (d, $^3J_{\mathrm{HH}}$ = 8.5 Hz, 1H; ArH), 9.99 (s, 1H; CHO).

[2,3-Bis[[2-hydroxy-4-(1-*N*,*N*,*N*,*N*-trimethyldodecyl-12-oxy-ammonium bromide)benzylidene] amino]-2-butenedinitrilato] Zn$^{\mathrm{II}}$ (1). To a solution of 12-(4-formyl-3-hydroxyphenoxy)-*N*,*N*,*N*-trimethyldodecan-1-ammonium bromide (0.542 g, 1.22 mmol) in ethanol (30.0 mL), diaminomaleonitrile (0.0660 g, 0.610 mmol) was added with stirring. The mixture was heated at reflux with stirring for 1 h, under a nitrogen atmosphere. To the red solution, zinc acetate dihydrate (0.134 g, 0.610 mmol) was added and the mixture was heated at reflux with stirring for 2 h, under a nitrogen atmosphere. After cooling, a purple precipitate product was collected by filtration, washed with ethanol, and dried *in vacuo* (0.324 g, 60%). $\mathrm{C_{48}H_{74}Br_2N_6O_4Zn}$ (1024.35): calcd C, 56.28; H, 7.28; N, 8.20%; found C, 56.73; H, 7.34; N, 8.30%. ESI: m/z = 1024 [M]$^+$. MALDI-TOF: m/z = 1968 [(M)$_2$ − Br]$^+$. ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ = 1.27–1.40 (m, 32H; CH_2), 1.64–1.73 (m, 8H; CH_2), 3.02 (s, 18H; N(CH_3)$_3{}^+$), 3.23–3.26 (m, 4H; CH_2–N(CH$_3$)$_3{}^+$), 3.99 (t, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 4H; OCH_2), 6.17 (d, $^4J_{\mathrm{HH}}$ = 2.0 Hz, 2H; ArH), 6.21 (dd, $^3J_{\mathrm{HH}}$ = 8.5 Hz, $^4J_{\mathrm{HH}}$ = 2.0 Hz, 2H; ArH), 7.33 (d, $^3J_{\mathrm{HH}}$ = 8.5 Hz, 2H; ArH), 8.36 (s, 2H; CH = N).

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