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Rosette formation by hydrogen bonding of 5,5-dialkylbarbituric acids with 2-amino-4,6-bis [5-(4′-aminophenyl)porphyrinatozinc]-1,3,5-triazines in solution

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Porphyrin appended triazines (**11a**, **11b**) and dialkylbarbituric acids (**2a**, **2b**) were synthesised. The rosette formation by three-point intermolecular hydrogen-bonding interaction between substituted triazines and barbituric acid derivatives has been characterised in solution by UV–vis, IR, TGA–DTA and ESI-MS spectroscopy. The association constants of different combinations of host–guest moieties in equimolar quantities were determined by ^{1}H NMR titration studies in $CDCl_3$ at room temperature. The nature of substituents either on triazine or on barbituric acid were found to play a crucial role in rosette formation.

Keywords: porphyrinatozinctriazines; self-assembly; 5,5-dialkylbarbituric acids; hydrogen bonding

Introduction

Non-covalent synthesis is a powerful synthetic method for the preparation of complex molecular structures in supramolecular chemistry (*1*). Multiple hydrogen-bond-mediated non-covalent synthesis is an emerging area to understand the mechanism of complex biological interactions and the development of newer materials (*2*). The selectivity in non-covalent synthesis has been achieved by preorganisation, peripheral crowding, and cooperative and directional nature of hydrogen bond in functional molecules (*3–5*). The design and synthesis of covalent porphyrinic arrays analogous to those found in nature for charge separation, electron transport (*6*) and signal or transduction (*7*) have been examined to understand the molecular mechanism and mimic their functions. The formation of multiple hydrogen bonds between complementary molecular components is widely used in the fabrication of supramolecular assemblies such as a linear strand (ribbon or tape) (*8–10*) an undulating strand or crinkled tape and cyclic rosette (*10*). The preparation of monomeric hydrogen bond recognition unit-bearing chromophores allows the self-assembly of both polymers and discrete arrays with various structures in high yields by appropriate combinations of the molecular building blocks. Designed porphyrin arrays have been formed by hydrogen bonding (*11*, *12*), axial metalloporphyrin coordination (*13*, *14*) and coordination of exocyclic ligands (*15*).

5,5-Diethylbarbiturate and related compounds are attractive targets for molecular recognition study due to their sedative and anti-convulsant activities. In continuation of our interest in self-assembly and non-covalent synthesis of porphyrinic compounds (*16*), we present the synthesis of 2-amino-4,6-bis[5-(4′-aminophenyl)porphinatozinc(II)]-1,3,5-triazine (**11a**) and 2-amino-4,6-bis[5-(4′-aminophenyl)10,15,20-triphenylporphyrinatozinc(II)]-1,3,5-triazine (**11b**) and their interactions with 5,5-dialkylbarbiturates (**2a**,**2b**) in solution (Figure 1). The results of ^{1}H NMR titrations (in $CDCl_3$) between host (**2a**, **2b**) and guest (**11a**, **11b**), and ESI-MS studies (in CH_2Cl_2–CH_3CN) of these hydrogen-bonded compounds, along with additional information gathered from UV–vis, IR and TGA–DTA is also presented.

Results and discussion

The 5,5-dialkyl substituted barbiturates (**2a**, **2b**) have been synthesised by condensing the corresponding dialkyl substituted diethylmalonate with urea in presence of sodium ethoxide in ethanol (*8*) (Scheme 1). The cyanuric chloride and fluoride are suitable building blocks for the synthesis of porphyrin appended triazine (*17*). The reaction of cyanuric chloride with ammonia gave 2-amino-4,6-dichloro-1,3,5-triazine, (Scheme 4) which in turn on reaction with 5-(4′-aminophenyl)-10,15,20-triphenylporphyrinatozinc(II) (Scheme 3) gave 2-amino-4,6-bis[5-(4′-aminophenyl)-10,15,20-triphenylporphyrinatozinc(II)]-1,3,5-triazine (**11b**) in 88% yield (Scheme 5). Similarly, the reaction of 5-(4′-aminophenyl)porphinatozinc(II) (Scheme 2) with 2-amino-4,6-dichloro-1,3,5-triazine

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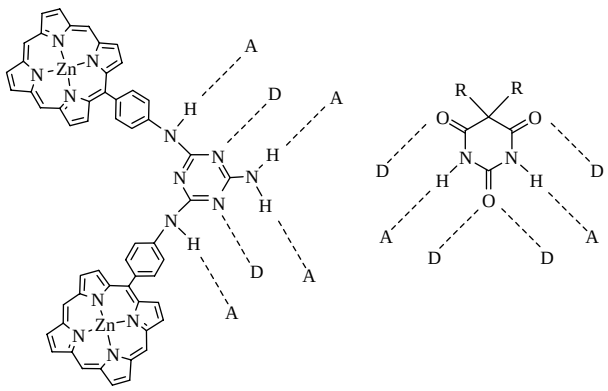
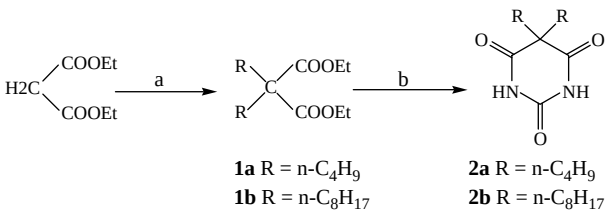


Figure 1. Two-way ADA and DAD arrays of functional porphine appended triazine and dialkyl substituted barbituric acid in formation of linear arrays and rosettes, respectively.

gave 2-amino-4,6-bis[5-(4′-aminophenyl)porphinatozinc(II)]-1,3,5-triazine, (**11a**) in 91% yield (Scheme 5).

In order to study the self-assembly by UV–vis spectra, 1 cm (10 mm) path length of cells allowing concentrations up to 2.14×10^{-5} mol l^{-1} was used. Equimolar concentrations (8.5×10^{-6} mol l^{-1}) of **2b** and **11b** in dichloromethane at 20 °C show 4 nm (419–423) red shift in Soret band and the relative intensity decreases by 35% with equal and consistent broadening (Figure 2). This is the evidence for self-assembly because the rotational conformations of **11b** are restricted to an eclipsed state, such that the effective cross-section per porphyrin **11b** is reduced. The relative Soret ε per **11b** decreases with increasing assembly concentration until it levels off at 2.14×10^{-5} mol l^{-1}, where a 5 nm red shift in Soret band and 45% decrease in intensity was recorded (Table 1). The red shift in Soret band and decrease in intensity was found different, for assemblies **11a**–**2b** and **11b**–**2a** (3 nm, 21%), and for **11a**–**2a** (2 nm, 11%). This shows that bulkier group substitution either on triazine or on barbiturate plays a dominating role in rosette formation in solution.

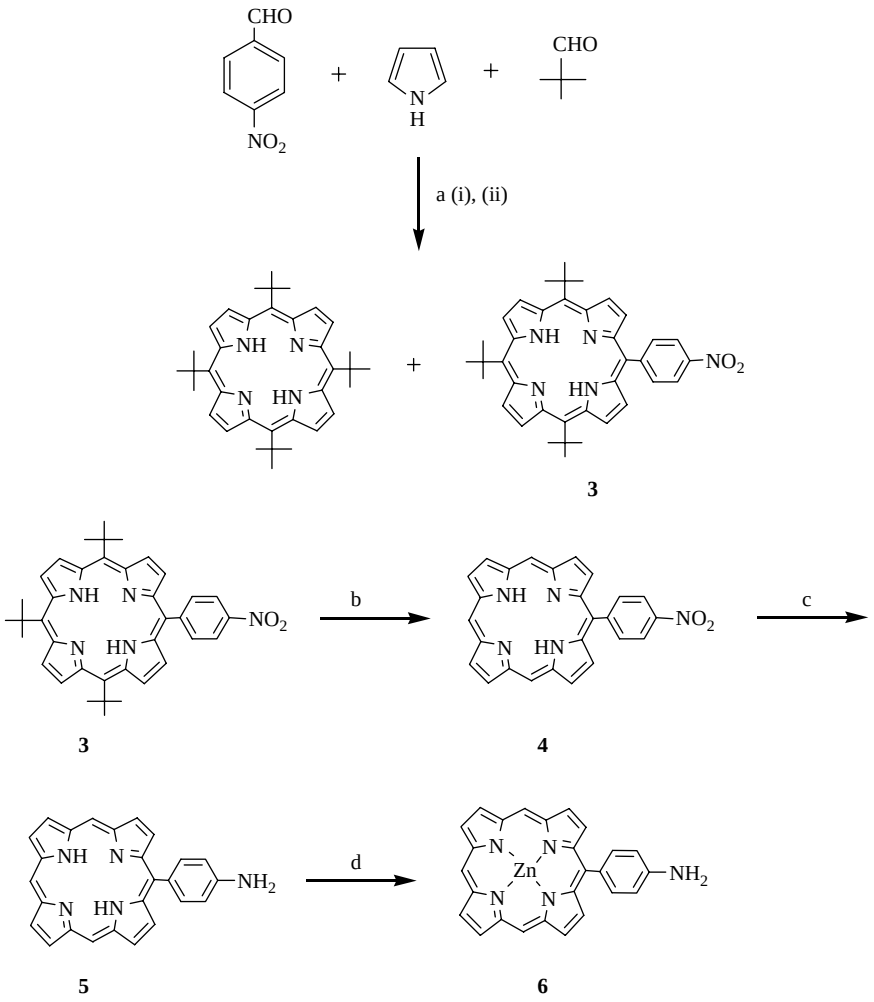
ESI-MS plays a prominent role in the direct detection of self-assembled species in solution (*18*). The electrospray mass spectra of the self-assembled species gave the protonated m/z^{++} parent peak (in 3:1; CH_2Cl_2:CH_3CN, 2.25×10^{-2} mol l^{-1}) in every combination of **2a**, **2b** and **11a**, **11b**. Cone voltage and source temperature of the instrument play an important role in the detection of aggregational behaviours. At high magnitude of above two parameters, we get the peaks of dissociated hetero-composite moieties. The best tuning parameters gave the expected protonated m/z^{++} peaks at 2740.9170 D for (**11b–2b**), (Figure 3) 2572.7177 D for (**2a–11b**), 2556.6171 D for (**2b–11a**) and 1888.4136 D for (**2a–11a**). No significant peaks were found at masses greater than or lower than (3 + 3) species; however, the total ion counts per 10 scans under the same experimental conditions were found to decrease in the above order. This is attributed to the stability and thus the binding constant of assembled moieties. The fact that no higher or lower order oligomers were obtained suggest that the predominant form under these experimental conditions was indeed the (3 + 3) species. In solvents with low hydrogen-bonding potentials, the added thermodynamic stability of the rosette as opposed to an open-chain polymer with enthalpically unfavourable 'unbounded' ends or entropically unfavourable higher order polymers, strongly argues in favour of the rosette structure.



1a R = n-C_4H_9 **2a** R = n-C_4H_9
1b R = n-C_8H_{17} **2b** R = n-C_8H_{17}

Scheme 1. Reagents and conditions (yields): (a) NaOEt/EtOH, 1-bromoalkane, reflux, 8 h, (70%) for **1a** and (72%) for **1b**; (b) NaOEt/EtOH, H_2NCONH_2, reflux, 12 h, N_2, 65% for **2a** and 62% for **2b**.

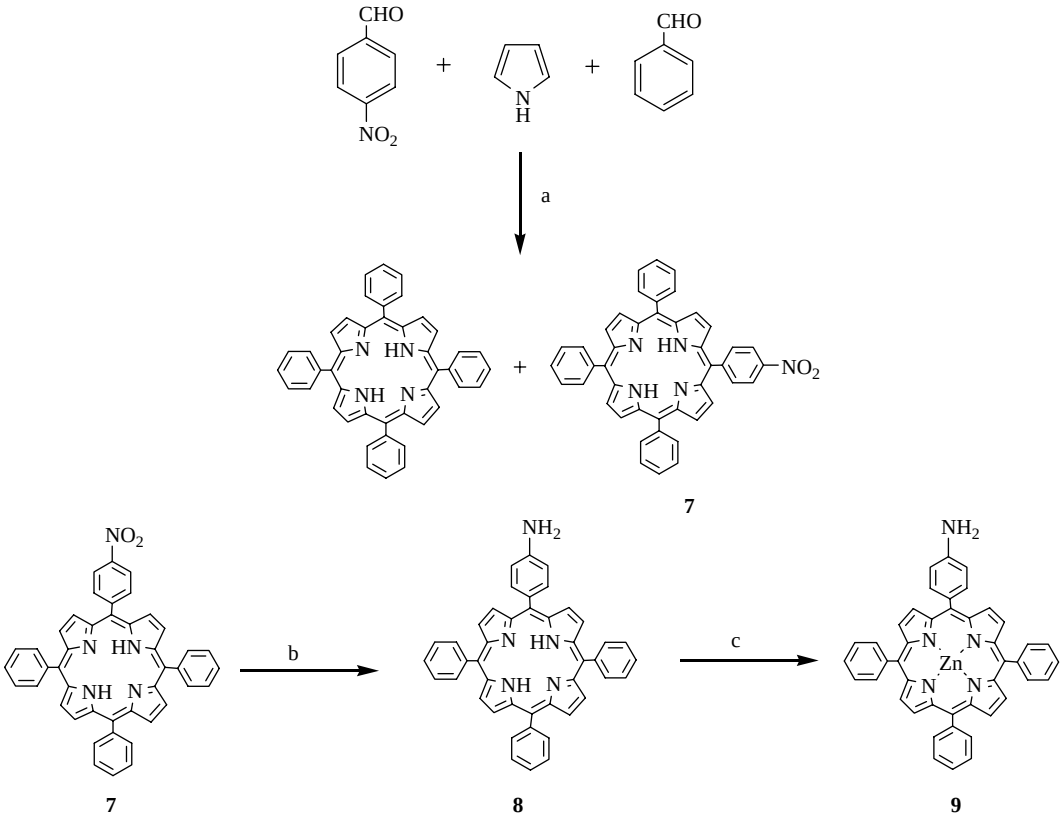
The equilibrium constant K_a may be determined by ^{1}H NMR experiments that monitor the chemical shift of suitable protons vs. the concentration of the complimentary moiety (*19*). Association constants of hydrogen-bonded complexes were determined from evaluation of ^{1}H NMR data by computer fitting with non-linear regression curves. For all donor–acceptor–donor (DAD) and acceptor–donor–acceptor (ADA) hetero complexes studied, a 1:1 stoichiometry was observed using Job plots (*20*) (Figure 4). Upon formation of assemblies, the NH protons of barbiturate components and NH_2 protons of triazine components get involved in hydrogen bonding and undergo a large downfield shift from 8.3 to 14.72 and from 4.1 to 5.5 ppm (δ), respectively (Figure 5). Since the peaks of NH protons of triazine components (**11a**, **11b**) were observed overlapping with resonances of other protons, therefore these protons were not followed for NMR titration. The efficacy of **2a**, **2b** for triazine derivatives (**11a**, **11b**) was evaluated by ^{1}H NMR titrations in $CDCl_3$. The change in the chemical shift of the NH protons of barbiturates (**2a**, **2b**) was followed as a function of increasing concentration of porphyrin appended triazine (**11a**, **11b**) until saturation of the chemical shift values was reached. The ^{1}H NMR chemical shifts of NH protons of **2a**, **2b** and NH_2 protons of **11a**, **11b** at zero concentration of composite components and their saturation chemical shifts have been tabulated in Table 2. The high association constant (4.5×10^3 M^{-1}) was observed for pair **2b–11b**. This may be attributed to the bulkier substitution on both, barbiturate and a triazine component which favours rosette formation in solution phase (*10*). The association constants of the composite of **2a**, **2b** and **11a**, **11b** were found to be 3.8×10^3 M^{-1}



Scheme 2. Reagents and conditions (yields): (a) (i) CH_2Cl_2, BF_3OEt_2, rt, 1 h, N_2; (ii) DDQ, reflux, 1 h, (10% of **3**); (b) H_2SO_4, 1-butanol, 90 °C, 30 min. (77%); (c) $SnCl_2$, concentration HCl, 65 °C, 2h, (90%); (d) Zn $(OAC)_2{\cdot}2H_2O$, DMF, reflux, 2 h, 95%.

(for **2b–11a**), $4.2 \times 10^3\,M^{-1}$ (for **2a–11b**) and $3.5 \times 10^3\,M^{-1}$ (for **2a–11a**). The estimated error was calculated to be $\leq \pm 10\%$ in each case. The least binding constant $3.5 \times 10^3\,M^{-1}$ (for **2a–11a**) was due to less bulkier substitution on the composite moieties. These observations are in agreement with the formation of a defined, closed supramolecular array rather than a polymeric chain of different lengths; as is also observed in other hydrogen-bond self-assembled systems (*11*). In IR spectrum too, this type of intermolecular hydrogen bonding can be recognised (*21*). In CH_2Cl_2 however, equimolar quantities ($2.25 \times 10^{-2}\,mol\,l^{-1}$) of the two composite moieties were associated and gave absorbances at $1624\,cm^{-1}$ (for unassociated carbonyl, $1676\,cm^{-1}$) and at $3393\,cm^{-1}$ (for monomer amino, $3469\,cm^{-1}$) in IR, showing a remarkable frequency decrease due to hydrogen bonding.

Melamine (M) and cyanuric acid (CA) form different structural motifs (*2*) (a cyclic rosette, a linear tape and a crinkled tape) that can be derived from the lattice. This lattice is remarkably stable (*22*); its DGA–DTA analysis shows major weight loss in the temperature range of 224.6–475.0 °C. This stability reflects the presumption that removing one molecule of melamine or cyanuric acid from the lattice requires breaking nine hydrogen bonds, each with energies approximately 30 kJ/mol (*23*). The TGA–DTA analysis of our assembled system showed a major weight loss in the temperature range of 142.1–240.9 °C, which is less than that for the melamine–cyanuric acid motif. This analysis also supports the cyclic rosette (containing a total of 18 hydrogen bonds) formation rather than polymeric linear tape (containing infinite hydrogen bonds) from barbiturate and triazine components.



Scheme 3. Reagents and conditions (yields): (a) propionic acid, reflux, 2 h, (9% of **7**); (b) $SnCl_2$, concentration HCl, 65 °C, 2 h, (94%); (c) Zn $(OAC)_2{\cdot}2H_2O$, DMF, reflux, 2 h, 95%.

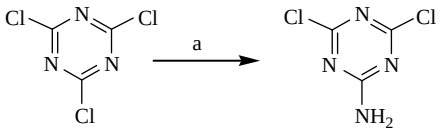
Conclusion

In conclusion, the self-assembly between DAD bearing units **2a**, **2b** and ADA bearing units **11a**, **11b** is studied in detail. It is found that a bulkier substitution on triazine or on barbituric acid or on both favours the cyclic rosette formation given by the stability of hydrogen-bonded cyclic rosettes in solution phase. In the pair with the lowest binding constant (**2a–11a**), the thermodynamic equilibrium is less shifted towards cyclic rosette than in pair (**2b–11b**). The ESI-MS molecular mass determination provided strong support in favour of the formation of supramolecular (3 + 3) cyclic rosette. The UV–vis, TGA–DTA and IR also support the intermolecular hydrogen bonding between all synthesised DAD-ADA hetero-composite moieties.

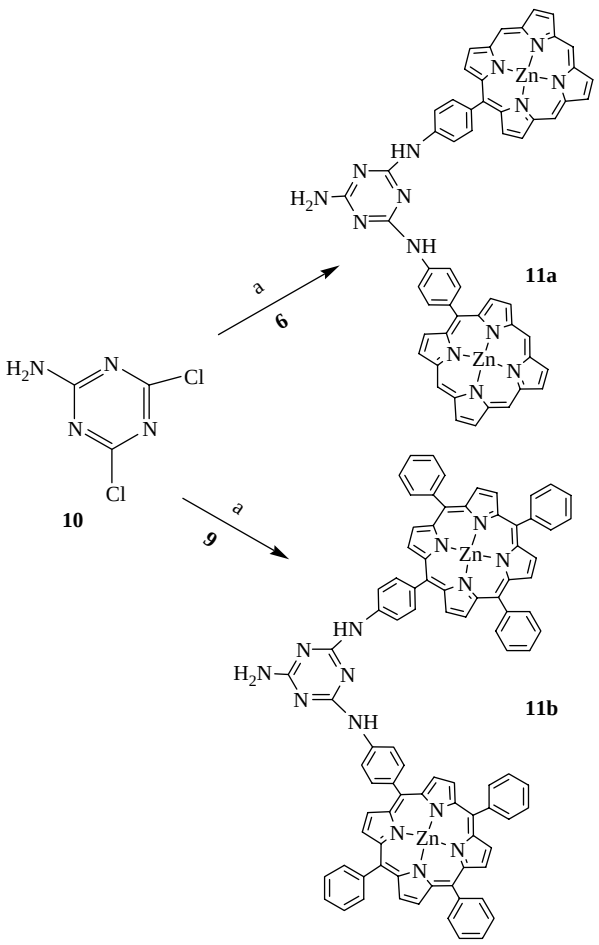
Experimental

General

All melting points are uncorrected, expressed in degree centigrade and recorded on Thomas Hoover Unimelt capillary melting point apparatus. The electronic transition spectra were recorded on a Perkin–Elmer (λ 35) UV–vis spectrophotometer, and the absorption maxima (λ_{max}) are expressed in nanometres. High-resolution mass spectra (ES) were recorded on a VG-Fisons 'Autospec' spectrometer. The infrared spectra were recorded on Perkin-Elmer spectrum FT-2000 spectrometer and ν_{max} are expressed in cm^{-1}. ^1H NMR and ^{13}C NMR were recorded on Bruker Avance-300 (300 MHz) spectrometer using tetramethylsilane (TMS) as internal standard and chemical shifts (δ) are expressed in ppm. ESI-MS were recorded using LC-TOF (KC-455) mass spectrometer of Waters. Column chromatography was performed using spectrochem silica gel 60–120 mesh for simple and 230–400 mesh for flash chroma-



Scheme 4. Reagents and conditions (yields): (a) acetone–ice water, NH_4OH, 0 °C, 2 h (70%).



Scheme 5. Reagents and conditions (yields): (a) 1,4-dioxane, DBU, reflux, 10 h, N_2 (91%) for **11a** and (88%) for **11b**.

tography. The solid compounds were dried under vacuum in the presence of P_2O_5. All reagents and solvents were of analytical grade and used without further purification.

*General synthesis of dialkyl diethylmalonate (**1a, 1b**)*

Diethylmalonate (7.68 g, 48 mmol) was added to a solution of sodium ethoxide (6.80 g, 100 mmol) in 100 ml of absolute ethanol with stirring at room temperature for 30 min. The alkylhalide (100 mmol) was added dropwise over a period of half an hour. After a short induction period, a mildly exothermic reaction was observed accompanied by the formation of a white precipitate (sodium halide). Then the reaction mixture was refluxed for 8 h. The reaction was cooled to room temperature and the residue was treated with water and allowed to separate into two layers. The upper layer was crude dialkyl diethylmalonate, separated and purified by flash chromatography (elution with petroleum ether) to give the title compounds in good yield.

*Compound **1a***

9.14 g (70%) as a colourless liquid. R_f 0.75 (petroleum ether); δ_H (300 MHz; $CDCl_3$) 4.16 (4H, q, $J = 7$ Hz, OEt), 1.84 (4H, m, *n*-C_4H_9), 1.28 (4H, m, *n*-C_4H_9), 1.22 (6H, t, $J = 7$ Hz, OEt), 1.12 (4H, m, *n*-C_4H_9), 0.88 (6H, t, $J = 7$ Hz, *n*-C_4H_9); ES-HRMS calcd for $(C_{15}H_{28}O_4{\cdot}Na)^+$295.1885, found 295.1881. Yield of **1b**. 13.15 g (72%) as a colourless liquid. R_f 0.90 (petroleum ether); δ_H (300 MHz; $CDCl_3$) 4.21 (4H, q, $J = 7$ Hz, OEt), 1.81 (4H, m, *n*-C_8H_{17}), 1.26 (4H, m, *n*-C_8H_{17}), 1.20 (6H, t, $J = 7$ Hz, OEt), 1.11 (4H, m, *n*-C_8H_{17}), 0.88 (6H, t, $J = 7$ Hz, *n*-C_8H_{17}); ES-HRMS calcd for $(C_{23}H_{44}O_4{\cdot}Na)^+$407.3137, found 407.3136.

*General synthesis of 5,5-dialkylbarbituric acid (**2a, 2b**)*

In the solution of 2.72 g (40 mmol) sodium ethoxide in 50 ml of absolute ethanol, 2.9 g (20 mmol) urea was added with stirring. The temperature of the reaction mixture was raised to 50–60 °C and dialkyl diethylmalonate (20 mmol) was added. The reaction was stirred and refluxed for 12 h under anhydrous conditions. Upon cooling, the sodium salt of dialkylbarbituric acid separated, was filtered off, dissolved in water and the free acid was precipitated by the addition of hydrochloric acid. The compound was filtered and recrystallised with acetone–petroleum ether to give the title compounds in quantitative yields. Compound **2a**. Yield 4.6 g (65%) as a colourless solid. Mp 159–161 °C (*8*); IR ν_{max} (KBr)/cm^{-1} 3444, 3350, 3261, 2806, 2653, 2474, 1676, 1624, 1460, 1153; δ_H (300 MHz; $CDCl_3$) 8.31 (2H, s, NH), 1.83 (4H, m, *n*-C_4H_9), 1.27 (4H, m, *n*-C_4H_9), 1.12 (4H, m, OEt), 1.12 (4H, m, *n*-C_4H_9), 0.91 (6H, t, $J = 7$ Hz, *n*-C_4H_9); ES-

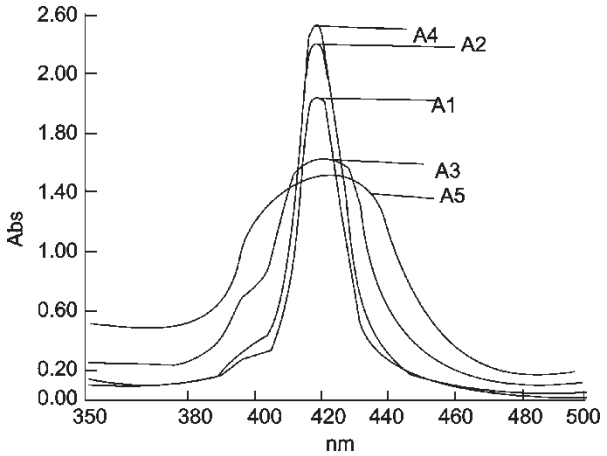


Figure 2. Electronic transition spectra of compound **9**; $\mathbf{A_1}$, **11b** (concentration 8.5×10^{-6} mol l^{-1}); $\mathbf{A_2}$, self-assembly formed by equimolar quantity (8.5×10^{-6} mol l^{-1}) of **2b** and **11b** in dichloromethane; $\mathbf{A_3}$, **11b** (concentration 2.14×10^{-5} mol l^{-1}); $\mathbf{A_4}$, self-assembly formed by equimolar quantity (2.14×10^{-5} mol l^{-1}) of **2b** and **11b** in dichloromethane; $\mathbf{A_5}$.

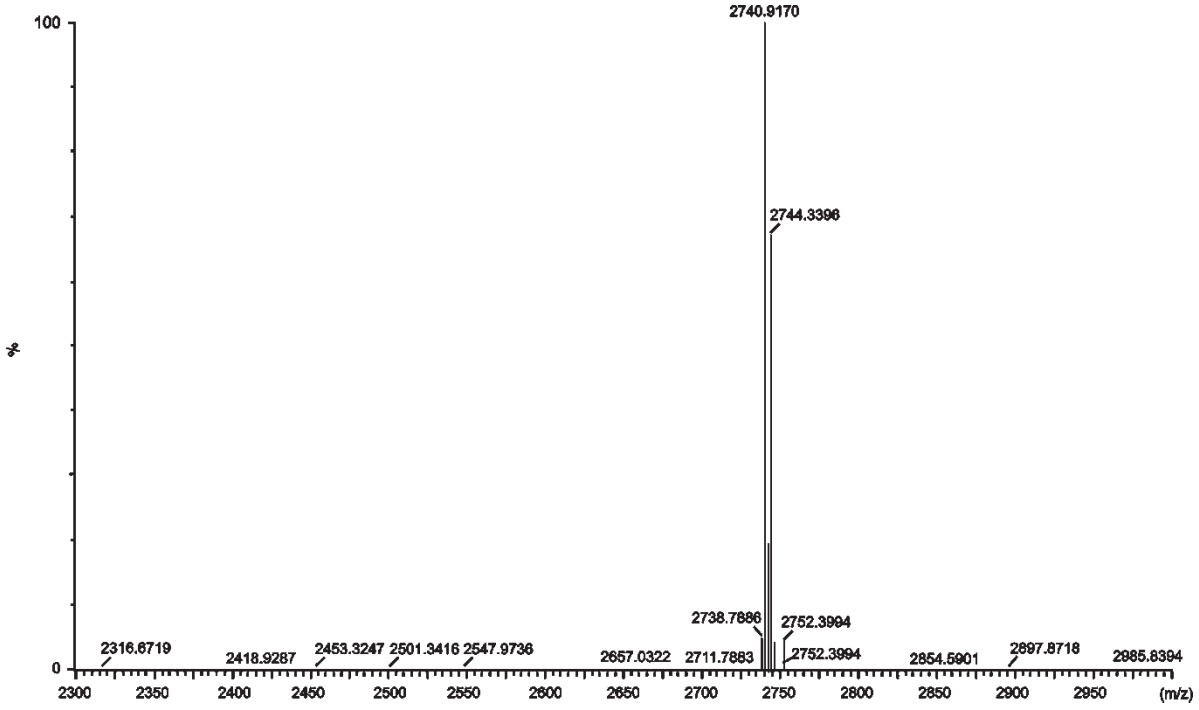


Figure 3. ESI-MS spectra in positive mode of equimolar (2.25×10^{-5} mol l^{-1}) of **2b** and **11b** (in CH_2Cl_2:CH_3CN; 3:1) resulted the protonated m/z^{++} parent peak at 2740.9170 D.

HRMS calcd for $(C_{12}H_{20}N_2O_3{\cdot}Na)^+$263.1372, found 263.1377. Compound **2b**. Yield 10.5 g (62%) as a colourless solid. Mp 118–120 °C; IR ν_{max} (KBr)/cm^{-1} 3443, 3351, 3261, 2802, 2651, 2474, 1676, 1624, 1462, 1153; δ_H (300 MHz; $CDCl_3$) 8.29 (2H, s, NH), 1.71 (4H, m, *n*-C_8H_{17}), 1.29–1.11 (24H, m, *n*-C_8H_{17}), 0.90 (6H, t, $J = 7$ Hz, *n*-C_8H_{17}); ES-HRMS calcd for $(C_{20}H_{36}O_3{\cdot}Na)^+$375.2624, found 375.2626.

*Synthesis of 5-(4′-nitrophenyl)-10,15,20-tritertiarybutylporphyrin (**3**)*

A 2-l three-necked, round-bottomed flask fitted with a reflux condenser and nitrogen inlet port was filled with 1 l of distilled CH_2Cl_2. Samples of pivalaldehyde (1.65 ml, 0.015 mol), *p*-nitrobenzaldehyde (0.755 gm, 0.005 mol) and pyrrole (1.38 ml, 0.02 mol) were added and the solution was stirred magnetically at room temperature under a slow steady stream of nitrogen. After 15 min, BF_3 etherate (0.5 ml of a 2.5 M solution in CH_2Cl_2, 10^{-3} M) was added and the reaction vessel was shielded from ambient lighting (*24*). After 1 h, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (3.045 g, 0.015 mol) in powder form was added all at once to the reaction vessel. The flask was immersed in a water bath preheated to 45 °C and the solution was refluxed for 1 h. The solution was then concentrated to about 50 ml by rotatory evaporation. TLC analysis (chloroform:petroleum ether 1:1) showed a mixture of two major isomers. Separation by column chromatography on silica gel eluting with chloroform:petroleum ether (1:1) provided the required compound **3** (0.29 g (10%, based on *p*-nitrobenzaldehyde). $R_f = 0.75$ (chloroform), IR (film, cm^{-1}) 1597, 1521 (ν asym NO_2), 1474, 1348 (ν sym NO_2), 966; δ_H (300 MHz; $CDCl_3$) 8.85 (2H, d, $J = 5$ Hz, β-pyrrole), 8.84 (4H, s, β-pyrrole), 8.67 (2H, d, $J = 5$ Hz, β-pyrrole), 8.53 (2H, d, $J = 8$ Hz, nitrophenyl), 8.30 (2H, d, $J = 8$ Hz, nitrophenyl), 1.27 (27H, s, *t*Bu), −3.97 (2H, s, NH); ES-HRMS calcd for $(C_{38}H_{41}N_2O_2{\cdot}H)^+$600.3338, found 600.3336; UV–vis (λ_{max} CH_2Cl_2, (log ε)): 447 (5.58), 551 (4.31), 596 (3.97), 621 (3.77), 693 (3.63).

Table 1. Electronic absorption bands of self-assembly and related compounds at different concentrations in dichloromethane.

Entry	Compounds	Q(0,0) (ε)	Q(1,0) (ε)	B(0,0) (ε)
1	**9**	586 (0.53)	547 (1.88)	419 (25.23)
2	**11b$_1$**	587 (0.61)	548 (1.92)	419 (28.63)
3	**SA-1**	589 (0.43)	549 (1.32)	423 (18.54)
4	**11b$_2$**	587 (0.63)	548 (2.02)	419 (29.71)
5	**SA-2**	589 (0.12)	549 (0.51)	424 (6.82)

Wave length (λ) in nm, ε in $dm^3\,mol^{-1}\,mm^{-1} \times 10^4$. **9**, 5-(4′-aminophenyl)-10,15,20-triphenylporphyrinato zinc; **11b$_1$**, 2-amino-4,6-bis[5-(4′-aminophenyl)-10,15,20-triphenylporphyrinato zinc]-1,3,5-triazine (concentration = 8.5×10^{-6} mol l^{-1}). **SA-1**, self-assembly formed by equimolar quantity (8.5×10^{-6} mol l^{-1}) of **2b** and **11b** in dichloromethane. **11b$_2$**, 2-amino-4,6-bis[5-(4′-aminophenyl)-10,15,20-triphenylporphyrinato zinc]-1,3,5-triazine (concentration = 2.14×10^{-5} mol l^{-1}). **SA-2**, self-assembly formed by equimolar quantity (2.14×10^{-5} mol l^{-1}) of **2b** and **11b** in dichloromethane.

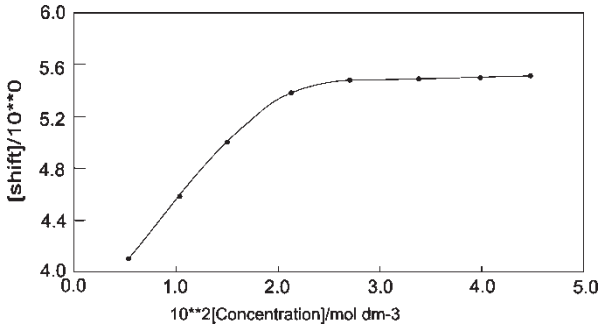


Figure 4. Non-linear regression curve, obtained by plotting change in chemical shift (δ, in ppm) of amino protons of **11b** upon complexation with **2b**, vs. concentration.

*Synthesis of 5-(4′-nitrophenyl)porphine (**4**)*

5-(4′-Nitrophenyl)-10,15,20-tritertiarybutylporphyrin, **3** (250 mg), dissolved in sulphuric acid (10 ml)/1-butanol (10 ml) mixture, was heated with stirring in an oil bath at 90 °C for 30 min (*25*). Methanol (50 ml) and chloroform (250 ml) were added to the cooled solution before being washed with dilute aqueous sodium hydroxide and water until neutrality. The chloroform layer was evaporated to dryness and the residue was purified by flash chromatography eluted with chloroform to get 0.125 g (70%) of the titled compound. δ_H (300 MHz; $CDCl_3$) 10.46 (3H, s, *meso*-CH), 9.24 (2H, d, $J = 5$ Hz, β-pyrrole), 8.98 (4H, s, β-pyrrole), 8.86 (2H, d, $J = 5$ Hz, β-pyrrole), 8.25 (2H, d, $J = 8$ Hz, nitrophenyl), 7.93 (2H, d, $J = 8$ Hz, nitrophenyl), −3.97 (2H, s, NH); ES-HRMS calcd for $(C_{26}H_{17}N_5O_2{\cdot}H)^+$432.1461, found 432.1462; UV–vis (λ_{max} CH_2Cl_2, (log ε)): 394 (5.12), 489 (4.13), 519 (3.51), 558 (3.77), 631 (3.16). The dramatic Soret shift (447–394 nm) from compound **3** was observed due to removal of three bulkier *tert*-butyl groups making the molecule planar.

*Synthesis of 5-(4′-aminophenyl)porphine (**5**)*

The mixture of 5-(4′-nitrophenyl)porphine **4**, 100 mg (0.23 mmol), 1 g tin chloride (in excess), in 20 ml concentration HCl was refluxed for 2 h (*26*). After cooling, the reaction mixture was filtered and given

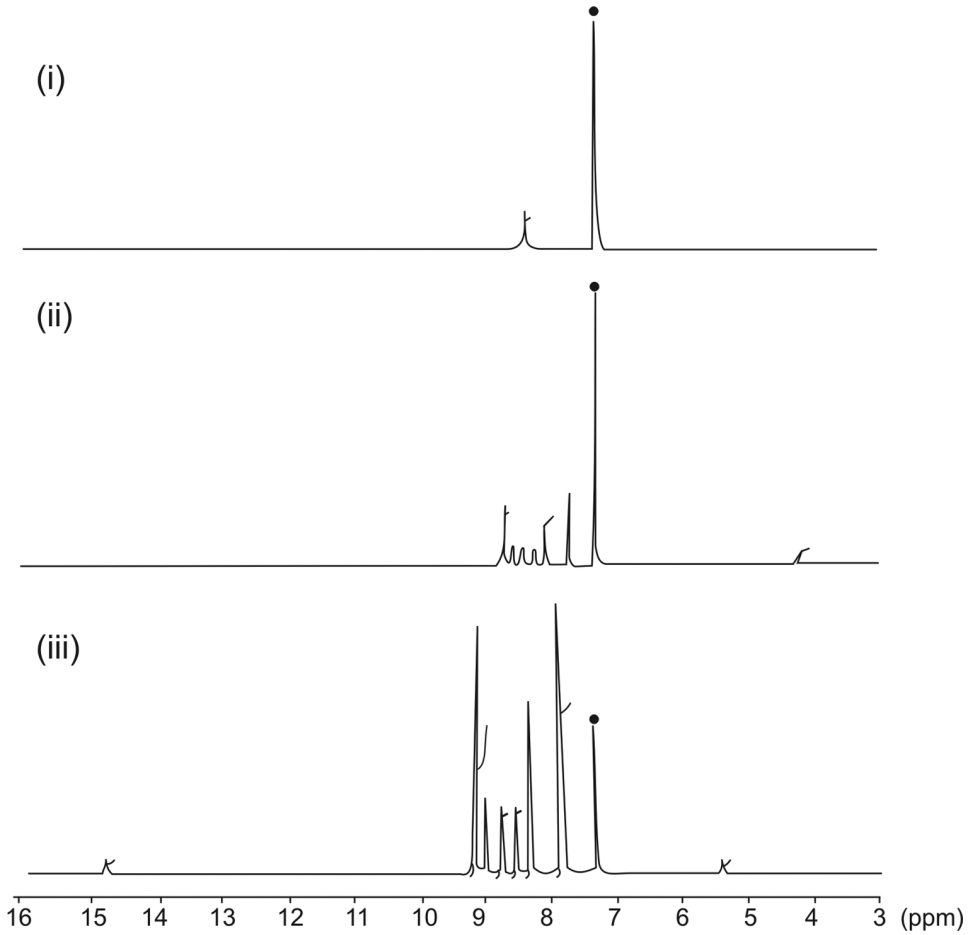


Figure 5. Partial ^{1}H NMR spectrum (300 MHz, $CDCl_3$, TMS) of: (i) **2b**, (ii) **11b**, (iii) 1:1 complexation of **2b** and **11b**. The amino protons signal of **11b** shifted from 4.11 to 5.51 ppm and amidic protons signal of **2b** from 8.33 to 14.72 ppm (δ).

Table 2. ^{1}H NMR chemical shifts of the NH_2 protons of **11a** and **11b** at zero concentration of the **2a** and **2b** and at their saturation, respectively.

	Substituted barbituric acid analogues	
Triazine derivatives	**2a**	**2b**
11a	4.31; 5.17	4.28; 5.19
11b	3.93; 5.44	4.11; 5.51

sufficient water washing until last washing showed an acidic character on pH paper. Recrystallisation of the crude compound with petroleum ether–ethyl acetate yielded 0.084 g (90%) pure compound **5**. $R_f = 0.60$ in chloroform. δ_H (300 MHz; $CDCl_3$) 10.36 (3H, s, *meso*-CH), 9.12 (2H, d, $J = 5$ Hz, β-pyrrole), 8.91 (4H, s, β-pyrrole), 8.82 (2H, d, $J = 5$ Hz, β-pyrrole), 8.21 (2H, d, $J = 8$ Hz, aminophenyl), 7.91 (2H, d, $J = 8$ Hz, aminophenyl), 5.30 (2H, br s, NH_2), −4.02 (2H, s, NH); ES-HRMS calcd for $(C_{26}H_{19}N_5{\cdot}H)^+$402.1719, found 402.1714; UV–vis (λ_{max} CH_2Cl_2, (log ε)): 394 (5.11), 488 (4.10), 520 (3.50), 558 (3.71), 630 (3.11).

*Synthesis of 5-(4′-aminophenyl)porphinatozinc(II) (**6**)*

Zinc (II) is inserted into the porphyrin by standard methods (*26*, *27*). Zinc acetate dihydrate, 400mg (in excess), is added in the solution of 80 mg 5-(4′-aminophenyl)porphine in 50 ml dimethylformamide. The solution was refluxed for 3h after which a small sample of reaction mixture was extracted with chloroform and analysed by using visible spectroscopy. The spectrum indicated that the metal insertion is complete with the four Q bands of free base ($\lambda = 488$, 520, 558 and 630 nm), collapsing to two peaks ($\lambda = 545$ and 590 nm); in ^{1}H NMR, the peak at δ −4.02 ppm (s, 2H, pyrrole NH) disappears. After cooling, the reaction mixture was filtered in order to remove excess of zinc salt and 250 ml of water added to the filtrate in order to precipitate the compound. The compound was filtered and washed with plenty of water and air-dried. The residue was chromatographed on silica gel (60–120 mesh) and eluted with chloroform to get the pure metallated compound, 88 mg (95%). $R_f = 0.30$ in chloroform:UV–vis (λ_{max} CH_2Cl_2, (log ε)): 394 (5.10), 545 (2.18), 590 (1.65). ES-HRMS calcd for $(C_{26}H_{17}N_5Zn{\cdot}H)^+$464.0854, found 464.0856.

*Synthesis of 5-(4′-nitrophenyl)-10,15,20-triphenylporphyrin (**7**)*

Pyrrole (5.5 ml, 80 mmol) was added to a solution of benzaldehyde (6 ml, 60 mmol) and *p*-nitrobenzaldehyde (3.02 g, 20 mmol) in propionic acid under stirring at a refluxing temperature for 2 h. The reaction mixture was cooled to room temperature and allowed to stand overnight. Filtration under suction pump on a Buchner funnel and water washing of reaction mixture afforded a purple crude product in quantitative yield. The TLC analysis (ethyl acetate:petroleum ether, 1:3) showed the mixture of two isomers. Separation by column chromatography on silica gel eluting with ethyl acetate:petroleum ether (1:4) yielded 1.05 g (4.0%, based on *p*-nitrobenzaldehyde) of the required compound. IR (film, cm^{-1}) 1598, 1520 (ν asym NO_2), 1474, 1349 (ν sym NO_2), 964; δ_H (300 MHz; $CDCl_3$) 8.85 (2H, d, $J = 5$ Hz, β-pyrrole), 8.84 (4H, s, β-pyrrole), 8.67 (2H, d, $J = 5$ Hz, β-pyrrole), 8.53 (2H, d, $J = 8$ Hz, nitrophenyl), 8.30 (2H, d, $J = 8$ Hz, nitrophenyl), 8.19 (6H, m, ArH), 7.70 (9H, m, ArH), −2.72 (2H, s, NH); MS (ESI) *m*/*z* (M + H^+, 660); UV–vis (λ_{max} CH_2Cl_2 (log ε): 418 (5.58), 515 (4.31), 551 (3.97), 589 (3.77), 646 (3.63).

*Synthesis of 5-(4′-aminophenyl)-10,15,20-triphenylporphyrin (**8**)*

The mixture of 300 mg (0.45 mmol) 5-(4′-nitrophenyl)-10,15,20-triphenylporphyrin, 2 g tin chloride (in excess) in 50 ml concentration HCl was refluxed for 2 h. After cooling, the reaction mixture was filtered and given sufficient water washing, until the last washing shows acidic character on the pH paper. Recrystallisation of the crude compound with petroleum ether–ethyl acetate yielded 0.27 gm (94%) of the pure compound **D**. $R_f = 0.45$ in chloroform/$R_{flit.} = 0.47$ in chloroform (*28*). δ_H (300 MHz; $CDCl_3$) 8.94 (2H, d, $J = 5$ Hz, β-pyrrole), 8.84 (2H, d, $J = 5$ Hz, β-pyrrole), 8.82 (4H, s, β-pyrrole), 8.23 (6H, m, ArH), 8.00 (2H, d, $J = 8$ Hz, aminophenyl), 7.76 (9H, m, ArH), 7.06 (2H, d, $J = 8$ Hz, aminophenyl), 4.02 (2H, br s, NH_2), −2.72 (2H, s, NH); MS (ESI) *m*/*z* (M + H^+, 630); UV–vis (λ_{max} CH_2Cl_2 (log ε): 421 (5.49), 516 (4.28), 551 (3.91), 589 (3.73), 647 (3.57).

*Synthesis of 5-(4′-amino phenyl)-10,15,20-triphenylporphyrinatozinc(II), (**9**)*

Zinc (II) is inserted into the porphyrin by standard methods. Zinc acetate dihydrate 687mg (3.16 mmol) is added in the solution of 200 mg (0.316 mmol) 5-(4′-aminophenyl)-10,15,20-triphenylporphyrin in 50 ml dimethylformamide. The solution was refluxed for 3 h after which a small sample of the reaction mixture was extracted and analysed by visible spectroscopy. The spectrum indicated that the metal insertion is complete with the four Q bands of free base ($\lambda = 517$, 551, 589 and 647 nm), collapsing to two peaks ($\lambda = 548$ and 587 nm). After cooling, the reaction mixture was filtered in order

to remove excess of zinc salt and 250 ml of water was added to the filtrate in order to precipitate the compound. This compound was filtered and washed with plenty of water and then air-dried. The residue was chromatographed on silica gel (60–120 mesh) and eluted with chloroform to get 200 mg (95%) of pure metallated compound. UV–vis (λ_{max} CH_2Cl_2, (log ε)): 424 (4.32), 554 (3.15), 596 (2.42). MS (ESI) *m/z* ($M + H^+$, 693.4).

*Synthesis of 2-amino-4,6-dichloro-1,3,5-triazine (**10**)*

2,4,6-Trichloro-1,3,5-triazine (cyanuric chloride), 2.5 g (13.5 mmol), was dissolved in acetone (20 ml) and poured into 20 ml of ice water to form a very fine suspension. Ammonium hydroxide solution (30 ml, 1N, 30 mmol) was added dropwise at a rate allowing keeping the temperature between 0 and 5 °C. The mixture was stirred for 30 min at 0 °C and additional for 30 min at room temperature. The precipitate was filtered off, washed with water (4 × 25 ml), and dried under a high vacuum giving a pure white solid compound **10**, 1.56 g (70%); mp 223–225 °C (lit.(*29*) 222–225 °C); IR ν_{max} (Nujol)/cm^{-1} 3488, 3341, 3178, 3116, 1725, 1685, 1647, 1589, 1570, 1530, 1463, 1377, 1302, 1084, 994, 916; δ_H (300 MHz; DMSO-d_6) 5.43 (2H, br s, NH_2); δ_c (75 MHz; DMSO-d_6) 166.8, 169.3; ES-HRMS calcd for $(C_3H_2N_4Cl_2{\cdot}H)^-$ 162.9578, found 162.9577.

*Synthesis of 2-amino-4,6-bis[5-(4′-aminophenyl)porphinatozinc(II)]-1,3,5-triazine (**11a**)*

In a 100 ml round-bottomed flask, equipped with an efficient condenser, charged 5-(4′-aminophenyl)-10,15,20-trimethyneporphyrinatozinc (II), 80 mg (0.17 mmol), and 2-amino-4,6-dichloro-1,3,5-triazine, 13 mg (0.08 mmol) in 30 ml dry 1,4-dioxane, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 30 μl (0.20 mmol) were added. The zinc porphyrin was used because of its higher stability and the enhanced nucleophilicity of the amino group; further with DBU, the yield was improved than with the reported sodium bicarbonate (*11*) and diisopropylethylamine, DIPEA (*30*). The reaction mixture was refluxed (110 °C) for 6 h under nitrogen. The mixture was cooled and poured into 150 ml of distilled water, where the required compound was precipitated. The precipitate was filtered on a suction pump and given sufficient washing with water and air-dried. The crude product was chromatographed on silica gel (60–120 mesh), eluted with chloroform:petroleum ether (1:2), which yielded 0.08 gm (91%) of compound **11a**. δ_H (300 MHz; $CDCl_3$) 10.37 (6H, s, *meso*-CH), 8.99 (4H, d, $J = 5$ Hz, β-pyrrole), 8.98 (8H, s, β-pyrrole), 8.83 (4H, d, $J = 5$ Hz, β-pyrrole), 8.61 (4H, d, $J = 8$ Hz, ArH), 8.38 (4H, d, $J = 8$ Hz, ArH), 7.75 (2H, br s, NH), 4.27 (2H, br s, NH_2); UV–vis (λ_{max} CH_2Cl_2 (log ε): 395 (4.91), 546 (1.98), 591 (1.12); IR ν_{max} (KBr)/cm^{-1} 3487, 3341, 3182, 3114, 3060, 2922, 2852, 2399, 1595, 1515, 1485, 1438, 1346, 1298, 1205, 1174, 1109, 1070, 993, 860, 844, 796, 748, 717, 700, 659; MS (ESI) *m/z* ($M + H^+$, 1019.2155).

*Synthesis of **11b** was as above*

Yield 0.23 g (88%). δ_H (300 MHz; $CDCl_3$) 8.98 (4H, d, $J = 5$ Hz, β-pyrrole), 8.96 (8H, s, β-pyrrole), 8.84 (4H, d, $J = 5$ Hz, β-pyrrole), 8.64 (4H, d, $J = 8$ Hz, ArH), 8.41 (4H, d, $J = 8$ Hz, ArH), 8.22 (12H, m, ArH), 7.77 (18H, m, ArH), 7.75 (2H, br s, NH), 4.21 (2H, s, NH_2); UV–vis (λ_{max} CH_2Cl_2 (log ε): 419 (4.42), 548 (3.31), 587 (2.32); MS (ESI) *m/z* ($M + H^+$, 1475.4133).

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