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ARTICLE TYPE

β-Substituted triarylborane appended porphyrins: photophysical properties and anion sensing

Rekha Sharma,[a] Prabhat Gautam,[a] Rajneesh Misra*[a] and Sanjeev K. Shukla[b]

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a Department of chemistry, Indian Institute of Technology, Indore, M.P., India.

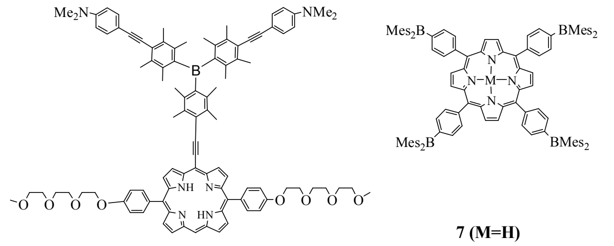
b Sophisticated Analytical Instrument Facilities, CSIR-Central Drug Research Institute, Lucknow 226031, India.

β-Substituted triarylborane porphyrins were designed and synthesized by the Pd-catalyzed Sonogashira cross-coupling reaction. The incorporation of triarylborane unit results in a red shifted absorbance and fluorescence. The sensing ability of these porphyrins were studied towards different anions. The triarylborane porphyrin **4** and **5** selectively detects fluoride ion as shown by the UV/vis absorption and fluorescence titration experiments. The binding constants for triarylborane porphyrin **4** and **5** in dichloromethane at 25°C were found to be 1.0×10^6 M^{-1} and 5.0×10^5 M^{-1} respectively.

Introduction:

In recent years triarylborane containing molecular systems have attracted considerable attention due to their applications in optoelectronic devices and anion sensing.[1-8] A variety of boron containing conjugated donor–acceptor systems have been documented in the literature for sensing application.[7-17]
Selective detection of fluoride ion is of wide interest because of their importance towards human health and impact on the environment.[18-19] The importance of this anion in the treatment of osteoporosis and dental care leads to the continuous pursuit of design and synthesis of new selective fluoride ion sensors.
Literature reveals couple of reports, where *meso* substituted[3-5] borylated porphyrins have been synthesized and studied as potential candidates for anion sensing.[20-21] Kubo *et al* reported the *meso* substituted triarylborane porphyrin using Sonogashira coupling reaction, which has been used for fluoride ion sensing (Chart 1).[20] Moreover Thilagar *et al* reported the synthesis and anion sensing properties of *meso*-substituted tetra triarylborane appended porphyrin (Chart 1).[21]

To the best of our knowledge, there are no reports on *β*-substituted borylated porphyrins for anion binding. Our group is interested in the design and synthesis of *β*- substituted porphyrins for various optoelectronic applications.[22] In this manuscript, we have incorporated triarylborane unit at the *β*-position of porphyrin which is in direct conjugation with the 18π-molecular system and results in significant perturbation of the photophysical properties. The *β*-substituted triarylborane porphyrin **4** and its metalated derivative **5** were synthesized by the Pd-catalyzed Sonogashira cross-coupling reaction and metalation reaction and their photophysical and anion binding properties were studied.



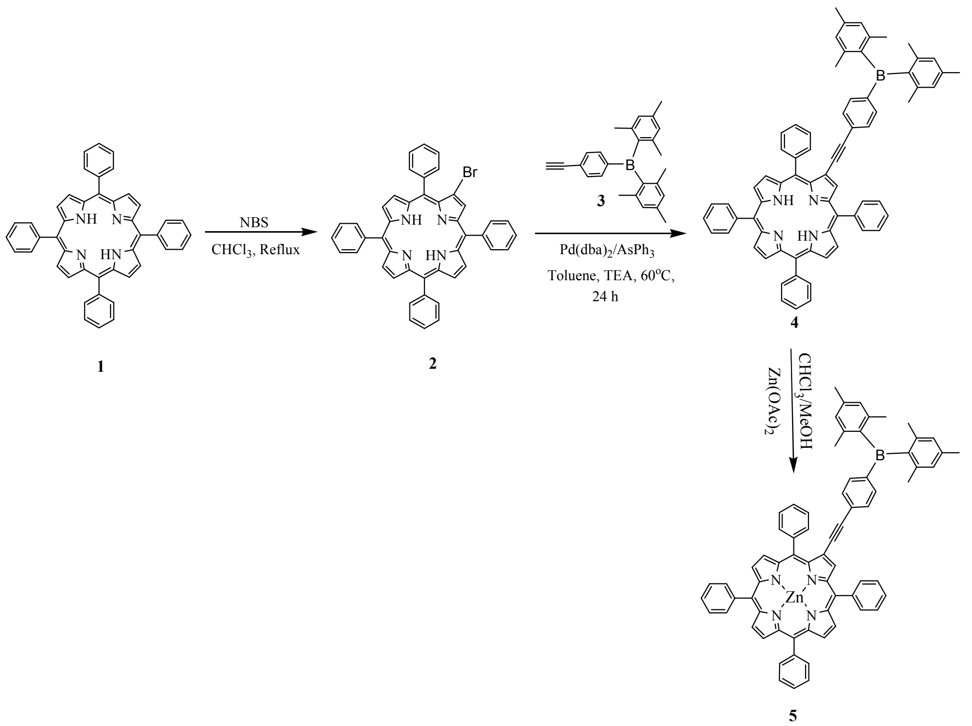
6

7 (M=H)
8 (M=Zn)

Chart 1. Structures of previously reported *meso* substituted triarylborane porphyrin.

Results and discussion:

The synthetic routes for the *β*-substituted triarylborane porphyrin **4** and its metalated triarylborane porphyrin **5** are shown in Scheme 1. The triarylborane porphyrin **4** was synthesized by the Pd-catalysed Sonogashira cross-coupling reaction of the *β*-bromo tetraphenyl porphyrin with the (4-ethynylphenyl)dimesitylborane **3** (Scheme 1). The 5,10,15,20-tetraphenylporphyrin (TPP) was synthesized by the condensation reaction of pyrrole, and benzaldehyde following the Lindsey procedure.[23]



Scheme 1: Synthesis of triarylborane porphyrin **4** and **5**

The bromination reaction of tetraphenylporphyrin was carried out using *N*-bromosuccinimide (NBS) in $CHCl_3$.[24] The β-bromo tetraphenyl porphyrin **2** was purified by the column chromatography using toluene/cyclohexane (30:70).[24] The precursor (4-ethynylphenyl) dimesitylborane **3** was synthesized by the reaction of 1,4-dibromobenzene with dimesitylboron fluoride in presence of *n*-butyllithium.[25]

The Sonogashira cross-coupling reaction of β-bromo porphyrin **2** with (4-ethynylphenyl)dimesitylborane **3** using the catalyst $Pd(dba)_2/AsPh_3$, resulted triarylborane porphyrin **4** in 50% yield.[26-27] The triarylborane porphyrin **4** was reacted with zinc acetate ($Zn(OAc)_2.2H_2O$) in refluxing chloroform/methanol (2:1) which resulted porphyrin **5** in 80% yield (Scheme 1). The triarylborane porphyrin **4** and **5** are readily soluble in common organic solvents. The triarylborane porphyrin **4** and **5** were well characterized by ^1H NMR, ^{13}C NMR and HRMS techniques.

Photophysical properties

The electronic absorption and emission spectra of the triarylborane porphyrin **4** and **5** were recorded in dichloromethane (Figure 1).

The triarylborane porphyrins **4** show boryl absorption band at 328 nm, intense Soret band at 428 nm, and four Q-bands in the region of 500 – 670 nm. The metalated triarylborane porphyrin **5** exhibit boryl absorption band at 333 nm, intense Soret band at 431 nm, and two Q-bands in the region of 550–600 nm. The substitution of the dimesitylborane on the β-position of porphyrin resulted in red shift of the Soret band and the Q-bands. The Soret band of triarylborane porphyrin **4** and **5** are red shifted by 10 nm compared to H_2TPP and ZnTPP respectively.

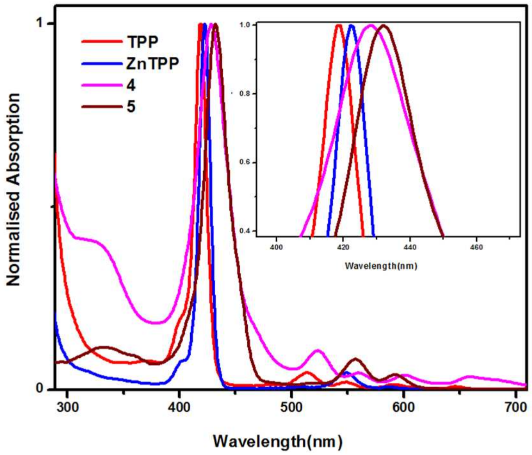


Figure 1. Electronic absorption spectra of the **TPP**, **ZnTPP** and triarylborane porphyrin **4** and **5** at 1.0 × 10^{-6} M, recorded in dichloro methane. The inset shows enlarged view.

The emission properties of the β-substituted triarylborane porphyrin **4** and **5** were studied by steady state fluorescence technique. Their emission spectra are shown in Figure 2. The triarylborane porphyrin **4** and **5** show considerable red shift in fluorescence maxima compared to TPP and ZnTPP respectively. The porphyrins **4** and **5** show enhanced fluorescence quantum yields of 0.20 and 0.12 respectively. These results indicate that there is considerable electronic communication between β-substituted boryl unit and the porphyrin core.

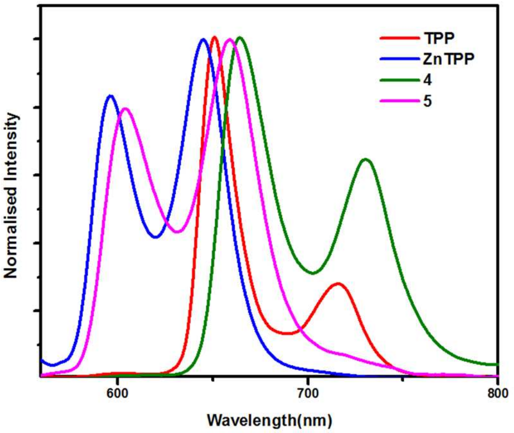


Figure 2. Emission spectra of **TPP**, **ZnTPP** and triarylborane substituted porphyrin **4** and **5** at 1.0 × 10^{-6} M concentration, the excitation wavelength was 418 nm for TPP, 422 nm for **ZnTPP**, 428 nm for **4**, and 432 nm for **5** in DCM.

Anion Binding Studies:

The sensing ability of the triarylborane-porphyrins **4** and **5** were investigated by absorption and emission studies, using various anions (F$^-$, Cl$^-$, Br$^-$, I$^-$ and CN$^-$) as their tetrabutylammonium salts. The absorption and emission studies show no significant change in the presence of Cl$^-$, Br$^-$, I$^-$ and CN$^-$ anions. However porphyrins **4** and **5** exhibit significant change in the absorption and emission spectra in the presence of fluoride anion. The binding constant for fluoride anion was determined from the emission data by using the Benesi–Hildebrand plot analysis.[28-30]

The titration result for triarylborane porphyrin **4** with fluoride anion is shown in Figure **3**. The absorption titration experiment of triarylborane porphyrin **4** shows blue shifted (ca. 420 nm) soret band upon increasing the concentration of TBAF. The emission titration spectra exhibits gradual quenching of the emission band at 663 and 730 nm upon increasing the fluoride ion concentration indicating the F$^-$ ion binding to the boron centre of porphyrin **4** (Figure 3)**.** The binding constant was found to be 1.0 × 10^6 M^{-1}, **(**log K= 6.0) by the Benesi–Hildebrand plot (Figure S1).

The electronic absorption spectra of fluoride ion titration of metalated triarylborane porphyrin **5** shows initial decrease in intensity of soret band, and gradual bathochromic shift of the Soret band from 432 nm to 443 nm (Figure 4). The Q-bands at 556 and 592 nm were also shifted to 578 and 618 nm respectively. In the emission spectra, the addition of fluoride ions to a solution of metalated triarylborane porphyrin **5** results in a substantial decrease in the intensity of the emission band at 604 and 659 nm. The binding constant towards the fluoride ion was found 5.0 × 10^5 M^{-1}, (log K= 5.69) using the Benesi–Hildebrand plot (Figure S1).

The *meso* substituted triarylborane porphyrin **6** with one triarylborane unit as reported by Kubo *et al* exhibits the binding constant 99700 M^{-1} (log K= 4.99) in THF, whereas the β-substituted porphyrin **4** and **5** with one triarylborane substitutent show the binding constant log K= 6.0 and log K= 5.69 respectively. This observation suggests that β-Substituted triarylborane porphyrins show better binding compared to *meso* substituted triarylborane porphyrin **6** which has donor group present on *meso* triarylborane substituents. Moreover, Thilagar *et al* have reported the binding of each triarylborane unit in porphyrin **7** and **8,** the binding constant of first triarylborane unit is log K1 = 5.2, which is comparable to that of β- substituted porphyrin **4** and **5.**

In order to gain further insight in the fluoride anion binding ^{1}H NMR titration studies were performed for the triarylborane-porphyrins **4** and **5**. The comparison of partial ^{1}H NMR spectra of porhyrins **4** and **5** before and after addition of F$^-$ ion is presented in Figure S10 and S11(see ESI for details).

The addition of fluoride ion in the triarylborane-porphyrin **4** results in lower frequency shift of peaks at 9.10 ppm and 6.90 ppm which are observed at 8.99 ppm and 6.62 ppm respectively. The inner NH proton peak of the porphyrin **4** is intact after binding with F$^-$ ion which shows the absence of deprotonation mechanism. The partial ^{1}H NMR spectra of porphyrin **5** shows that the peaks at 9.26 and 6.88 ppm are shifted in the lower frequency region at 8.98 ppm and 6.61ppm respectively upon addition of F$^-$ ion, which confirms that the fluoride ion is binding at the boron centre of the porphyrins.

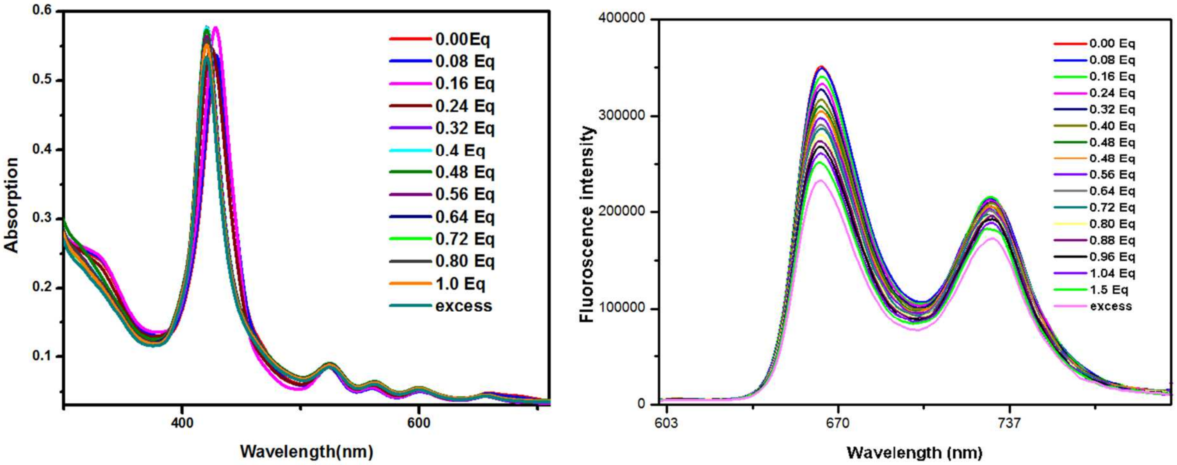


Figure 3. Absorption and Fluorescence titration spectra of triarylborane porphyrin **4** with TBAF in 1.0 ×10^{-6} M DCM solution at λ_{ex} = 428 nm

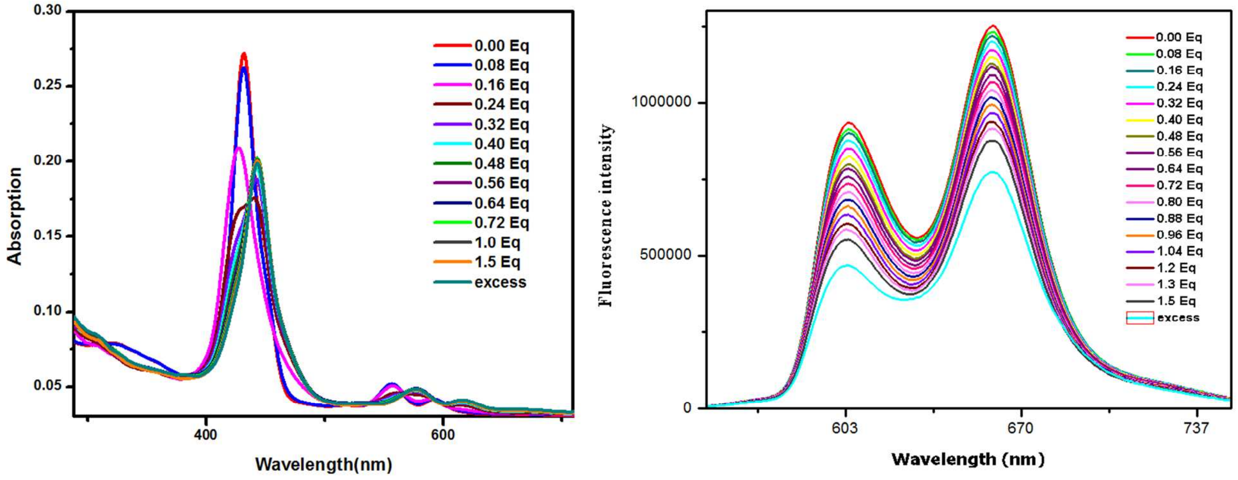


Figure 4. Absorption and Fluorescence titration spectra of metalated triarylborane porphyrin **5** with TBAF in 1.0×10^{-6} M DCM solution at $\lambda_{ex} = 432$ nm

Table 1. Absorption and emission data of triarylborane porphyrin **4** and **5**

Compound	**λ_{abs}(nm)^a**				**λ_{em}(nm)**	**$^c\Phi_f$**
	boryl abs.band	**Soret band**	**$^b\varepsilon$(M^{-1}cm^{-1})$\times10^3$**	**Q-bands**		
TPP	-	418	-	515, 551, 589, 647	650,716	0.11
ZnTPP	-	422	-	549,587	595,645	
4	328	428	577	523,559,602,658	663,730	0.20
5	333	432	439	556,592	604,659	0.12

[a] Measured in dichloromethane at T = 25 °C, λ_{abs} (nm): absorption maximum of the Soret band. [b]ε, extinction coefficient. [c]Determined by using H_2TPP as a standard ($\Phi_{st} = 0.11$)

Table 2: Comparative study of binding constants

Compound	[a]Binding constant	Solvent
Porphyrin **6**[b]	99700(±0.02)M^{-1}; log K= 4.99	THF
Porphyrin **7**[b]	log K_1 = 5.2, log K_2 = 11.0, log K_3^F = 16.5, log K_4^F = 21.6	DCM
Porphyrin **8**[b]	log K_1 = 5.3, log K_2 = 10.6, log K_3 = 16.1, log K_4 = 21.4	DCM
Porphyrin **4**	1.0(±0.05)× 10^6 M^{-1}; log K= 6.0	DCM
Porphyrin **5**	5.0 (±0.05)× 10^5 M^{-1}; log K= 5.69	DCM

[a]All values are derived experimentally. [b] Literature reported values.

Conclusion

In summary, *β*-substituted triarylborane porphyrin **4** and its Zn-metalated derivative **5** were designed and synthesized for selective anion detection. The absorption and emission studies exhibit strong electronic communication. The *β*-substituted triarylborane porphyrin reported here are potential candidate for optoelectronic application and their detailed study is currently in progress in our laboratory.

Experimental section

Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere using standard schlenk method. Triethylamine (TEA) was received from commercial source, and distilled on KOH prior to use. ^{1}H NMR (400 MHz) was recorded on the Bruker Avance (III) 400 MHz, using $CDCl_3$ as solvent. Tetramethylsilane (TMS) was used as reference for recording ^{1}H (of residual proton; $\delta = 7.26$ ppm), spectra in $CDCl_3$. UV-visible absorption spectra of all compounds in Dichloromethane were recorded on a Carry-100 Bio UV-visible Spectrophotometer. HRMS was recorded on Brucker-Daltonics, micrO TOF-Q II mass spectrometer. The quantum yields (Φ) were calculated using H_2TPP ($\Phi = 0.11$) as references. The association constant of the metal complex formed in solution has been estimated by using the standard Benesi−Hildebrand equation.

$$\frac{1}{I - I_0} = \frac{1}{I_1 - I_0} + \frac{1}{(I_1 - I_0)\,K_a(M)}$$

where I_0 is the intensity before addition of anion, I is the intensity in the presence of F^-, I_1 is intensity upon saturation with anion, and K_a is the association constant of the complex formed. The solutions of anions were prepared (1×10^{-3} M) in CH_2Cl_2.

Fluorescence quantum yield.

The fluorescence quantum yields (Φ_F) of compounds **4-5** were calculated (eqn (1)) by the steady-state comparative method using H_2TPP as a standard ($\Phi_{st} = 0.11$).

$$\Phi_F = \Phi_{st} \times S_u/S_{st} \times A_{st} / A_u \times n^2D_u/n^2D_{st} \text{ (Eq. 1)}$$

where Φ_F is the emission quantum yield of the sample, Φ_{st} is the emission quantum yield of the standard, A_{st} and A_u represent the absorbance of the standard and the sample at the excitation wavelength, respectively, while S_{st} and S_u are the integrated emission band areas of the standard and the sample, respectively, and nD_{st} and nD_u are the solvent refractive index of the standard and the sample, and u and st refer to the unknown and the standard, respectively.

Synthesis and Characterization

Synthesis of Compound **4**: A solution of 2-bromo-5,10,15,20-tetraphenylporphyrin (100 mg, 0.14 mmol) and 4-ethynylphenyl dimesitylborane 3 (65 mg, 0.187 mmol) in toluene/triethylamine 5:1 (60 mL), was deareated for 30 min with argon bubbling and then, $Pd(dba)_2$ (40 mg, 0.07 mmol) and $AsPh_3$ (170 mg, 0.55 mmol) were added. The solution was deareated for further 5 min; after that, reaction was left under argon at 60 °C. After completion, the mixture was cooled at room temperature and the solvent was evaporated. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2/Hexane. R_f value = 0.5 (DCM-Hexane 1:1). The product was further recrystalized from dichloromethane/methanol to give porphyrin 4 in 50% yield. Mp> 280°C, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.09 (s, 1H), 8.89 (s, 2H), 8.83 (d, 1H, *J* = 4.9 Hz), 8.80-8.74 (m, 3H), 8.25-8.18 (m, 8H), 7.80-7.73 (m, 9H), 7.67 (t, 2H), 7.58 (t, 1H), 7.49 (d, 2H, *J* = 4.9 Hz), 7.34 (d, 2H, *J* = 8.1 Hz), 6.88(s, 4H), 2.36 (s, 6H), 2.07(s, 12H), -2.66 (s, 2H). ^{13}C NMR (100 MHz, CDCl3): δ = 142.08, 142.04, 141.82, 141.68, 141.19, 140.92, 138.81, 135.77, 134.61, 134.56, 134.45, 131.51, 128.85, 128.26, 127.93, 127.81, 127.31, 126.82, 126.78, 126.74, 120.49, 120.16, 120.14, 120.12, 99.21, 88.38, 23.51, 21.31. HRMS (ESI) m/z, calcd for MH^+ ($C_{70}H_{55}BN_4$): 962.4525; found: 962.4520.

Synthesis of Compound **5**:
A solution of $Zn(OAc)_2.2H_2O$ (15 mg, 0.06 mmol) in MeOH (2 mL) was added to a solution of compound 4 (20 mg, 0.02 mmol) in 15 mL of chloroform and the reaction mixture was stirred for overnight at room temperature. The reaction mixture was concentrated in vacuo and further purified by column chromatography using dichloromethane/hexane. The porphyrin **5** was obtained as a purple colour solid in 80% yield. Mp> 280°C, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.26 (s, 1H), 8.97-8.86 (m, 5H), 8.78 (d, 1H,), 8.28-8.15 (m, 8H), 7.81-7.70 (m, 9H), 7.66 (t, 2H), 7.59 (d, 1H), 7.51 (d, 2H, *J* = 9.8 Hz), 7.38 (d, 2H, *J* = 7.9 Hz), 6.89 (s, 4H), 2.36 (s, 6H), 2.08 (s, 12H). ^{13}C NMR (100 MHz, CDCl3): δ = 150.04, 149.79, 149..68, 149.05, 147.10, 145.85, 141.54, 140.92, 140.62, 139.85, 138.26, 138.04, 137.74, 134.70, 133.38, 133.35, 133.12, 131.81, 131.33, 131.21, 130.75, 130.47, 127.60, 127.20, 126.63, 126.52, 126.36, 125.58, 124.56, 120.44, 120.08, 119.95, 113.03, 98.30, 87.51, 32.79, 30.90, 30.57, 28.66, 28.33, 28.12, 27.97, 22.45, 21.66, 20.24, 13.10. HRMS (ESI) m/z, calculated for MH^+($C_{70}H_{53}BN_4Zn$): 1025.3739; found: 1025.3922.

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Notes and references

*Department of Chemistry, Indian Institute of Technology Indore, 452017, India. Fax: +91 731 2361 482; Tel: +91 731 2438 710 * E-mail rajneeshmisra@iiti.ac.in*

†Electronic Supplementary Information (ESI) available: General experimental methods, and copies of ^{1}H NMR, and HRMS spectra of all new compounds.

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