

Supporting Information

**Synthesis, characterization and cation-induced dimerization of new
aza-crown ether-appended metalloporphyrins**

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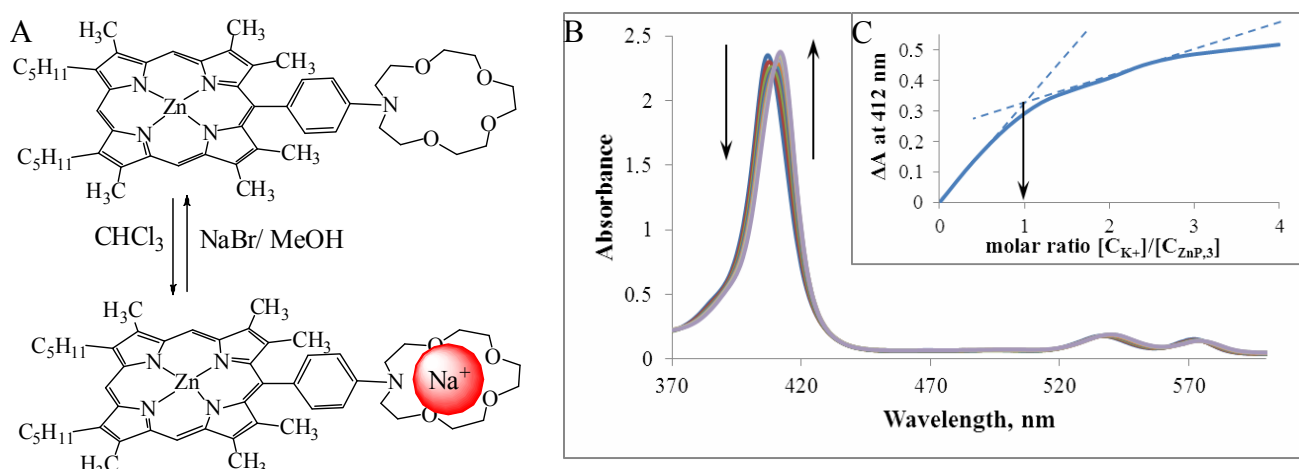
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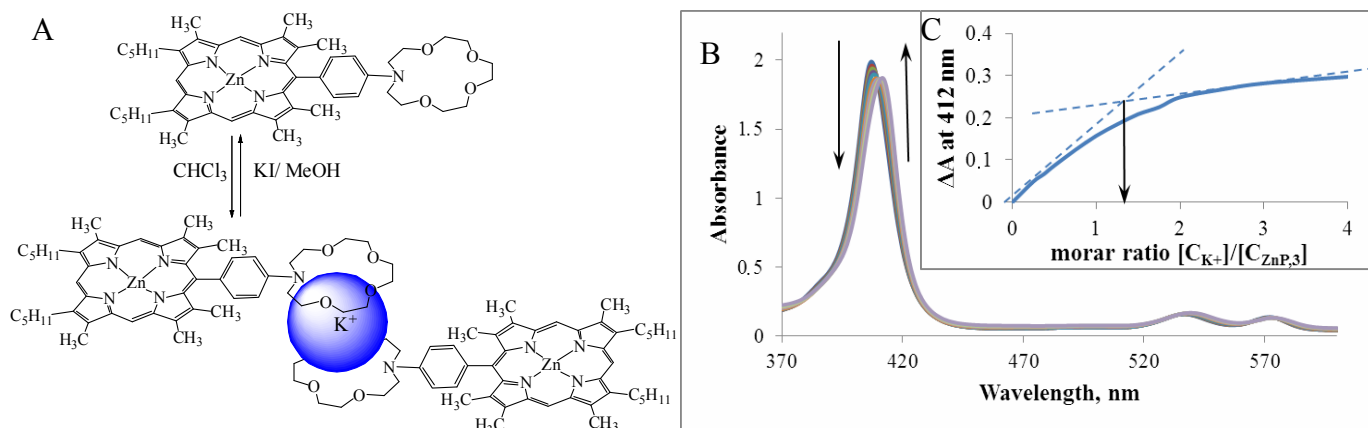
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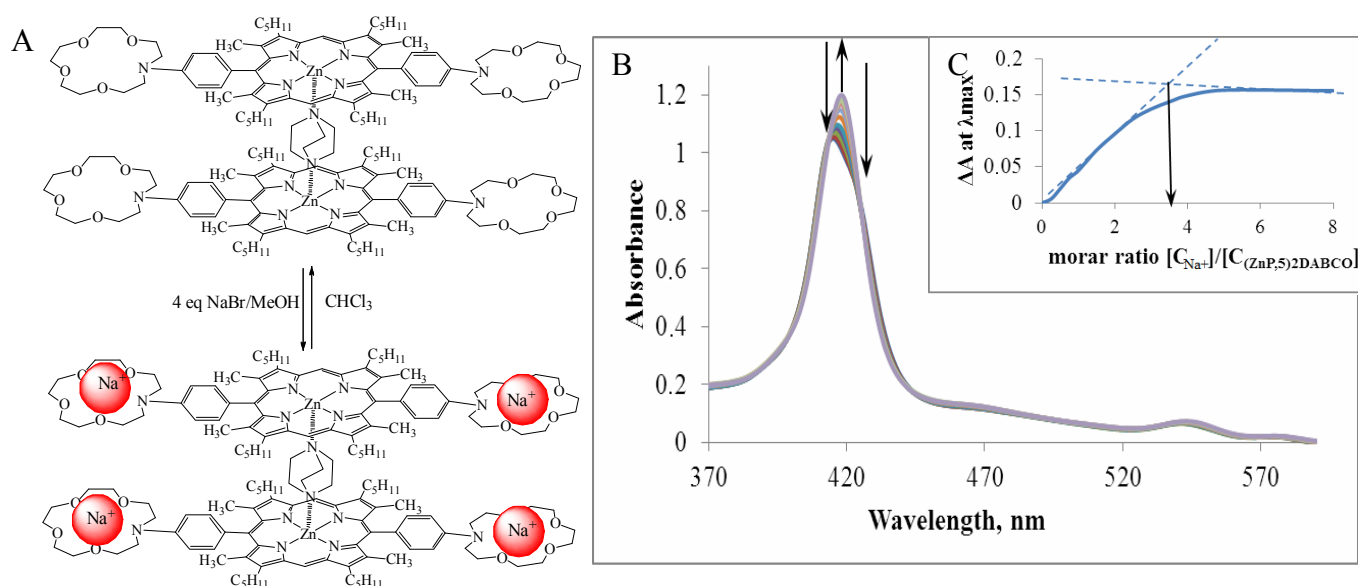
1. Experimental Details of the spectrophotometric titration of ZnP,3 and ZnP,5 with alkali cations and DABCO in CHCl₃/MeOH



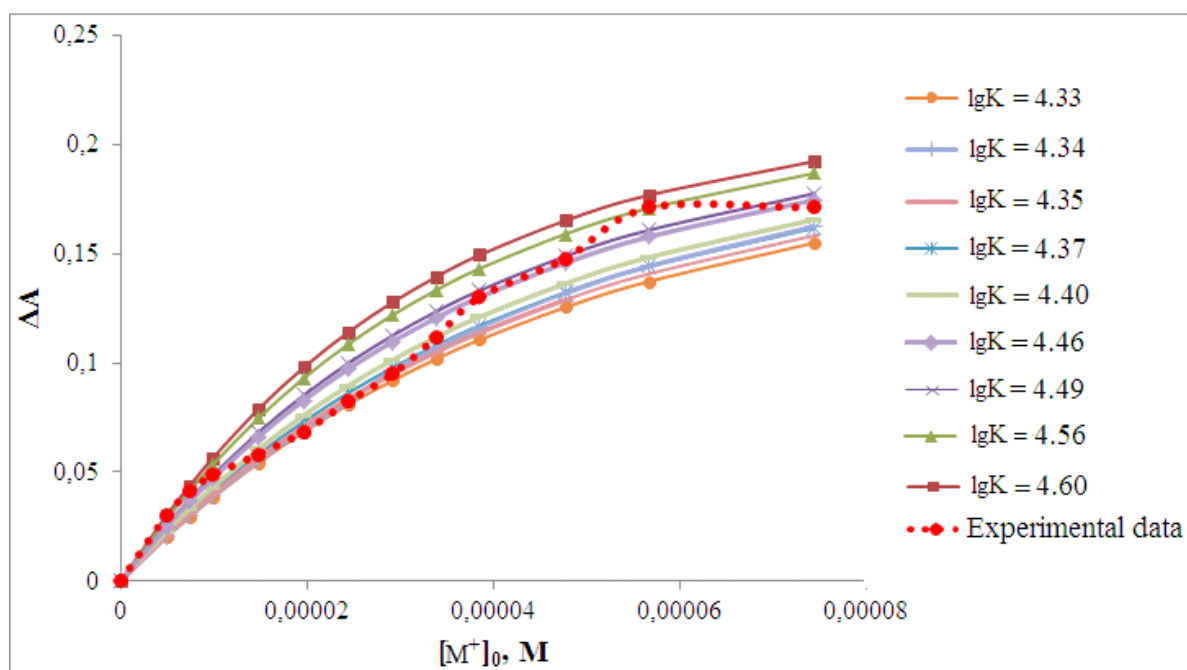
S.1. Structural scheme of complexation **ZnP,3** with sodium cations (A). Spectral changes of **ZnP,3** ($[\text{ZnP,3}] = 2 \times 10^{-5} \text{ M}$) at addition of 0 – 4 equiv of NaBr in CHCl₃/MeOH (20:1) (B). Spectrophotometric titration curve at $\lambda=412 \text{ nm}$ (C).



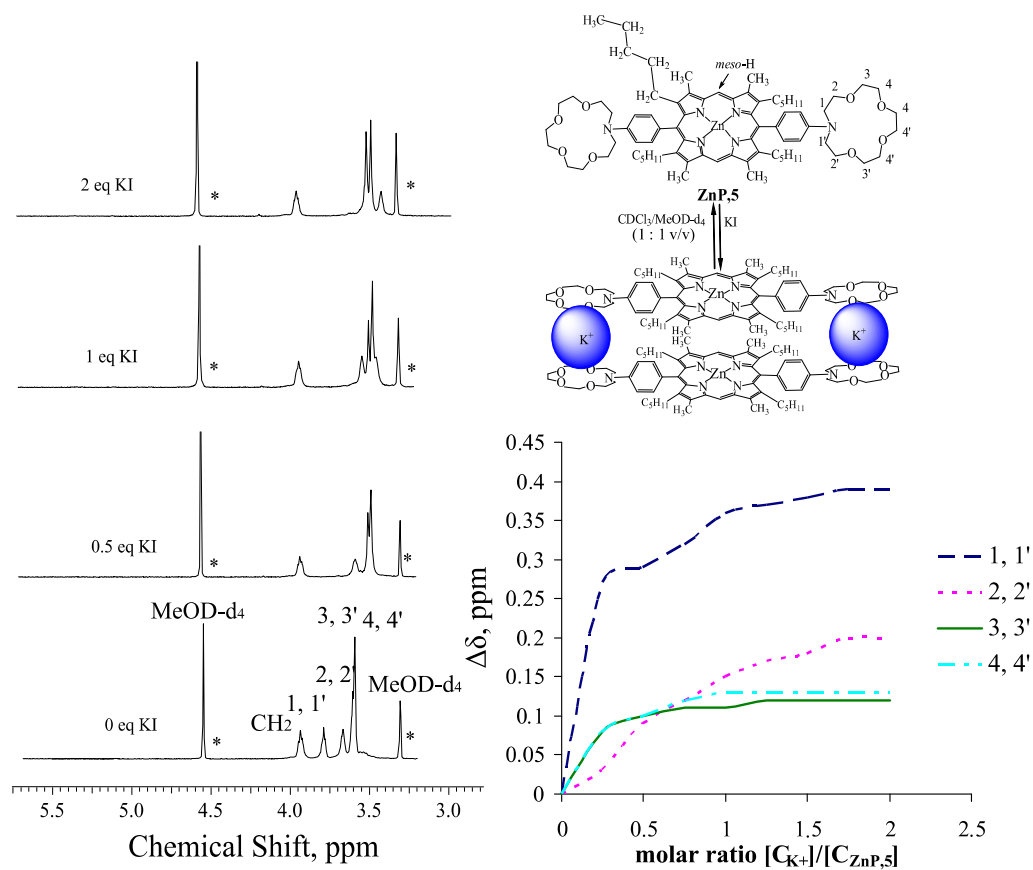
S.2. Structural scheme of cation-induced dimerization of **ZnP,3** by potassium cations (A). Spectral changes of **ZnP,3** ($[\text{ZnP,3}] = 2 \times 10^{-5} \text{ M}$) on addition of 0 – 4 equiv of KI in CHCl₃/MeOH (20:1) (B). Spectrophotometric titration curve at $\lambda=412 \text{ nm}$ (C).



S.3. Structural scheme of complexation of with sodium cations (A). Spectral change at formation of 1:4 complexes of (ZnP,5)₂DABCO with Na⁺ in CDCl₃/MeOH (20:1 v/v) (B). Spectrophotometric titration curve of (ZnP,5)₂DABCO at λ_{max} (C).

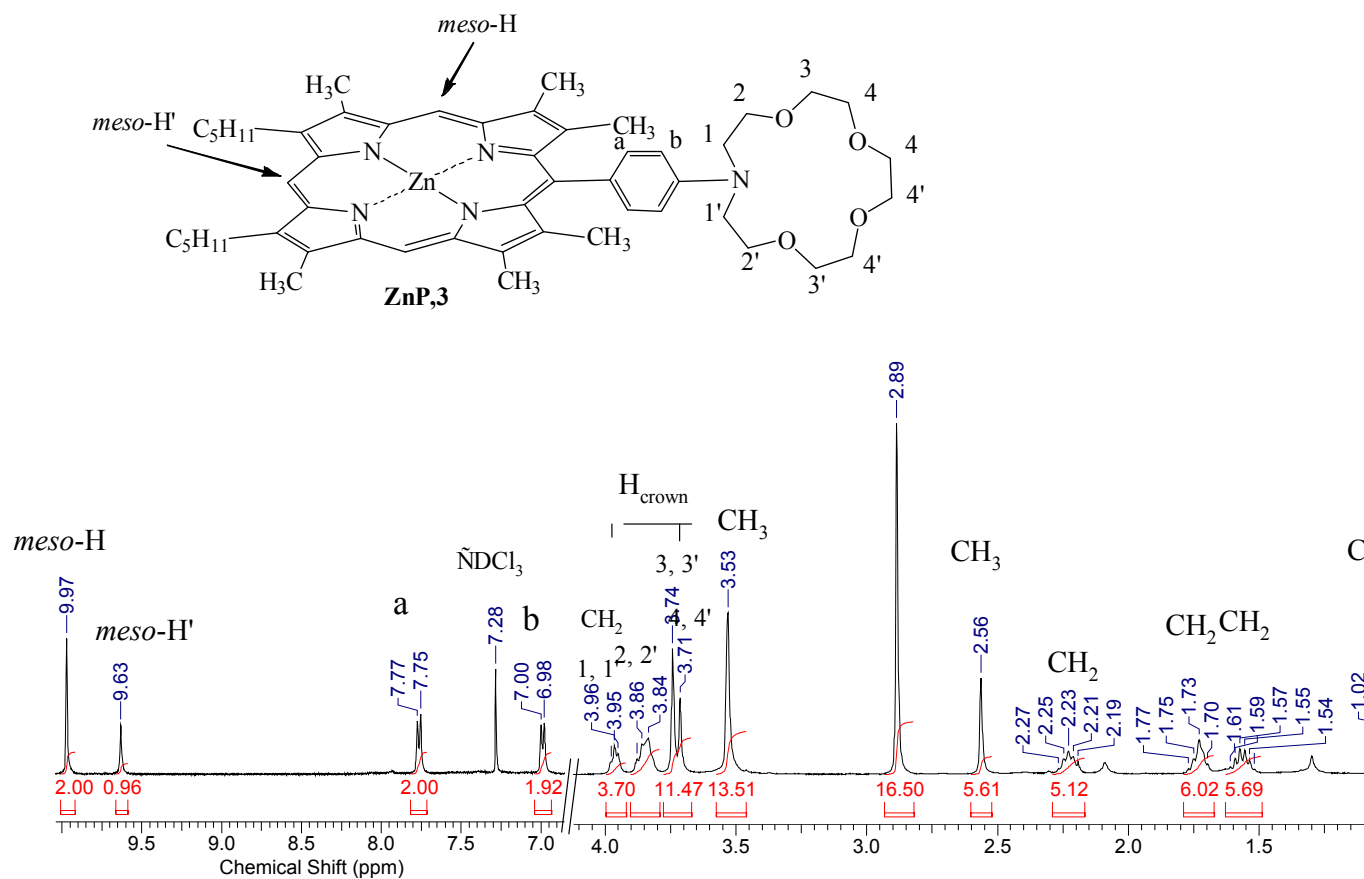


S.4. Difference in absorbance values ΔA vs. the concentrations of the added potassium cations to solution of (ZnP,3)₂DABCO for various values of stability constants.

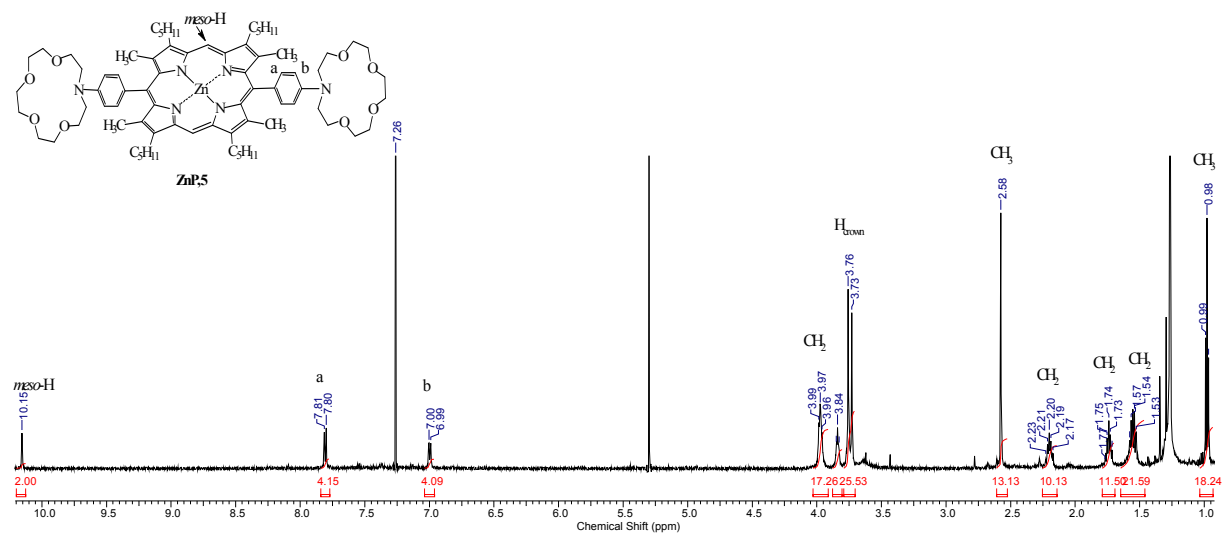


S. 5. ^1H NMR titration (600 MHz) at 298 °K of **ZnP,5** in $\text{CDCl}_3/\text{MeOD-d}_4$ (v/v = 1:1) on addition of KI in $\text{CDCl}_3/\text{MeOD-d}_4$ at 30°C; $[\text{ZnP,5}] = 1.2 \times 10^{-2}$ M, The solvent peak is marked. Insert: ^1H NMR titration curve of **ZnP,5** (change of chemical shifts of methylene hydrogens of aza-crown ether units).

2. Experimental data ^1H NMR of ZnP,3 and ZnP,5 and their complexes

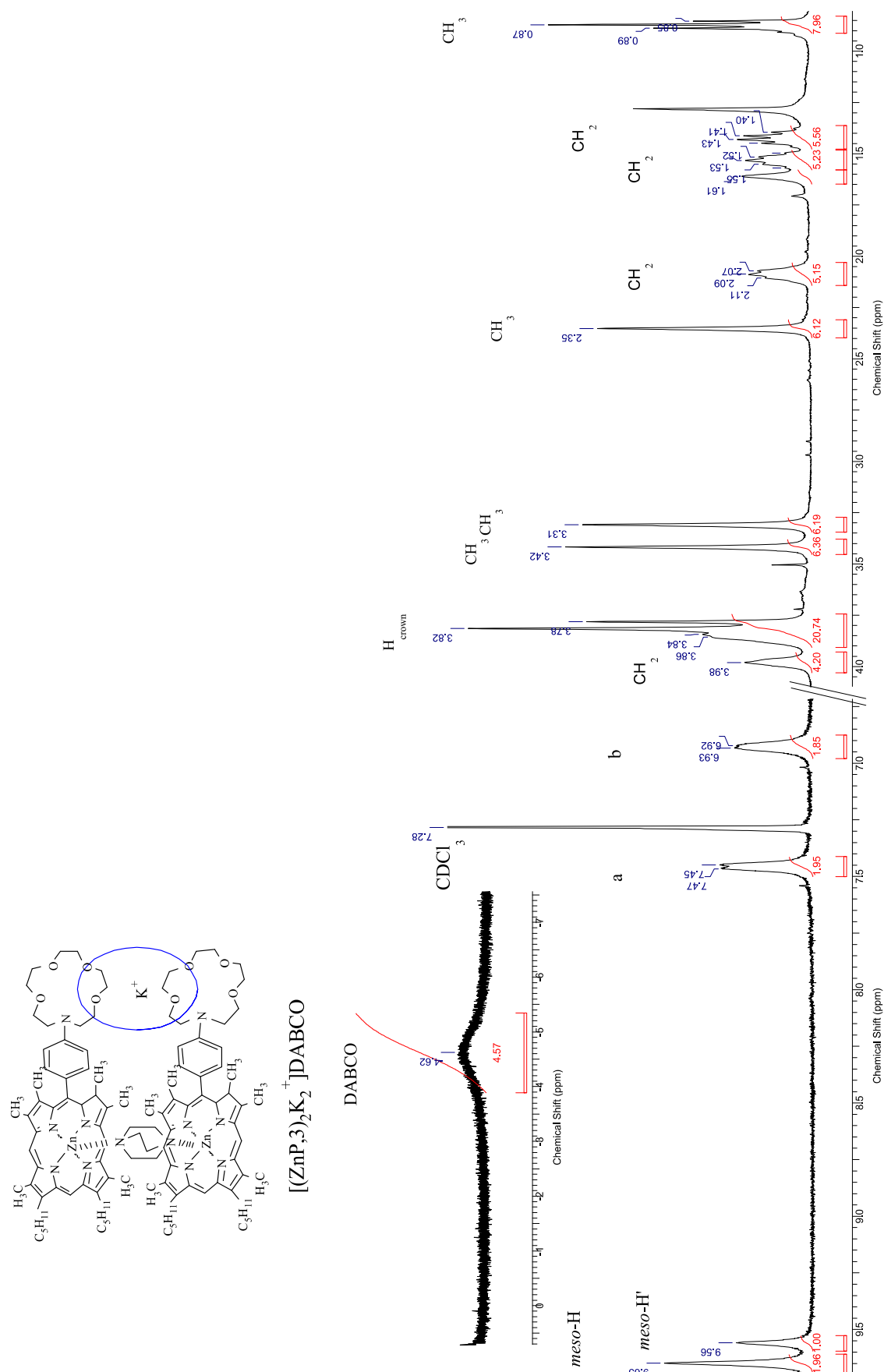


S. 6. ^1H NMR data of ZnP,3

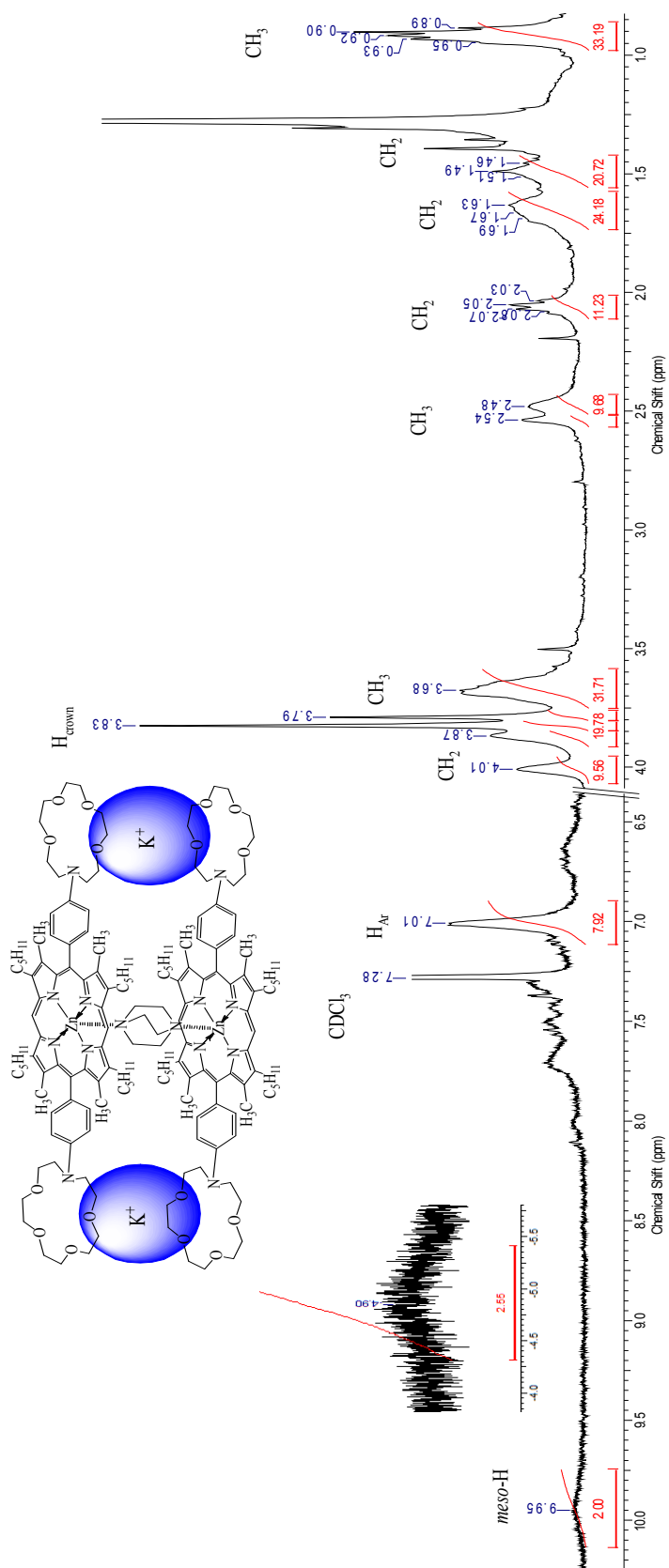


S. 7. ¹H NMR data of ZnP,5

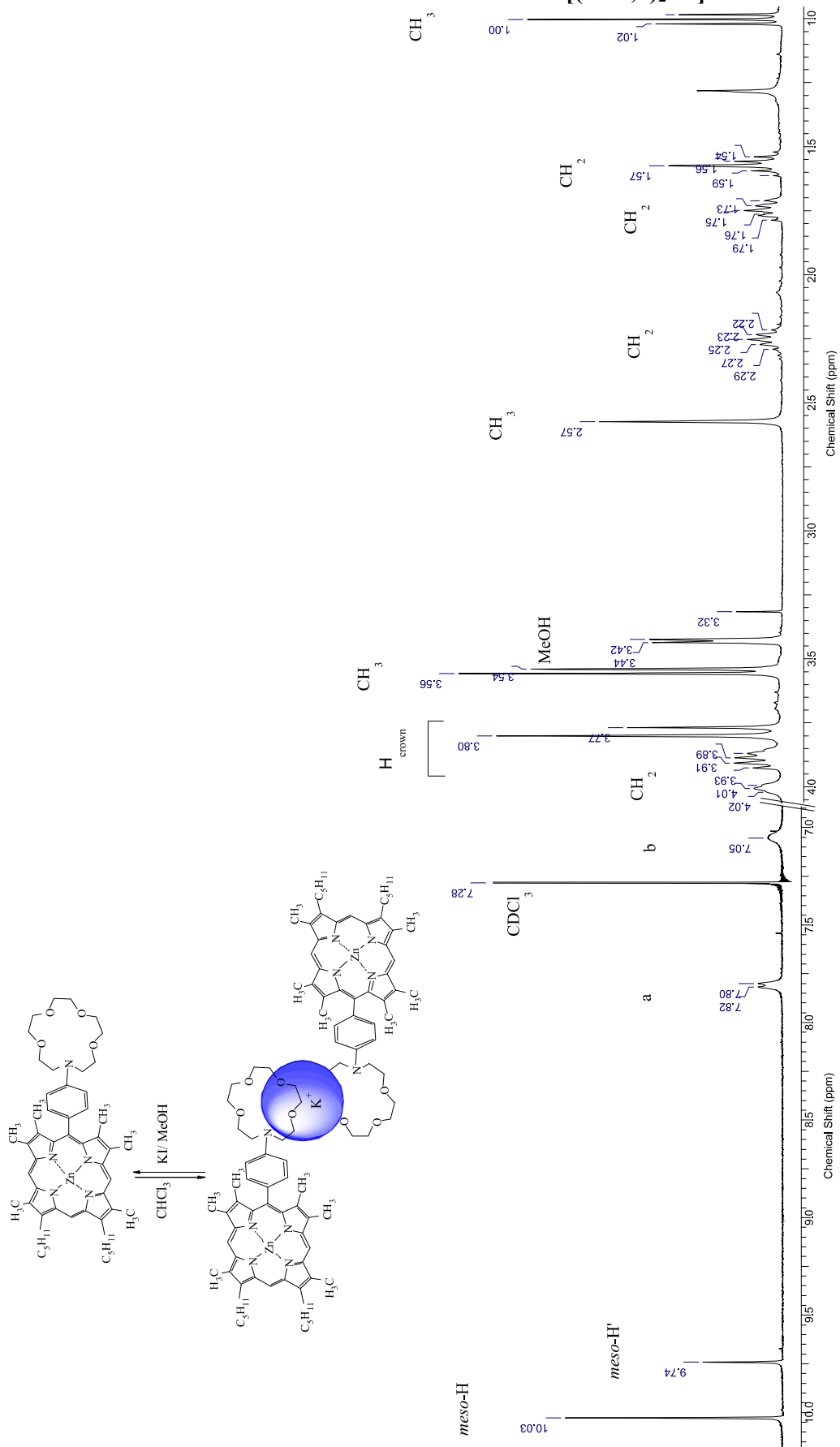
S.8. ^1H NMR data of $[(\text{ZnP},3)_2\text{K}^+]\text{DABCO}$



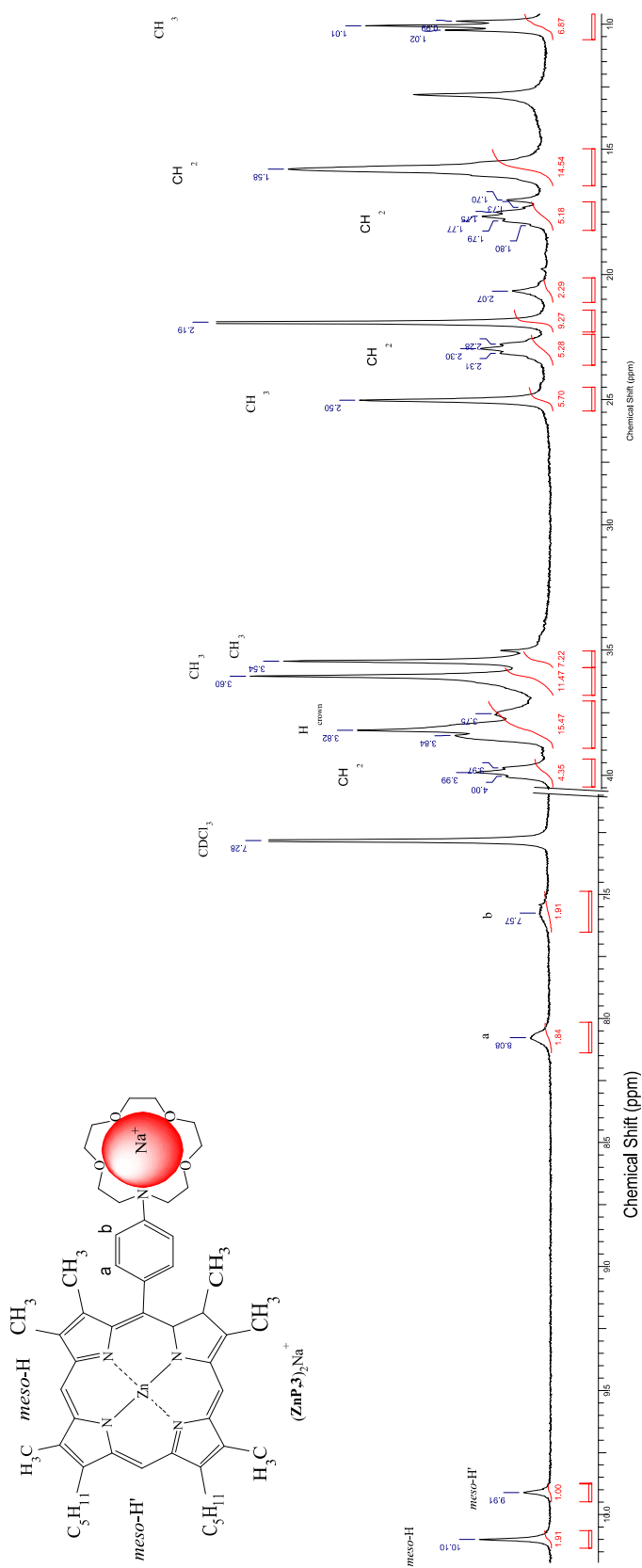
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S. 10. ^1H NMR data of $[(\text{ZnP},3)_2\text{K}]^+$



S. 11. ^1H NMR spectrum of $[(\text{ZnP},3)_2\text{Na}^+]$



3. Experimental data of synthesis of **ZnP,5** collected in Table 2

*Zn 5,15-bis[4'-(1,4,7,10-tetraoxa-13-aza-cyclopentadec-13-yl)-phenyl]-3,7,13,17-tetramethyl-2,8,12,18-tetrapenthyll porphyrinate (**ZnP,5**).*

Entry 1. 2-(dicyclohexylphosphino)-2'-(N,N-dimethylamino)biphenyl (DavePhos) 4 mol % (0.9 mg, $2.3 \cdot 10^{-3}$ mmol), 4 mol % Pd(dba)₂ (1.3 mg, $2.3 \cdot 10^{-3}$ mmol), and sodium tert-butoxide (7.8 mg, 0.16 mmol) were placed in a dried, resealable round-bottom flask, which was backfilled with argon. A stock solution of 2.3 equivalents of aza-15-crown-5 ether in dioxan (0.4 mL, 0.33 M, 0.13 mmol) was added via syringe. Then **ZnP,2** (59 mg, 58 μmol) was added in Ar flow. The flask was purged with argon for 3 min. The flask was sealed, and its contents were heated at 100°C with stirring for 32 hours. The reaction path was monitored by TLC. The reaction mixture was then cooled to room temperature, taken up in dichloromethane (10 mL), filtered, and concentrated in a vacuum. The crude product was purified by column chromatography on silica gel using gradient elution by 0-2% mixture of CH₂Cl₂ - MeOH as an eluting solvent. First fire-engine red fraction ($R_f = 0.95$) was by-product of β-H elimination **ZnP,6** (25%), second dark red fraction ($R_f = 0.57$) was by-product **ZnP,4** (14%), third dark red fraction ($R_f = 0.43$) was **ZnP,5** which was isolated as a solid (9.3 mg, 16 %). ¹H NMR (CDCl₃, 298 K, 300 MHz): δ = 10.16 (2H, s, *meso*-H), 7.83 (4H, d, J=8,44 Hz, H_{Ar}), 7.01 (4H, d, J=8,44 Hz, H_{Ar}), 4.03 (8H, t, J₁=6.75 Hz, J₂=6.95 Hz, CH₂), 3.98 (8H, t, J₁=8.34 Hz, J₂=6.82 Hz, NCH₂), 3.89 (8H, t, J₁=5.94 Hz, J₂=6.32 Hz, CH₂O), 3.81 (16H, s, C₂H₄O(CH₂O)₂), 3.78 (8H, s, CH₂O), 2.59 (12H, s, CH₃), 2.19-2.13 (8H, m, CH₂), 1.73-1.68 (8H, m, CH₂), 1.54-1.49 (8H, m, CH₂), 1.01 (12H, t, J₁=7.26 Hz, J₂=7.26 Hz, CH₃). ¹³C NMR (125 MHz, CDCl₃): δ = 148.57, 147.57, 146.27, 142.84, 139.30, 138.33, 133.84, 114.08, 110.66, 97.19, 71.41, 70.24, 68.83, 52.71, 33.85, 33.08, 32.55, 31.94, 31.52, 30.14, 29.71, 29.53, 29.38, 29.18, 28.96, 26.76, 22.84, 22.71, 15.55, 14.21, 14.15. UV-Vis (CHCl₃): λ, nm (10⁻³ ε, dm³mol⁻¹cm⁻¹): 414 (107), 541 (7.43), 574 (3.96). ESI MS: calcd m/z=1295.7436 for C₇₆H₁₀₆N₆O₈Zn, found 1295.7384.

Entry 2. Preparation procedure as above for a twofold increase in catalyst loading was applied. DavePhos 8 mol% (1.8 mg, $4.6 \cdot 10^{-3}$ mmol), Pd(dba)₂ 8 mol % (2.6 mg, $4.6 \cdot 10^{-3}$ mmol), 1.4 equivalent of sodium tert-butoxide (7.8 mg, 0.16 mmol), 2.3 equivalents of aza-15-crown-5 ether 26.7 mg (0.13 mmol) and **ZnP,2** 59 mg (58 μmol) were refluxed in dried dioxane under Ar for 37 hours. After cooling reaction mixture was filtrate and purified by column chromatography as stated above. Yields of products were 25% **ZnP,6**; 25% **ZnP,6**; 28% **ZnP,5**.