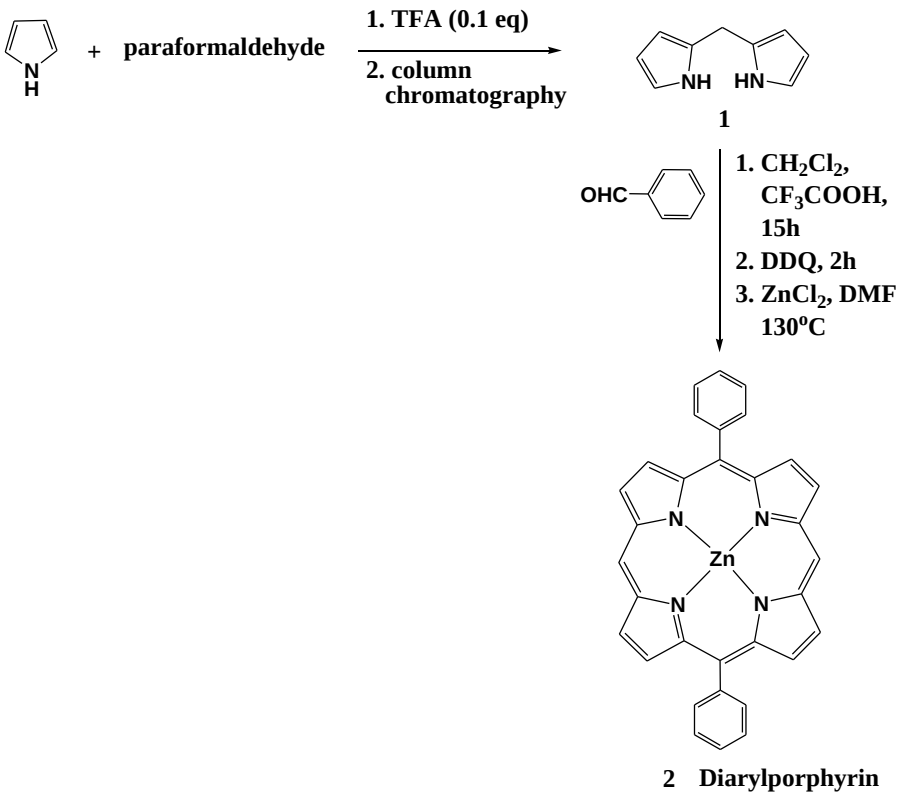
Supporting information:

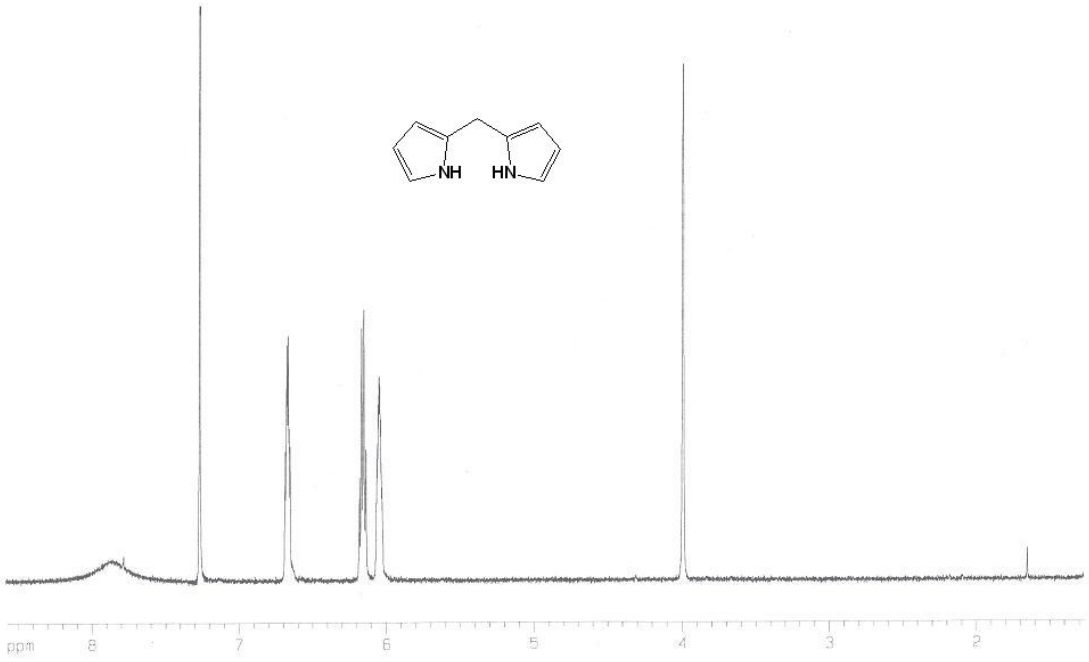
1. Syntheses:

(i) zinc(II)-5,15-diphenylporphyrin



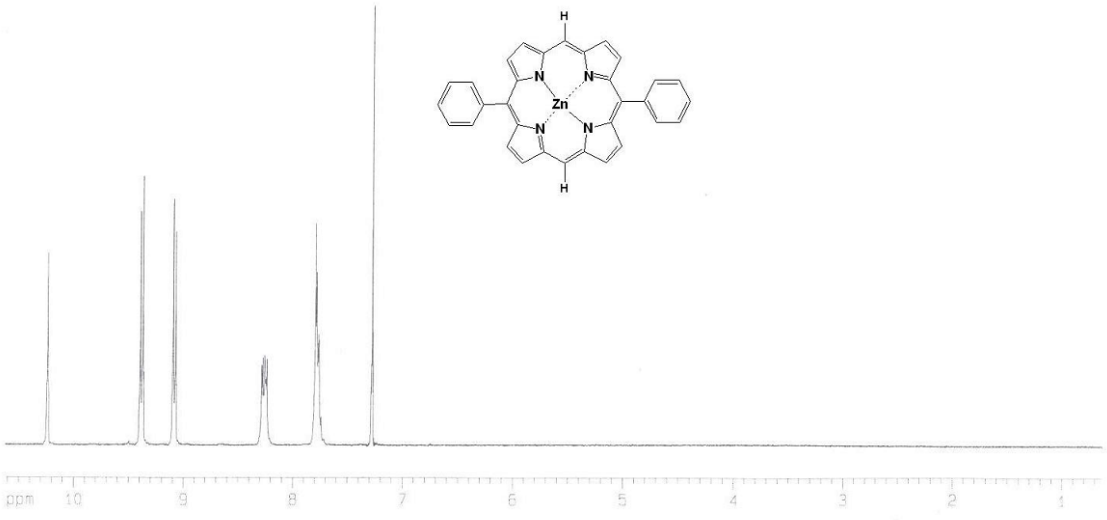
2 Diarylporphyrin

Dipyrromethane (**1**):[1] A solution of pyrrole (60 mL, 864 mmol) and paraformaldehyde (648 mg, 21.6 mmol) were treated with acetic acid (AcOH, 90 mL) and methanol (MeOH, 30 mL) at room temperature under argon. The mixture was stirred for 20 hours. The solution was then diluted with dichloromethane (300 mL), washed with water (100 mL x 2), 0.1 M KOH solution (100 mL x 2), and dried over sodium sulphate. The solvents were evaporated and the unreacted pyrrole was removed by distillation. The crude product was purified by flash column chromatography, eluting with CH_2Cl_2/NEt_3. to give the desired compound 1 (1.33 g, 42%) as colorless crystals. M.p. 74-75^{o}C; ^{1}H n.m.r ($CDCl_3$): δ 3.96 (s, 2H), 5.98 (m, 2H), 6.15 (q, *J* = 2.9 Hz, 2H), 6.64 (m, 2H), 7.82 (br, s, 2H). ^{13}C n.m.r ($CDCl_3$): δ 26.1, 106.5, 108.2, 117.4, 129.2; LR-MS (CI, +ve, CH_2Cl_2/MeOH): *m/z* 146.1 $[M+H]^+$. The nmr spectrum is shown below.



Synthesis of zinc-5,15-diphenylporphyrin (**2**). Synthesis was performed by adapting a method described by Lindsey and co-workers.[2] A flame-dried three-necked round-bottom flask equipped with a stir bar was charged with dipyrrylmethane **1** (600 mg, 3.5 mmol) and benzaldehyde (378 mg, 3.57 mmol) in anhydrous dichloromethane (700 mL). The solution was then degassed with an argon stream for 15 minutes. Trifluoroacetic acid (184 mL, 2.9 mmol) was added and the reaction mixture was vigorously stirred in the dark for 15 hours at room temperature. DDQ (1.1 g, 4.8 mmol) was added to the reaction and the mixture was stirred for a further 30 minutes. Triethylamine (3 mL) was added to neutralize the reaction mixture. The solvent were removed under reduced pressure and the crude residue was dissolved immediately into anhydrous DMF (50 mL). $ZnCl_2$ (1.0 g, 7.35 mmol) was added and the mixture was heated at 130°C under argon for 2 hours. The reaction mixture was cooled to room temperature and poured into water (500 mL). The purple precipitate was collected by filtration and further purified using flash column chromatography, eluting with CH_2Cl_2 to give the desired product **2** (200 mg, 17%). ^{1}H n.m.r ($CDCl_3$): δ 10.5 (s, 2H, *meso*-H), 9.45 (d, J = 4.48 Hz, 4H), 9.17 (d, J = 4.40 Hz, 4H), 8.3 (m, 4H), 7.8 (m, 6H); LR-MS (CI, +ve, CH_2Cl_2/MeOH): *m/z* 525.84 $[M+H]^+$.

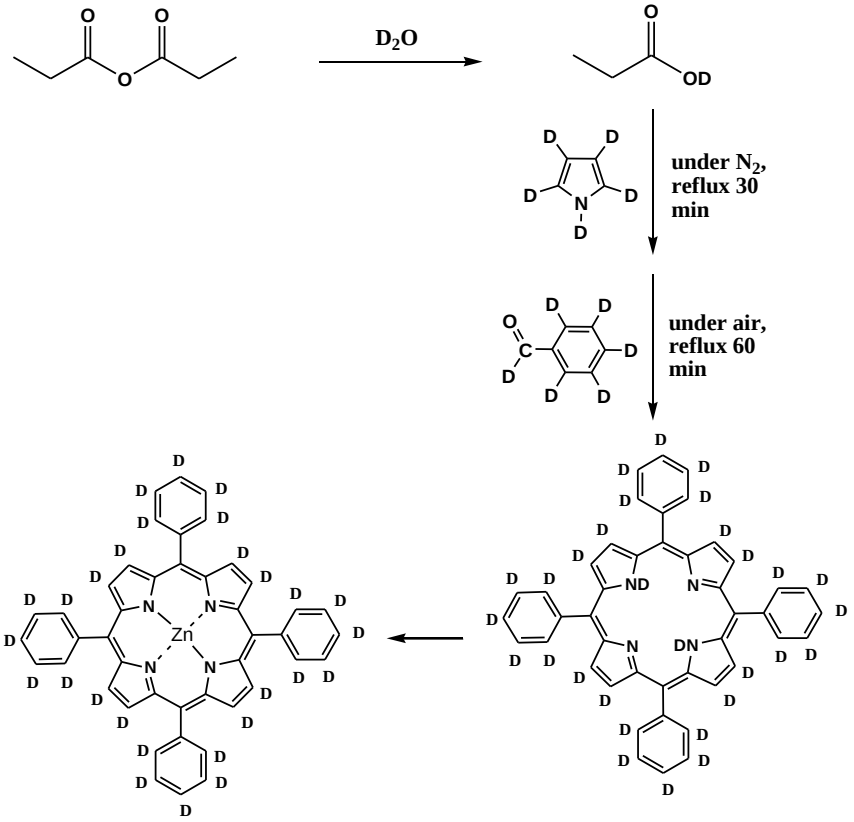
The nmr spectrum of zinc-5,15-diphenylporphyrin is shown below.



1. Wang, Q. M.; and Bruce, D. W., *Synlett* **1995**, 1267.

2. Rao, P. D., Dhanalekshmi, S., Littler, B. J., B. J. Littler, and J. S. Lindsey *J. Org. Chem.* **2000**, *65*,7323.

(ii) Deuterated D_2TPP-d_{28} and ZnTPP-d_{28}:



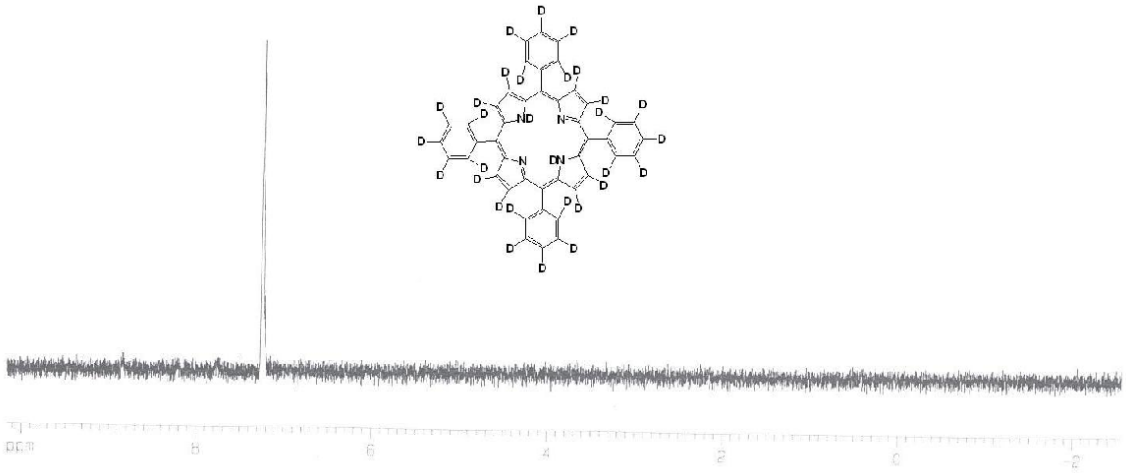
Synthesis of fully deuterated free base-5, 10, 15, 20-tetraphenylporphyrin (TPP-d_{30}):

To propionic anhydride (6.25 mL, 0.049 mol) was added D_2O (0.855 mL, 0.049 mmol) under nitrogen atmosphere, and the mixture was heated under reflux for 30 min to give d_1-propionic acid. To this solution, d_5-pyrrole (0.1 g, 0.001 mmol) and d_6-benzaldehyde (0.147 g, 0.001 mmol) was added, and the resulting mixture was heated under reflux for 1 h. The reaction mixture was left to cool the resulting precipitate, consisting of crude d_{30}-TPP, was collected by filtration. The precipitate was redissolved in degassed dichloromethane and treated with DDQ (500 mg) for 2 hours at room temperature. The chlorin-free deuterated porphyrin was purified twice by column chromatography on silica, the first using dichloromethane eluent followed by a second (G60 SiO_2, hexane/CH_2Cl_2, (1:5)) to give the desired deuterated porphyrin **4** (28 %) as a crystalline purple solid. ^{1}H n.m.r ($CDCl_3$): no peaks were observed. UV/Vis - ($CHCl_3$, nm), Soret band at 405 and 499, 530, 571, 639 are the Q-bands; LR-MS (ESI, +ve, $CDCl_3$/d_4-MeOD): Calculated *m/z* 646.5; Observed *m/z* 646.5 $[M+D]^+$.

Synthesis of fully deuterated zinc(II)-5, 10, 15, 20-tetraphenylporphyrin (ZnTPP-d_{28}):

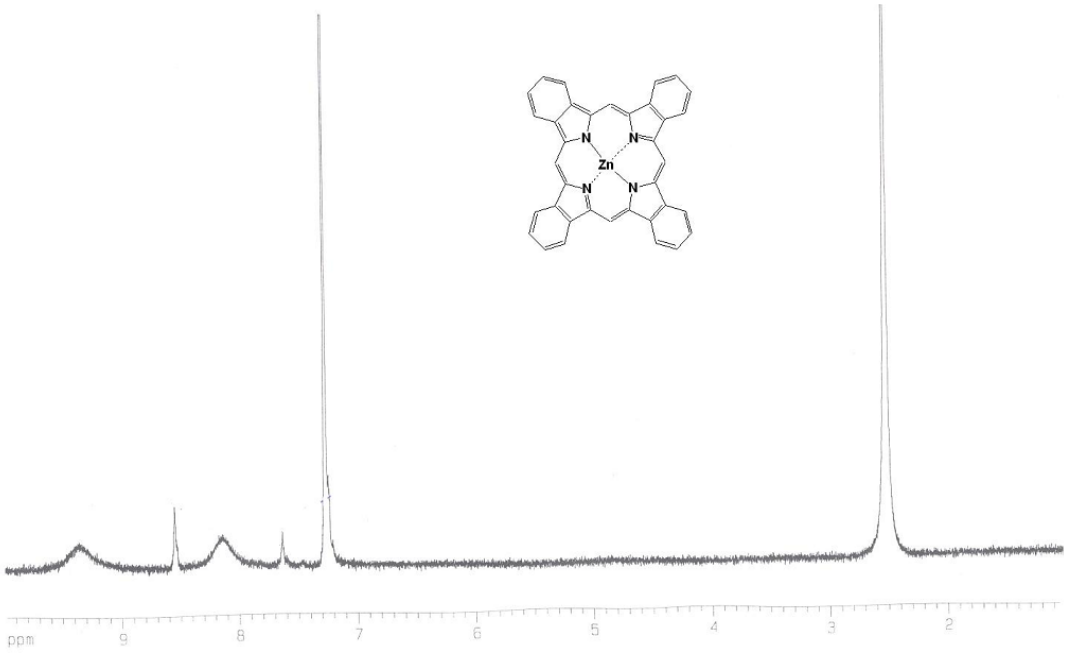
To a solution of d_{30}-TPP (10.9 mg, 16.9 μmol) in $CDCl_3$ (2 mL) saturated zinc acetate in d_4-methanol (3 mL) was added and stirred at 25°C for 18 h in darkness. Upon completion, the solvent system was removed by rotary evaporation. The crude mixture was taken up in chloroform (5mL) and filtered through a cotton wool plug to removed residual zinc salts present. The collected porphyrinic material was purified further by passage through a short silica plug (SiO_2, $CHCl_3$), giving the desired d_{28}-zinc(II) porphyrin (4) as a pink/purple solid (8.9 mg, 75 %) after solvent removal. ^{1}H n.m.r (400 MHz, $CDCl_3$): no peaks were observed. LR-MS (ESI, +ve, $CDCl_3$/d_4-MeOD): Calculated *m/z* 704.3; Observed *m/z* 704.3 $[M]^+$.

The nmr spectrum of TPP-d_{30} is shown below.



2. Purification of ZnTBP:

To remove the impurity in the crude material from Sigma-Aldrich, ZnTBP (20 mg) was dissolved in 2 mL chloroform and loaded onto an alumina column (10g of neutral alumina, 5% pyridine in $CHCl_3$) and the ZnTBP eluted as a broad band. Using UV-visible spectroscopy it was determined that the first fractions collected were devoid of the absorbance at 460 nm. The later fraction, which contain the impurity were discarded. The fractions deemed pure were concentrated by rotary evaporation, leaving dark violet crystals that were washed with hexane (3 × 10 mL) to give pure ZnTBP (13 mg). UV-vis$_{max}$ in $CHCl_3$ (nm): 628, 578, 431, and 407; Q band $\varepsilon(0\text{-}0)/\varepsilon(0\text{-}1) = 7.63$; B band $\varepsilon(0\text{-}0)/\varepsilon(0\text{-}1) = 10.0$; $f_Q/f_B = 0.162$. The nmr spectrum is shown below.



3. Representative spectra:

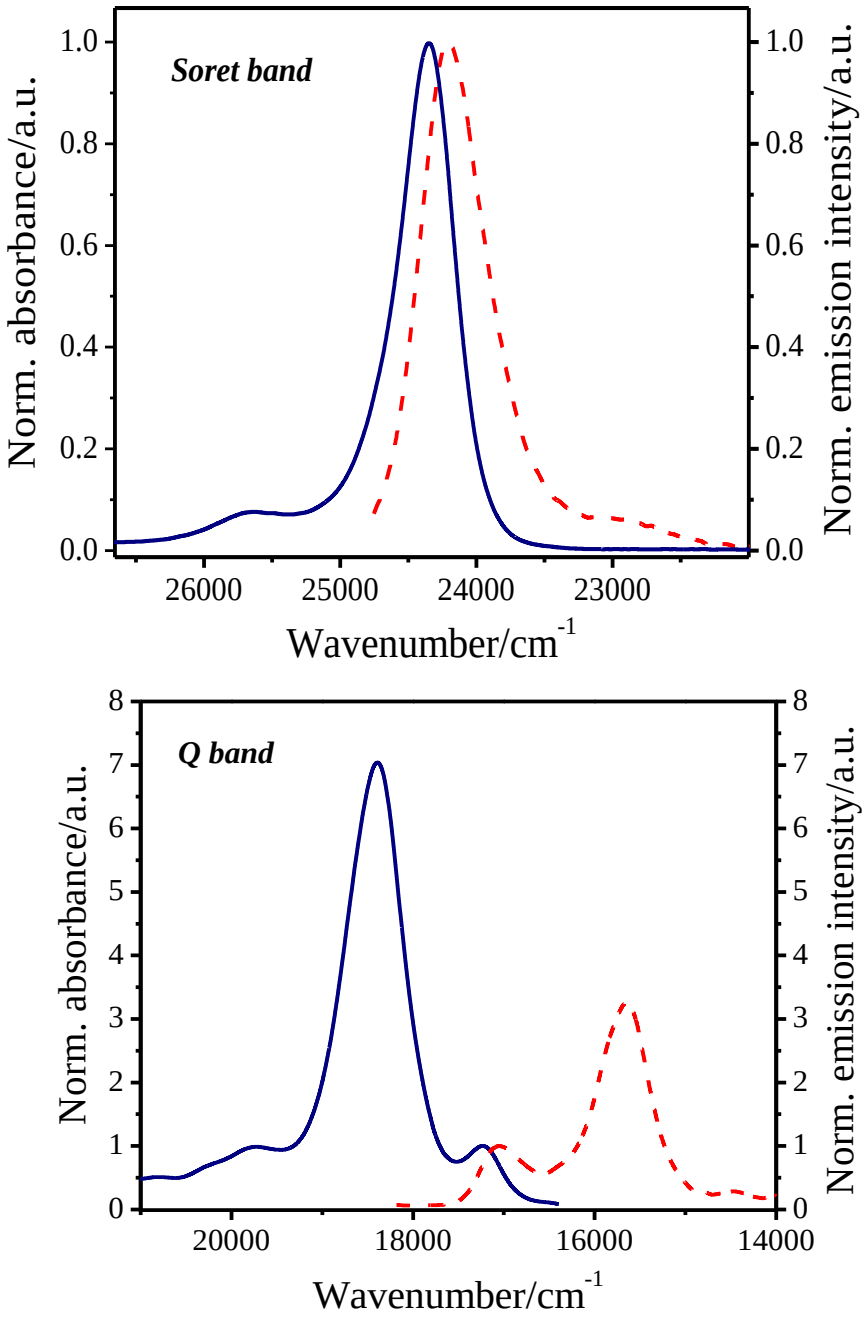


Figure 8 (a) normalized Soret band (upper) and Q band (bottom) absorption and emission spectra of ZnDPP in ethanol. The excitation wavelength is 400 nm.

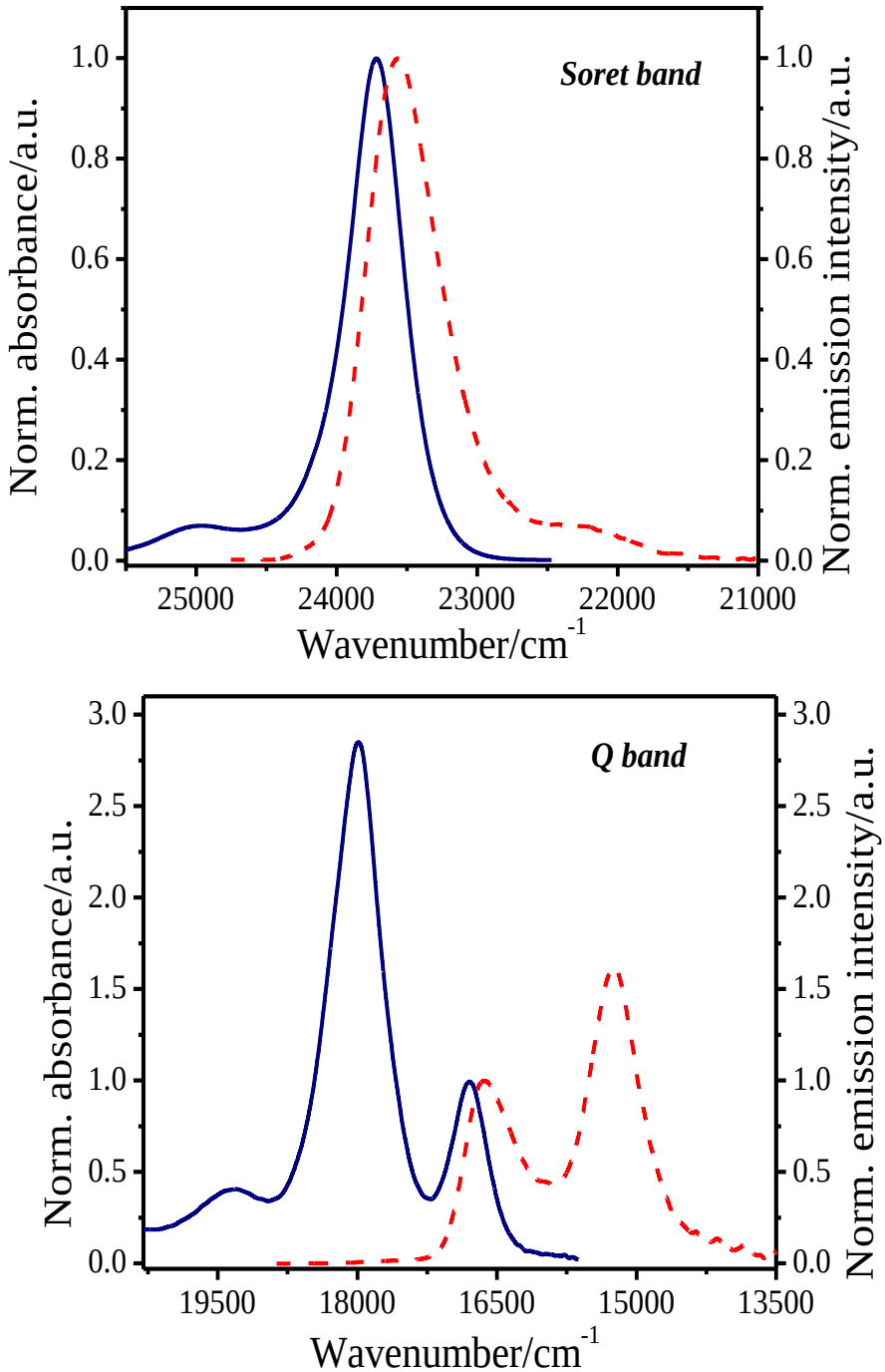


Figure 8 (b) normalized Soret band (upper) and Q band (bottom) absorption and emission spectra of ZnTPP-d_{28} in ethanol. The excitation wavelength is 400 nm.

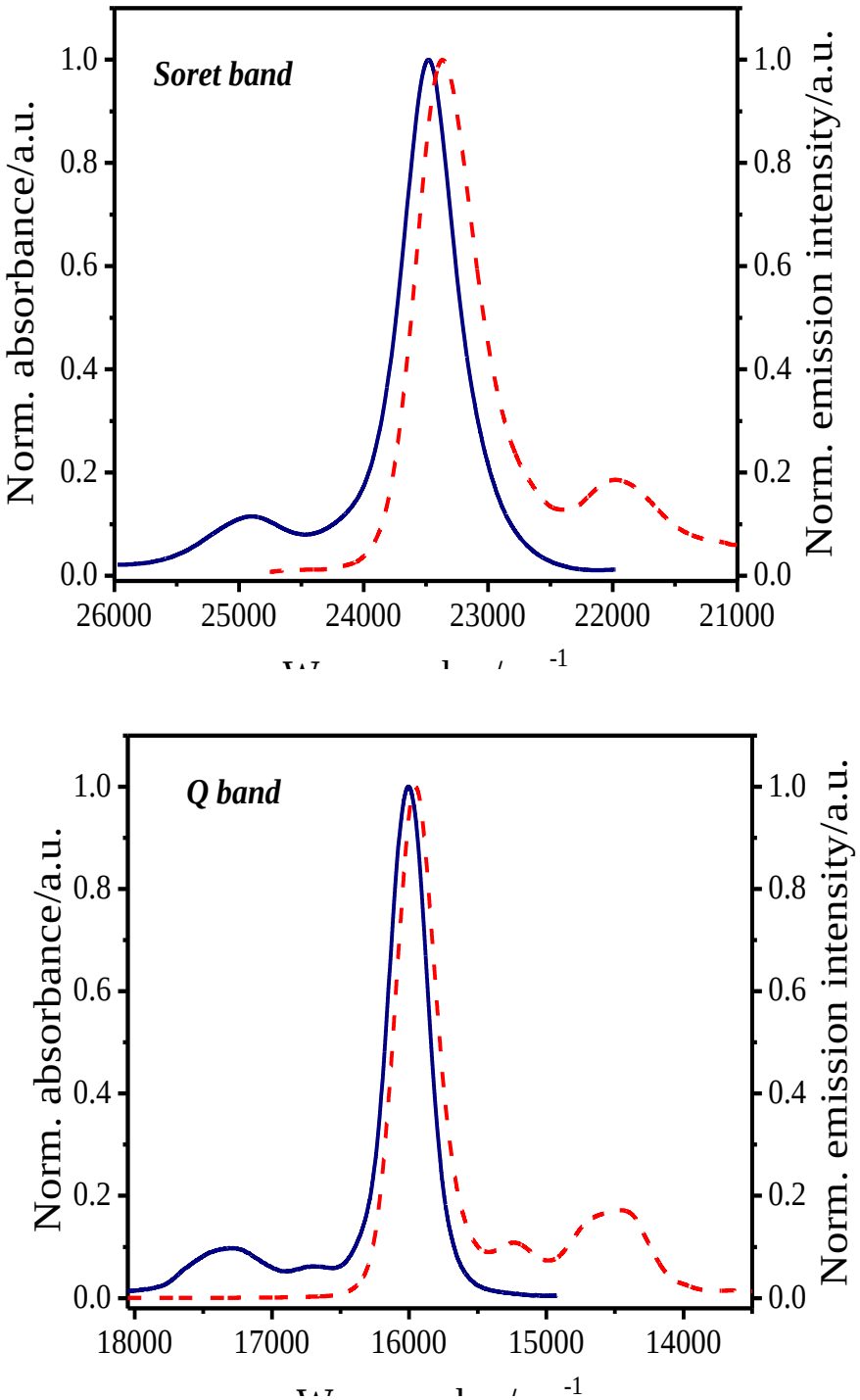


Figure 8 (c) normalized Soret band (upper) and Q band (bottom) absorption and emission spectra of ZnTBP in DMF. The excitation wavelength is 400 nm.