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Synthesis, characterization and fluorescence *turn-on* behavior of new porphyrin analogue: *meta*-benzporphodimethenes[☆]

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ABSTRACT

New fluorescence *switch-on* *meso*-substituted free base *meta*-benzporphodimethenes were synthesized, characterized via acid catalyzed condensation reaction and metallated with Zn^{2+} . Their photophysical properties were also studied. The fluorescence spectra analysis demonstrates substituent's independent behaviour on emitting λ_{max} . The average Stokes shift of 33 nm was observed. Crystal structure of 8 was obtained and gave expected perturbed geometry.

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1. Introduction

Fluorescent molecules for the recognition of metal ions are of great interest for chemist as well as biologist because of their significant role in biological and environmental process [1–18]. Bioimaging with the help of these fluorescent molecules is an important and powerful approach to achieve target specific information which paves the way to understand the structural and functional properties of cells, organs, and living organism in the context of molecular biology, diagnostics and therapeutics [19–26]. The fluorescent techniques are always promising and better tool for analysis because of its high resolution; ease of use and cheaper than other analytical techniques [27]. Different kind of fluorescent sensor have been developed and synthesized like fluorescent proteins [28,29], dyes [30], metal complexes [31], and nanoparticles [32]. The coordination of metal ion with fluorophore increases the fluorescence intensity of chromophore, called chelation-enhanced fluorescence, CHEF. Mostly sensors like fluorescein [33,34], dansyl [35–38], anthracene [11,13], and BIODPY [39] shows CHEF. These CHEF based sensors emit lower than 600 nm and constitute background fluorescence. Still, there is a crunch and in need of development of sensors emitting above 600 nm or even low and zero background fluorescence, high penetration and lesser scattering in optically diffuse samples which in turn may induce lesser tissue damage [40–42]. Deficiency of Zn, Cd, Cu or other transition metals in trace amount can lead to

human or animal diseases [27,43]. So, sincere efforts of environmental, biological scientist and chemist in this direction need to be required for the development of fluorescent molecular sensor for the detection of these trace metals. Out of these trace elements, Zinc is the most abundant transition elements after iron in human body [44]. Zinc plays various important roles in several biological processes such as neurotransmission, signal transduction and gene expression [45]. Literature on homeostasis of zinc is lesser known but structural chemistry explored greatly by chemist because of the spectroscopically silent nature of $d^{10} Zn^{2+}$ [46]. Zn^{2+} fluorescent probes are of three main categories small-molecules, genetically encoded, and hybrid probes. But out of these three classes small-molecule sensors are of higher choice. Again small molecules sensors were further divided into two systems: intensity based and ratiometric probes. Intensity base probes undergo a change in fluorescence intensity upon binding with Zn^{2+} [46]. Bruckner and co-workers showed 300 fold enhancements in fluorescence intensity after Zn^{2+} binding with quinoline based moiety [47]. Varieties of fluorophores have been developed with low background and turn-on fluorescence suitable for biological imaging like proteins [48–49] and peptides based [50]. Other approaches have also been implemented like fluorescein [33–34], Zinpyr family and their modified derivatives [51], ZnAF probes [52], coumarin [53], rhodamine [54], tricarboyanine [55], 4-aminophthalimide [56]. Li, Lin and their co-workers recently developed ZNBR1-3 probes based on benzoessorufin and ZIMIR, respectively [57]. LuoZin-3 probe was recently used by Kornfeld for imaging Zn^{2+} in an optically transparent living organism and later for time lapse imaging and revealed exquisite Zn^{2+} transients [58]. Lippard and Chyan laboratory recently used fluorescent probes, Zinpyr modified

[☆] Dedicated to Professor Sabyasachi Sarkar on his 69th Birthday.

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family, for Zn^{2+} levels in prostate cancer [59]. Large number of fluorescent probes have been developed and used in biological imaging but almost all suffer from high background fluorescence and low CHEF. In this direction, Hung and co-workers developed a fluorescence probe, *meta*-benzoporhodomethene, had no background emission and upon binding with Zn^{2+} shows tremendous increase in fluorescence intensity and represented turn-on probe for Zn^{2+} sensor [60–61]. The change in magnitude of fluorescence intensity with binding of Zn^{2+} with fluorophore can be tuned on manipulation of fluorophore. This can be accomplished in two different ways, first on changing *meso* substituent's or modification on pyrrole β -carbon atoms to tune the electron density. In this paper, we report on the extension of the synthesis of *meta*-benzoporhodomethenes, with various *meso*-substituents and their effects on photophysical properties upon binding with Zn^{2+} have been studied.

2. Experimental section

2.1. Reagents

Pyrrole and substituted aldehydes (liquid) were distilled prior to use. α , α' -dihydroxy-1, 3-diisopropylbenzene (TCI) and boron trifluoride ethyl ether complex, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone were used as supplied. Solvents and all other reagents were used as such without purification. $CDCl_3$ was used as supplied. Basic alumina oxide and silica gel were obtained from Merck.

2.2. General information

Absorption spectra were recorded with Shimadzu UV-1800 at room temperature. Fluorescence spectra were recorded by JobinYvon Horiba Fluorolog-3 spectrofluorometer equipped with double-grating at excitation and emission monochromators and an R928P photomultiplier tube (PMT). The excitation source was a 450 W CW xenon lamp. Fluorescence decay profiles were recorded using time-correlated single photon counting (TCSPC) system (DeltaFlex-01-DD, Horiba JobinYvon IBH Ltd) coupled with Delta Diode Laser. NMR spectra were recorded on Bruker and Jeol Delta. Fourier transform infrared (FTIR) spectra were obtained in the wavenumber range of 4000–400 cm^{-1} by using a Nicolet 380 FTIR spectrometer with the KBr pellet technique. NMR spectra were referenced to residual solvent signals. ESI-mass spectra were recorded on Waters Synapt G2 HDMS. Column chromatography was carried out on Merck silica gel with gravity-feel-column technique. Thin-layer chromatographies were performed on Merck silica gel 60 F254 precoated aluminium sheets.

2.3. Synthesis of **1–8**

A solution of α , α' -dihydroxy-1, 3-diisopropylbenzene (98 mg, 0.50 mmol), substituted aldehyde (102 mL, 1.01 mmol), and pyrrole (104 mL, 1.51 mmol) were dissolved in CH_2Cl_2 (150 mL). The resulted solution was treated with $BF_3 \cdot OEt_2$ (13 μ L, 0.10 mmol) and stirred at room temperature. DDQ (374 mg, 1.65 mmol) was added into the reaction mixture after 2 h and continuously stirred for another 2 h at room temperature. The reaction mixture was quenched with triethylamine and the solvent was removed in vacuo. The crude mixture was dissolved in a minimum amount of CH_2Cl_2 and was purified using silica gel column chromatography (450 mL) eluting with mixture of CH_2Cl_2 and *n*-hexane to give **1–8** as a red powder. The yields obtained for compound (% yield) are as follows: **1** (17%), **2** (14%), **3** (17%), **4** (17%), **5** (16%), **6** (17%), **7** (16%), **8** (17%).

2.4. Synthesis of Zn^{2+} -**1–8**

1 (10 mg) was dissolved in 25 mL CH_2Cl_2/CH_3CN (1:2). To this solution anhydrous zinc chloride (51.3 mg, 0.376 mmol) was pre-dissolved in CH_3CN , added 1 drop of 2, 6-lutidine into the solution. After 2 min of

stirring, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and excess zinc salt was extracted using distilled water. The organic layer was collected and solvent was removed in vacuo and crystallized in *n*-hexane to afford bluish green product. All zinc complexes reported here were prepared with same procedure. The yields obtained for Zn^{2+} -**1–8** was Zn^{2+} -**1** (98%), Zn^{2+} -**2** (98%), Zn^{2+} -**3** (97%), Zn^{2+} -**4** (98%), Zn^{2+} -**5** (97%), Zn^{2+} -**6** (98%), Zn^{2+} -**7** (98%), and Zn^{2+} -**8** (98%).

Spectroscopic analyses of free base *meta*-benzoporhodomethenes and their zinc complex. **1**: λ_{max} (log ϵ) 548 (4.31), 517 (4.27), 353 (4.55). ESI-MS (m/z): 600.0937 ($M + 1$), 1H NMR: 12.32 (br, 1H, NH), 7.93 (s, 1H, 22-ArH), 7.24–7.39 (m, 11H, (2,3,4-ArH + *meso*Ar-H), 6.81 (ab quartet $^3J_{H,H} = 4.88$ Hz, HH, 8,9,18,19-Pyrr H), 6.15 (s, 2H, 13,14-Pyrr H), 1.72 (s, 12H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 20 $^\circ C$): 181.79, 153.72, 152.44, 151.77, 147.41, 143.63, 138.84, 138.58, 138.22, 136.53, 133.59, 131.79, 128.68, 127.38, 125.24, 123.15, 121.27, 42.10, 29.06. IR (KBr, 25 $^\circ C$): 3290.6 (N–H Stretch), 2929.5 (C–H Stretch, sp^3 Hybridised), 1691.9 (C=N Stretch), 1582.7, 1502.9 (C=C Stretch Aromatic), 1383.1 (C–H Bending, sp^3 Hybridised out of plane), 799.9, 756.9 (C–H Bending, Aromatic, out of plane), 717.0 (C–Cl Stretch). Zn^{2+} -**1**: 639 (4.477), 594 (4.216), 351 (4.499). IR (in KBr, 25 $^\circ C$): 2975.5 (C–H Stretch, sp^3 Hybridised), 1672.9 (C=N Stretch), 1545.8, 1491.2 (C=C Stretch Aromatic), 1360.4 (C–H Bending, sp^3 Hybridised, out of plane), 964.1, 804.6 (C–H Bending, Aromatic, out of plane), 713.5 (C–Cl Stretch). Compound **2**: 542 (4.078), 513 (4.05), 351 (4.344). ESI-Mass (m/z): 690.0589 ($M + 1$), 1H NMR: 12.32 (br, 1H, NH), 7.94 (s, 1H, 22-ArH), 7.31–7.57 (m, 11H, (2,3,4-ArH + *meso*Ar-H), 6.83 (ab quartet $^3J_{H,H} = 5.90$ Hz, HH, 8,9,18,19-Pyrr H), 6.16 (s, 2H, 13,14-Pyrr H), 1.74 (s, 12H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 20 $^\circ C$): 182.68, 152.00, 147.06, 138.57, 137.10, 136.45, 133.29, 131.02, 128.52, 127.11, 125.60, 123.56, 123.29, 121.24, 42.25, 28.98. IR (KBr, 25 $^\circ C$): 3281.3 (N–H Stretch), 2924.1 (C–H Stretch, sp^3 Hybridised), 1586.6, 1484.4 (C=C Stretch Aromatic), 1382.8 (C–H Bending, sp^3 Hybridised out of plane), 798.1, 735.7, 703.8 (C–H Bending, Aromatic, out of plane). Zn^{2+} -**2**: 638 (4.45), 594 (4.19), 350 (4.48). IR (in KBr, 25 $^\circ C$): 2969.3 (C–H Stretch, sp^3 Hybridised), 1712.0 (C=N Stretch), 1547.9, 1489.4 (C=C Stretch Aromatic), 1360.6 (C–H Bending, sp^3 Hybridised, out of plane), 967.3, 802.2 (C–H Bending, Aromatic, out of plane), 465.9 (C–Br Stretch). Compound **3**: 538 (4.22), 508 (4.19), 321 (4.32). ESI-Mass (m/z): 670.0478 ($M + 1$). 1H NMR: 12.16 (br, 1H, NH), 8.06 (s, 1H, 22-ArH), 7.28–7.41 (m, 9H, (2,3,4-ArH + *meso*Ar-H), 6.82 (doublet $^2J_{H,H} = 4.59$ Hz, HH, 9,18-Pyrr H), 6.56 (doublet $^2J_{H,H} = 4.59$ Hz, HH, 8,19-Pyrr H), 5.86 (s, 2H, 13,14-Pyrr H), 1.81 (s, 12H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 20 $^\circ C$): 184.33, 162.24, 159.69, 152.99, 146.25, 144.66, 137.77, 135.65, 130.61, 127.94, 127.08, 125.92, 123.59, 123.15, 120.16, 118.37, 111.48, 111.24, 42.50, 29.82, 28.73. IR (in KBr, 25 $^\circ C$): 3300.4 (N–H Stretch), 2967.7 (C–H Stretch, sp^3 Hybridised), 1678.9 (C=N Stretch), 1591.0, 1480.9 (C=C Stretch Aromatic), 1381.7 (C–H Bending, sp^3 Hybridised out of plane), 828.6, 796.8 (C–H Bending, Aromatic, out of plane), 709.0 (C–Cl Stretch). Zn^{2+} -**3**: 649 (4.517), 602 (4.26), 348 (4.608). IR (in KBr, 25 $^\circ C$): 2880.9 (C–H Stretch, sp^3 Hybridised), 1675.2 (C=N Stretch), 1555.1, 1488.8 (C=C Stretch Aromatic), 1321.5 (C–H Bending, sp^3 Hybridised, out of plane), 906.3, 835.5, 797.6 (C–H Bending, Aromatic, out of plane), 718.7 (C–Cl Stretch). Compound **4**: 533 (4.24), 507 (4.213), 320 (4.372). ESI-Mass (m/z): 604.1306 ($M + 1$). 1H NMR: 12.18 (br, 1H, NH), 7.97 (s, 1H, 22-ArH), 7.35–7.45 (m, 3H, (2,3,4-ArH), 6.91–7.05 (m, 6H, ArH), 6.83 (doublet $^2J_{H,H} = 4.40$ Hz, HH, 9,18-Pyrr H), 6.70 (doublet $^2J_{H,H} = 4.22$ Hz, HH, 8,19-Pyrr H), 6.00 (s, 2H, 13,14-Pyrr H), 1.79 (s, 12H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$, 20 $^\circ C$): 184.35, 162.17, 159.75, 153.00, 146.25, 144.65, 137.78, 135.66, 130.63, 127.95, 127.51, 127.08, 125.94, 123.61, 123.16, 120.18, 118.40, 111.50, 111.26, 42.51, 29.83, 28.74. IR (in KBr, 25 $^\circ C$): 3282.8 (N–H Stretch), 2924.0 (C–H Stretch, sp^3 Hybridised), 1621.6 (C=N Stretch), 1589.3 (C=C Stretch Aromatic), 1381.0 (C–H Bending, sp^3 Hybridised out of plane), 783.6, 753.9, 706.8 (C–H Bending, Aromatic, out of plane),

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