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One Pot Syntheses of Butadiyne bridged Bipyrrole derivatives and Bisporphyrin

M. V. Nanda Kishore and Pradeepta K. Panda*[a]

Abstract: A facile one-pot synthesis of butadiyne bridged bipyrroles could be achieved from 2-iodopyrroles and trimethylsilylacetylene via a modified Sonogashira coupling and in-situ aerial oxidative coupling of the acetylenic pyrroles in 31-72% yields, depending upon the substituents on pyrrole. The acetylene bridged diacids obtained from hydrolysis of the corresponding ester derivatives were highly stable, unlike most of the reported oligopyrrolic diacids. This protocol could be easily extended towards the synthesis of butadiyne bridged bisporphyrin.

Introduction

Acetylene bridged biaryls, in particular bipyrroles has emerged as an attractive building block for the synthesis of new class of expanded porphyrins e.g. **1-2** possessing interesting photophysical properties (Figure 1). [1] Whereas, bisporphyrins such as **3** bridged via acetylene(s) also emerged as potential nonlinear optical materials (Figure 1), [2] along with their utility as

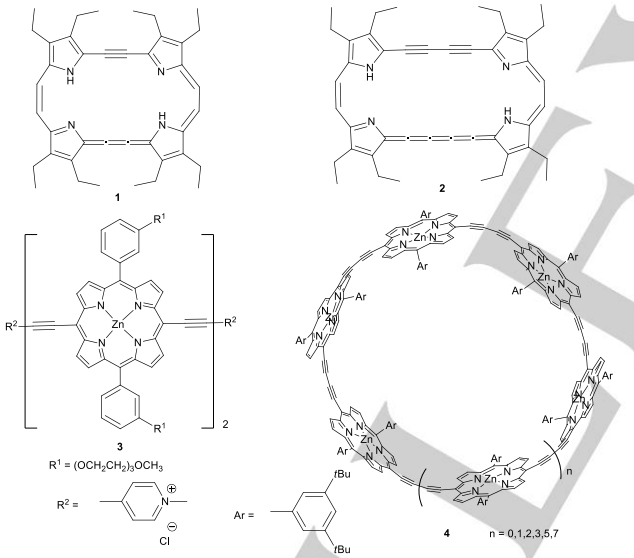


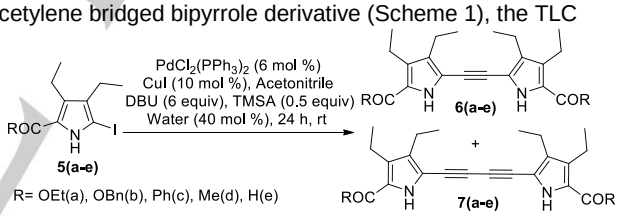
Figure 1. Some examples of acetylene bridged bipyrrole derivatives, bisporphyrins and porphyrin nanorings.

a platform to synthesize novel multiporphyrinic derivatives,[3] porphyrin nanorings **4**,[4] supramolecular nesting[5a] and charge storage/transport,[5b-e] which display many interesting properties, viz. as photosensitizers for two photon photodynamic therapy,[2d-e] tracking molecular motion, create artificial protein-like molecules, etc. However, there are only very few reports regarding their efficient synthesis.[1a,6]

While most of the synthetic approaches, consist of multiple steps involving Pd/Cu-cocatalyzed Sonogashira coupling of iodo arenes (i.e. pyrroles or porphyrins) with trimethylsilylacetylene (TMSA), followed by deprotection of the silyl protecting group and then either another Sonogashira coupling to generate the monoacetylene bridged bipyrrole (or bisporphyrin) derivatives or else Pd-catalyzed oxidative coupling to yield the diacetylene (butadiyne) bridged bipyrrole (or bisporphyrin) derivatives. Herewith, we report a very efficient one pot synthesis of butadiyne bridged bipyrroles and bisporphyrin.

Results and Discussion

The motivation towards this work came during our attempts to synthesize acetylene bridged bipyrrolic systems following the one-pot synthetic protocol for symmetrical bisarylethynes reported by Mio et al. via modified Sonogashira coupling reaction.[7] Interestingly, during our attempt to synthesize the acetylene bridged bipyrrole derivative (Scheme 1), the TLC



Scheme 1. Synthesis of acetylene bridged bipyrroles

analysis revealed a small amount of starting material, iodopyrrole **5a** (never got consumed completely, in spite of extended reaction time or higher temperature), along with another yellow fluorescent spot close to the desired blue fluorescent product **6a** (Table 1, entry 1). Even modulation of reaction conditions via change of solvent and addition of water after some time could not help suppressing the formation of the latter product **7a** completely (Table S1). Successful isolation of

Table 1. Yields of compounds **6** and **7** from Scheme 1

entry	R	Scheme 1 (% yield)	
		6	**7**
1	OEt (a)	71	7
2	OBn (b)	65	13
3	Ph (c)	58	22
4	Me (d)	52	18
5	H (e)	44	-

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this compound via column chromatography revealed similar ^{1}H NMR spectrum as the desired acetylene bridged bipyrrole derivative **6a** (Figure S16 and S25). However, ^{13}C NMR spectrum (Figure S26) displayed an additional carbon signal (at 74.85 ppm for C≡C). The similarity in ^{1}H NMR spectra and the additional carbon signal in ^{13}C NMR spectrum, led us to believe presence of one more alkyne bond in the molecule, which was confirmed by mass analysis showing peak at 459.2260 (Figure S27) for the corresponding $[M + Na]^{+}$ species. Finally, the identity of the compound could be unequivocally resolved through single crystal X-ray diffraction analysis (obtained by slow evaporation of dichloromethane solution of **7a**). The structure shows both pyrroles are in opposite direction, yet in same plane, whereas, in case of **6a** (crystals obtained under similar condition) the pyrroles are pointed towards the same direction (Figure 2). While, the presence of unreacted starting material can be attributed to the formation of diacetylene (or butadiyne) bridged bipyrroles, the formation of the latter may be

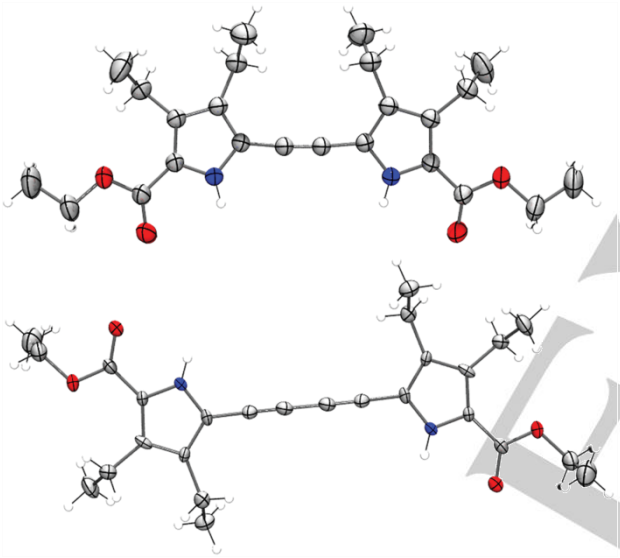
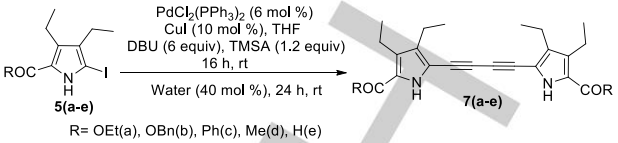


Figure 2. ORTEP diagrams of **6a** (top) and **7a** (bottom). Thermal ellipsoids are scaled up to 35% probability level. Color code: grey = Carbon, white = Hydrogen, blue = Nitrogen and red = Oxygen.

ascribed to the presence of trace amount of oxygen in the reaction medium, which might have promoted the oxidative coupling. While we are working on this theme, Graça H. Vicente and co-workers reported synthesis of 1,2-dipyrrolylethynes following this strategy.[8] However, comparatively lower yields reported by them do not rule out the formation of the butadiyne derivatives in their cases also. Following this protocol several functionalized acetylene bridged bipyrrole derivatives **6a-e** could be synthesized in varying yields depending on the nature of the substituents on the α-position of the 3,4-diethylpyrrole moiety (Table 1, entry 1-5). In most of the cases, we could able to isolate minor quantities of butadiyne bridged bipyrroles **7**.

Encouraged by the above results and owing to the importance of the butadiyne bridged derivatives,[1,9] we wished to explore if they can be exclusively synthesized in one-pot. In order to achieve our desired target, we increased the quantity of TMSA to 1.2 equivalents and exposed the reaction mixture to air after



Scheme 2. Synthesis of butadiyne bridged bipyrroles

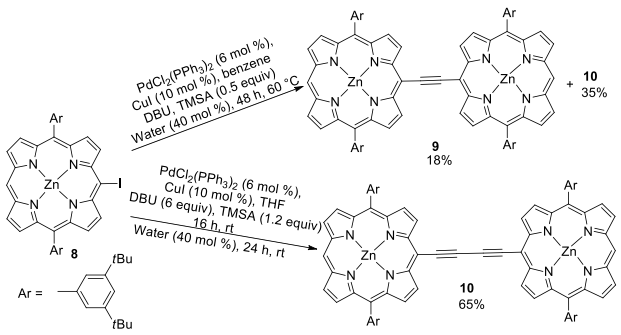
the regular modified Sonogashira coupling (Scheme 2). Reaction of 5a under this condition resulted in the exclusive formation of the desired bipyrrole **7a** in 72% yield. Similarly, other iodopyrrole derivatives **5b-e** (Table 2, entry 2-5) also produced quite good yields of diacetylene bridged bipyrrole derivatives **7b-e** (31 - 67%). The decrease in yield in case of **7e** (Table 2, entry 5) can be attributed to strong deactivating nature

Table 2. Yields of compounds **7** from Scheme 2

entry	R	**7** (% yield)
1	OEt (a)	72
2	OBn (b)	67
3	Ph (c)	61
4	Me (d)	54
5	H (e)	31

of the formyl substituent at the α-position of the pyrrole moiety. The reaction could be easily performed upto 10 g scale in case of **5a** to synthesize **7a** in good yield (60%). The plausible mechanism for the diacetylene bridged bipyrrole synthesis involves a general Sonogashira coupling of TMSA in first step, a base mediated deprotection of TMS group in the second step and oxidative Glaser coupling of thus formed acetylenic pyrrole in presence of palladium and copper.[10]

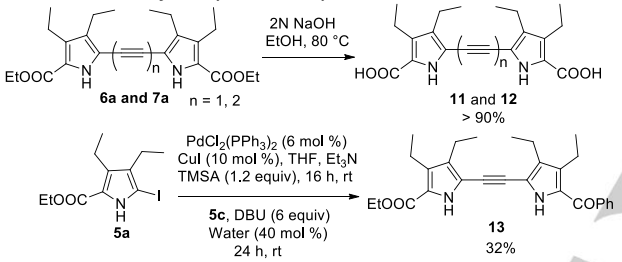
Versatility of this approach could be verified by employing it towards the synthesis of acetylene and butadiyne bridged porphyrins. Here, following the route in Scheme 1, we could obtain the acetylene-bridged bisporphyrin **9** as the minor product on the other hand to our surprise, the butadiyne bridged bisporphyrin **10** formed as the major product (Scheme 3). This may be attributed to the relatively dilute condition we need to



Scheme 3. Synthesis of acetylene and butadiyne bridged bisporphyrins.

adopt for this reaction in order to solubilize the porphyrin in benzene (reaction in THF resulted in much reduced yield) and this may led to the presence of relatively increased oxygen concentration and hence promoting the formation of latter via oxidative coupling. We believe, if carried out in larger scale and also presence of longer alkyl/alkoxy chain(s) at porphyrin periphery to enhance its solubility should result in increased yield of the monoacetylene bridged bisporphyrin (our reaction is not rigorously optimized). However, second route (as in Scheme 2) exclusively yielded the butadiyne-bridged bisporphyrin **10** in quite good yield (65%). To our knowledge, this is the most versatile method for the synthesis of these important bipyrrole based precursors having no protecting group on pyrrolic N and bisporphyrin derivatives.[6,10]

Hydrolysis of **6a** and **7a** resulted in almost quantitative isolation of **11** and **12** (Scheme 4). Unlike other oligopyrrolic diacids,[11] these diacids were found to be very stable under ambient condition and hence could be rigorously characterized (Figure S57-S62). We could also successfully demonstrate coupling between two differently substituted pyrroles to isolate bipyrrole **13** in moderate yield (Scheme 4).



Scheme 4. Synthesis of acetylene bridged bipyrrole acid derivatives and differently substituted acetylene bridged bipyrrole.

Conclusions

In conclusion, we have demonstrated a simple approach towards the synthesis of several butadiyne bridged bipyrrole derivatives, along with their acetylene bridged counterparts. The protocol not only could be easily scaled up, but also could be successfully extended to porphyrinic system, indicating its versatility. As all the bipyrrolic derivatives are without N-protection and also endowed with useful functional groups at their α-positions, they can be used directly or with minimal synthetic manipulation as building blocks towards synthesis of novel π-extended porphyrinoids, retaining the acetylene bridged conjugation. Presently, our efforts are underway in this direction.

Experimental Section

General Information. Commercially available solvents were distilled before use. Reagents were purchased from Sigma Aldrich and used as received without further purification unless otherwise stated. Solvents for the reaction were dried according to literature methods. Compounds ethyl 5-iodo-3,4-diethylpyrrole-2-carboxylate **5a**,[12] benzyl 3,4-diethylpyrrole-2-carboxylate **15b**,[13] 5-iodo-3,4-diethylpyrrole-2-carboxaldehyde **5e**,[6a] 3,4-diethylpyrrole **14**,[14] and 5-iodo-10,20-Bis(3,5-di-*tert*-butylphenyl) porphyrinato Zinc (II) **8**[15] were prepared according to the reported procedures. NMR spectra were recorded on a Bruker Avance-400 and 500 MHz FT NMR spectrometers using tetramethylsilane (TMS, δ = 0) as an internal standard at room temperature. Mass spectral determinations were carried out by Bruker Maxis Spectrometer by ESI technique. Melting points were determined on MR-Vis+ visual melting point range apparatus from LABINDIA instruments private limited. IR spectra were recorded on a JASCO-FT-IR model 5300 and NICOLET 5700 FT-IR spectrometers. All UV-Vis spectra were recorded using Perkin Elmer Lambda-750 UV-VIS spectrometer and fluorescence spectra were recorded in Fluorolog-3-221 spectrofluorometer. Fluorescence spectra were recorded by exciting all acetylene bridged bipyrroles and bisporphyrins in the wavelength range of 265-269 nm and 497-502 nm, respectively. Quantum yield (ϕ_f) calculations were done using 9,10-diphenylanthracene in ethanol as reference for acetylene bridged bipyrroles and tetraphenylporphyrin in toluene for bisporphyrins.[16]

Crystallographic data for **6a** and **7a** were collected on BRUKER SMART-APEX CCD diffractometer. Mo α (λ = 0.71073 Å) radiation was used to collect X-ray reflections on the single crystal. Data reduction was performed using Bruker SAINT software.[17] Intensities for absorption were corrected using SADABS[18] and refined using SHELXL-2014/7[19] with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on O and N were experimentally located in difference electron density maps. A check of the final CIF file using PLATON[20] did not show any missed symmetry. Crystallographic data (including the structure factor) for structures **6a** and **7a** in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1500784-1500785. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

General procedure for the synthesis of 2-benzoyl/acyl substituted 3,4-diethylpyrroles 15c and 15d (Scheme S1).[21] To a three neck round bottom flask having a dropping funnel and a reflux condenser N,N-dimethylbenzamide (DMBz) (3.3 g, 22 mmol)/ N,N-DMAc (3.1 mL, 33 mmol) was added. The flask was immersed in an ice bath, $POCl_3$ (2 mL, 22 mmol)/ (3.1 mL, 33 mmol) was added slowly through syringe. The ice bath was removed and the complex was stirred for another 24 h/15 min at room temperature. DCE (5 mL) was added and the ice bath was replaced. When the internal temperature has been lowered to 5 °C, 3,4-diethylpyrrole (2.46 g, 20 mmol)/ (3.69 g, 30 mmol) dissolved in DCE (20 mL) was added slowly to cooled reaction mixture. After the addition was complete, the ice bath was replaced with heating mantle. The mixture was refluxed for 4 h, then cooled to 25-30 °C and a saturated solution of sodium acetate (9 g, 110 mmol)/ (13.5 g, 165 mmol) was added slowly to the reaction mixture. The reaction mixture was again refluxed for 4 h, during which there is a copious evolution of HCl gas. After the completion of reaction it was extracted thrice with DCM. The combined organic layers were washed with saturated aq sodium carbonate solution and dried over anhyd sodium carbonate. The crude product was purified using silica gel via column chromatography with 20% EtOAc + 80% Hexane as eluent to get the desired products.

15c: 3.8 g, 84%; pale yellow liquid; FTIR data (in cm^{-1}): 3246, 2963, 1617; ^{1}H NMR (400 MHz, $CDCl_3$ δ in ppm): 8.76 (s, 1H), 7.66 (m, 2H), 7.52 (m, 1H), 7.46 (m, 2H), 6.81 (d, J = 2.8 Hz, 1H), 2.50 (m, 4H), 1.22 (t, J = 7.6 Hz , 3H), 1.01 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ δ in ppm): 186.5, 140.2, 134.1, 131.0, 128.3, 128.0, 121.6, 18.3, 18.0, 15.4, 14.7; HRMS m/z calculated for $[M+Na]^+$ $C_{15}H_{17}NONa$: 250.1208, found 250.1210.

15d: 4.7 g, 95%; off-white crystalline solid; mp 96-98 °C ; FTIR data (in cm^{-1}): 3203, 2967, 1615; ^{1}H-NMR (400 MHz, $CDCl_3$ δ in ppm) : 9.04 (s,

1H), 6.76 (d, J = 3.2 Hz, 1H), 2.76 (q, J = 7.6 Hz, 2H), 2.47 (s, 3H), 2.45 (q, J = 7.6 Hz, 2H), 1.2 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$ δ in ppm): 187.6, 131.6, 128.9, 127.3, 121.0, 27.2, 18.6, 17.8, 15.8, 14.7; HRMS m/z calculated for $[M+H]^+$ $C_{10}H_{16}NO$:166.1232 found 166.1229.

General procedure for the synthesis of iodopyrrole derivatives 5(b-d) (Scheme S2):[12] To sodium bicarbonate solution (3.125 g, 38 mmol in 58.5 mL water) in a two neck round bottom flask bearing a reflux condenser with a nitrogen inlet and a pressure equalizing dropping funnel, the pyrrole derivative (10 mmol) in DCE was added and heated at 90 °C. To this, KI_3 solution (KI - 3.65 g, 22 mmol + I_2 - 2.79 g, 11 mmol in 30 mL water) was added dropwise and stirred for 90 min at 80 °C. Later the reaction mixture was extracted twice with DCM. The organic layer was washed with saturated sodium thiosulphate solution and dried over anhyd sodium sulfate. The solvent was evaporated on a rotary evaporator and the crude product was subsequently purified by column chromatography using silica gel and 10% EtOAc + 90% Hexane as eluent to obtain the pure compounds.

5b Yield: 3 g, 78%; white solid; mp 94-95 °C; FTIR data (in cm^{-1}): 3265, 2964, 1671; ^{1}H NMR (400 MHz, $CDCl_3$ δ in ppm): 8.94 (s, 1H), 7.38 (m, 5H), 5.31, (s, 2H), 2.77 (q, J = 7.6 Hz, 2H), 2.38 (q, J = 7.6 Hz, 2H), 1.13 (t, J = 7.6 Hz, 3H), 1.08 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ δ in ppm): 160.0, 136.1, 133.7, 131.7, 128.6, 128.3, 122.8, 73.1, 66.0, 19.8, 18.8, 15.8, 15.5; HRMS calcd. for $[M+H]^+$ $C_{16}H_{19}NO_2I$:384.0461, found 384.0461.

5c Yield: 2.9 g, 83%; yellow solid; mp 120-121 °C ; FTIR data (in cm^{-1}): 3236, 2962, 1604; ^{1}H NMR (400 MHz, $CDCl_3$ δ in ppm): 9.05 (s, 1H), 7.66 (m, 2H), 7.54 (m, 1H), 7.46 (m, 2H), 2.52 (q, J = 7.6 Hz, 2H), 2.42 (q, J = 7.6 Hz, 2H), 1.11 (t, J = 7.6 Hz, 3H), 0.99 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ δ in ppm): 185.3, 139.5, 134.3, 132.4, 131.3, 128.4, 128.1, 76.8, 19.8, 18.8, 15.8, 15.3; HRMS calcd. for $[M+H]^+$ $C_{15}H_{17}NOI$:354.0355, found 354.0359.

5d Yield: 2.4 g, 83%; off-white solid; mp 118-120 °C; FTIR data (in cm^{-1}): 3238, 2964, 1621; ^{1}H NMR (400 MHz, $CDCl_3$ δ in ppm): 9.29 (s, 1H), 2.77 (q, J = 7.6 Hz, 2H), 2.46 (s, 3H), 2.39 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H), 1.09 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ δ in ppm): 186.4, 133.4, 132.0, 131.8, 76.8, 27.0, 19.7, 19.2, 16.3, 15.4; HRMS calcd. for $[M+H]^+$ $C_{10}H_{15}NOI$:292.0198, found 292.0199.

General procedure for the synthesis of dipyrrolyl ethynes 6(a-e):[7] To an oven dried two necked round bottom flask $PdCl_2(PPh_3)_2$ (42 mg, 0.06 mmol), CuI (19 mg, 0.1 mmol) and iodopyrrole derivative (1 mmol) were added and flushed with N_2. Nitrogen purged acetonitrile (5 mL) and DBU (0.9 mL, 6 mmol) were added and the reaction mixture was kept for freeze-pump thaw cycle for 3 times. To this reaction mixture TMSA (71 µL, 0.5 mmol) and water (7 µL, 40 mol%) were added and stirred in dark for 24 h at room temperature. After completion of the reaction, the product was partitioned between ethyl acetate and dil. HCl. The organic layer was washed with brine and dried over anhyd sodium sulfate. Evaporation of solvent under reduced pressure gave crude product, which was purified by silica gel column chromatography to yield the titled compounds.

6a Eluent:10% EtOAc + 90% Hexane, Yield: 146 mg, 71%; off-white solid; mp 180-181 °C; FTIR data (in cm^{-1}): 3290, 2962, 2199, 1660; ^{1}H NMR (400 MHz, $CDCl_3$ δ in ppm): 8.87 (s, 2H), 4.33 (q, J = 7.6 Hz, 4H), 2.75 (q, J = 7.6 Hz, 4H), 2.56 (q, J = 7.6 Hz, 4H), 1.37 (t, J = 7.6 Hz, 6H), 1.17 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$ δ in ppm): 160.7, 132.6, 132.5, 119.4, 114.1, 85.1, 60.2, 18.2, 18.1, 15.7, 14.5; HRMS m/z calcd. for $[M+H]^+$ $C_{24}H_{33}N_2O_4$:413.2440, found 413.2442. UV-Vis data ($CHCl_3$), λ_{max} (in nm): 265 (4.20), 344 (4.59), 369 (4.51); Fluorescence ($CHCl_3$), λ_{max} (in nm): 382, 400; ϕ_f : 0.005.

6b Eluent:10% EtOAc + 90% Hexane, Yield: 174 mg, 65%; light brown solid; UV-Vis data ($CHCl_3$), λ_{max} (in nm): 265 (4.25), 346 (4.57), 371 (4.49) ; Fluorescence ($CHCl_3$), λ_{max} (in nm): 384, 401; ϕ_f : 0.01. All data matched with previously reported compound, except the emission studies which was not reported earlier.[1b]

6c Eluent:15% EtOAc + 85% Hexane, Yield: 138 mg, 58%; yellow solid; mp 196-197 °C; FTIR data (in cm^{-1}): 3300, 2966, 1593, 1414; ^{1}H NMR (400 MHz, $CDCl_3$ δ in ppm): 8.83 (s, 2H), 7.69 (d, J = 6.8 Hz, 4H), 7.55 (t, J = 7.2 Hz, 2H), 7.48 (t, J = 7.2 Hz, 4H), 2.58 (m, 8H), 1.22 (t, J = 7.6 Hz, 6H), 1.05 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$ δ in ppm): 185.8, 139.6, 134.0, 133.5, 131.5, 128.5, 128.3, 128.1, 115.8, 86.1, 18.4, 18.1, 15.7, 15.5; HRMS m/z calcd. for $[M+H]^+$ $C_{32}H_{33}N_2O_2$:477.2542, found 477.2546. UV-Vis data ($CHCl_3$), λ_{max} (in nm): 254 (4.40), 393 (4.57); Fluorescence ($CHCl_3$), λ_{max} (in nm): 448; ϕ_f : 0.003.

6d Eluent:15-30% EtOAc in Hexane, Yield: 92 mg, 52%; brown solid; mp 233-234 °C; FTIR data (in cm^{-1}): 3237, 2962, 1610, 1427; ^{1}H NMR (400 MHz, DMSO-d_6 δ in ppm): 11.93 (s, 2H), 2.69 (q, J = 7.6 Hz, 4H), 2.51 (q J = 7.6 Hz, 4H), 2.40 (s, 6H), 1.09 (m, 12H); ^{13}C NMR (100 MHz, DMSO-d_6 δ in ppm): 187.8, 132.2, 131.7, 129.1, 114.7, 85.7, 28.1, 18.4, 17.8, 16.4, 16.0; HRMS m/z calcd. for $[M+H]^+$ $C_{22}H_{29}N_2O_2$:353.2229, found 353.2232. UV-Vis data ($CHCl_3$), λ_{max} (in nm): 256 (4.18), 281 (4.13), 373 (4.55), 393 (4.52); Fluorescence ($CHCl_3$), λ_{max} (in nm): 413, 433; ϕ_f : 0.379.

6e Eluent:15-30% EtOAc in Hexane, Yield: 141 mg, 44%; yellow solid; UV-Vis data ($CHCl_3$), λ_{max} (in nm): 257 (4.08), 287 (4.13), 384 (4.56), 403 (4.56); Fluorescence ($CHCl_3$), λ_{max} (in nm): 421, 439; ϕ_f : 0.43. All data matched with previously reported compound, except the emission studies which was not reported earlier.[1a]

General procedure for the synthesis of dipyrrolyl butadiynes 7(a-e): To an oven dried two necked round bottom flask $PdCl_2(PPh_3)_2$ (42 mg, 0.06 mmol), CuI (19 mg, 0.1 mmol) and iodopyrrole derivative (1 mmol) were added and flushed with N_2 gas. Nitrogen purged THF (5 mL) and DBU (0.9 mL, 6 mmol) were added and the reaction mixture was kept for freeze-pump thaw cycle for 3 times. To this reaction mixture TMSA (170 µL, 1.2 mmol) was added and stirred in dark for 16 h. Water (18 µL) was added and again stirred in dark for 24 h at room temperature under aerobic condition. After completion of the reaction product was partitioned between ethyl acetate and dilute HCl. The organic layer was washed with brine and dried over anhyd sodium sulfate. Evaporation of solvent under reduced pressure provided crude product, which was purified by silica gel column chromatography using 20-40% EtOAc in Hexane to yield the desired compounds.

7a Yield: 156 mg, 72%; yellow solid; mp 208-209 °C; FTIR data (in cm^{-1}): 3273, 2966, 2129, 1666; ^{1}H NMR (400 MHz, $CDCl_3$ δ in ppm): 9.02 (s, 2H), 4.34 (q, J = 7.2 Hz, 4H), 2.73 (q, J = 7.2 Hz, 4H), 2.56 (q, J = 7.2 Hz, 4H), 1.37 (t, J = 7.2 Hz, 6H), 1.16 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$ δ in ppm): 160.4, 135.1, 132.4, 120.3, 113.1, 79.0, 74.9, 60.4, 18.2, 15.8, 15.6, 14.4; HRMS m/z calcd. for $[M+Na]^+$ $C_{26}H_{32}NaN_2O_4$:459.2260, found 459.2260. UV-Vis data ($CHCl_3$), λ_{max} (in nm): 320 (4.51), 334 (4.62), 360 (4.59), 389 (4.50); Fluorescence ($CHCl_3$), λ_{max} (in nm): 443, 471; ϕ_f : 0.005.

7b Yield: 188 mg, 67%; yellow solid; mp 175-176 °C; FTIR data (in cm^{-1}): 3287, 2958, 2131, 1666; ^{1}H NMR (400 MHz, $CDCl_3$ δ in ppm): 9.08 (s, 2H), 7.38 (m, 10H), 5.31 (s, 4H), 2.72 (q, J = 7.6 Hz, 4H), 2.53 (q, J = 7.6 Hz, 4H), 1.14 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$ δ in ppm): 160.1, 135.9, 135.2, 133.0, 128.6, 128.3, 119.9, 113.4, 79.0, 74.8, 66.3, 18.2, 18.1, 15.7, 15.7; HRMS m/z calcd. for $[M+H]^+$ $C_{36}H_{37}N_2O_4$:561.2753, found 561.2754. UV-Vis data ($CHCl_3$), λ_{max} (in nm): 257 (4.42), 283

(4.41), 336 (4.68), 362 (4.65), 391 (4.56); Fluorescence ($CHCl_3$), λ_{max} (in nm): 408, 424, 481, 503; ϕ_f : 0.004.

7c Yield: 153 mg, 61%; yellow solid; mp 210-212 °C; FTIR data (in cm^{-1}): 3233, 2966, 1595; ^{1}H NMR (400 MHz, $CDCl_3$ δ in ppm): 8.89 (s, 2H), 7.68 (d, J = 7.2 Hz, 4H), 7.56 (t, J = 6.8 Hz, 2H), 7.48 (t, J = 7.2 Hz, 4H), 2.58 (q, J = 7.6 Hz, 8H), 1.21 (t, J = 7.6 Hz, 6H), 1.05 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$ δ in ppm): 185.7, 139.3, 136.0, 133.8, 131.7, 128.8, 128.6, 128.2, 114.7, 79.7, 75.2, 18.4, 18.1, 15.6; HRMS m/z calcd. for $[M+H]^+$ $C_{34}H_{33}N_2O_2$:501.2542, found 501.2545. UV-Vis data ($CHCl_3$), λ_{max} (in nm): 261 (4.43), 389 (4.68), 419 (4.59); Fluorescence ($CHCl_3$), λ_{max} (in nm): 458; ϕ_f : 0.003.

7d Yield: 102 mg, 54%; yellow solid; mp 266-268 °C; FTIR data (in cm^{-1}): 3269, 2972, 1620; ^{1}H NMR (400 MHz, DMSO-d_6 δ in ppm): 12.15 (s, 2H), 2.67 (q, J = 7.2 Hz, 4H), 2.48 (q, J = 7.2 Hz, 4H), 2.39 (s, 6H), 1.11 (t, J = 7.2 Hz, 6H), 1.05 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6 δ in ppm): 188.0, 134.7, 131.5, 129.9, 112.9, 78.7, 76.4, 28.1, 18.3, 17.8, 16.3, 15.9; HRMS m/z calcd. for $[M+H]^+$ $C_{24}H_{29}N_2O_2$:377.2229, found 377.2230. UV-Vis data ($CHCl_3$), λ_{max} (in nm): 287 (4.21), 359 (4.61), 377 (4.62), 406 (4.53); Fluorescence ($CHCl_3$), λ_{max} (in nm): 448; ϕ_f : 0.006.

7e Yield: 54 mg, 31%; yellow solid; UV-Vis data ($CHCl_3$), λ_{max} (in nm): 281 (4.29), 368 (4.61), 385 (4.61); Fluorescence ($CHCl_3$), λ_{max} (in nm): 430; ϕ_f : 0.256. All data matched with previously reported compound, except the emission studies, which was not reported earlier.[1c]

Preparation of acetylene bridged porphyrin dimer 9: To a Schlenk flask fitted with a tight rubber septum was added Zn(II) complex of iodoporphyrin (88 mg, 0.1 mmol), $PdCl_2(PPh_3)_2$ (4 mg, 6 mol%), CuI (2 mg, 10 mol%). Dry benzene (5 mL) and DBU (5 mL) were added and the solution was degassed by freeze-pump thaw cycles. TMSA (7 µL, 0.05 mmol) and water (1 µL, 40 mol%) were added and stirred under inert atmosphere for 48 h at 60 °C. The mixture was washed with water and the organic layer was evaporated in vacuum to obtain the crude product, which was subjected to column chromatography using silica gel and DCM-Hexane-Et_3N (1:1:0.01) mixture as eluent to obtain both mono and diacetylene bridged dimers. The pure compound **9** was obtained as a green solid using preparative TLC (14 mg, 18%), along with **10** (27 mg, 35%). UV-Vis data ($CHCl_3$), λ_{max} (nm): 415 (5.03), 478 (5.17), 551 (4.21), 652 (4.33), 690 (4.39); Fluorescence (1% pyridine in toluene), λ_{max} (nm): 735; ϕ_f : 0.094. All data matched with previously reported compound, except the quantum yield, which is measured in different solvent and is of similar order.[22]

Preparation of butadiyne bridged porphyrin dimer 10: To a Schlenk flask fitted with a tight rubber septum was added Zn(II) complex of iodoporphyrin (44 mg, 0.05 mmol), $PdCl_2(PPh_3)_2$ (2 mg, 6 mol%), CuI (1 mg, 10 mol%). THF (4 mL) and DBU (0.5 mL) were added and the solution was degassed by freeze-pump thaw cycles. TMSA (11 µL, 0.075 mmol) was added and stirred in dark for 16 h. Water (2 µL) was added and the reaction mixture was stirred under aerobic condition for 24 h at room temperature. The reaction mixture was washed with water and the organic layer was evaporated in vacuum to obtain the crude product. It was further subjected to silica gel column chromatography using DCM-Hexane (1:2) as eluent to obtain the desired dimer 10 as a green solid (25 mg, 65%). UV-Vis data ($CHCl_3$), λ_{max} (in nm): 448 (5.07), 480 (4.90), 562 (4.06), 634 (4.19), 679 (4.33); Fluorescence (toluene), λ_{max} (in nm): 682; ϕ_f : 0.12. All data matched with previously reported compound, except the quantum yield, which so far is not reported precisely.[2c,6b]

General procedure for the synthesis of acetylene bridged bipyrrole acid derivatives 11 and 12: To a two neck round bottomed flask fitted with a rubber septum **6a** or **7a** (1 mmol) was added and dissolved in minimum amount of ethanol by refluxing. Subsequently, the reaction mixture was cooled and 2N NaOH (400 mg, 10 mmol) solution was added and again refluxed under nitrogen atmosphere for 10-12 h until a clear solution was obtained. The reaction mixture was cooled and diluted with water. To the ice cooled reaction mixture, dilute HCl was added dropwise under constant stirring to obtain clear precipitate, which was filtered and dried overnight under vacuum to provide the titled compounds.

11 Yield: 322 mg, 91%; grey solid; mp > 250°C (decomposes); FTIR data (in cm^{-1}): 3300, 2961, 2930, 1660; ^{1}H NMR (400 MHz, Methanol-*d4*, δ in ppm): 2.76 (q, J = 7.2 Hz, 4H), 2.58 (q, J = 7.2 Hz, 4H), 1.16 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$ δ in ppm): 162.5, 132.4, 131.1, 119.0, 114.5, 84.5, 17.6, 17.5, 14.9; HRMS m/z calcd. for $[M+Na]^+$ $C_{20}H_{24}N_2NaO_4$: 379.1634 found 379.1635. UV-Vis data (MeOH), λ_{max} (in nm): 262 (4.09), 338 (4.46), 360 (4.40); Fluorescence (MeOH), λ_{max} (in nm): 393; ϕ_f : 0.007.

12 Yield: 366 mg, 96%; light brown solid; mp > 250°C (decomposes); FTIR data (in cm^{-1}): 3300, 2962, 1661; ^{1}H NMR (400 MHz, Methanol-*d4*, δ in ppm): 2.74 (q, J = 7.2 Hz, 4H), 2.55 (q, J = 7.6 Hz, 4H), 1.17 (t, J = 7.6 Hz, 6H), 1.12 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$ δ in ppm):163.5, 135.3, 133.5, 121.6, 114.4, 79.2, 75.9, 18.9, 18.9, 16.2, 16.2; HRMS m/z calcd. for $[M+Na]^+$ $C_{22}H_{24}N_2NaO_4$: 403.1634 found 403.1633. UV-Vis data (MeOH), λ_{max} (in nm): 314 (4.47), 329 (4.52), 354 (4.46), 381 (4.36); Fluorescence (MeOH), λ_{max} (in nm): 470, 498; ϕ_f : 0.004.

Synthesis of differently substituted acetylene bridged bipyrrole 13: To an oven dried two necked round bottom flask $PdCl_2(PPh_3)_2$ (42 mg, 0.06 mmol), CuI (19 mg, 0.1 mmol) and **5a** (1 mmol) were added and flushed with N_2 gas. Nitrogen purged THF (5 mL) and triethylamine (0.9 mL) were added and the reaction mixture was kept for freeze-pump thaw cycle for 3 times. To the reaction mixture TMSA (170 µL, 1.2 mmol) was added and stirred in dark for 16 h. To the reaction mixture **5c**, DBU (1.8 mL) and water (14 µL) were added and again stirred for 24 h at rt. Subsequently, the reaction mixture was partitioned between ethyl acetate and dil. HCl. The organic layer was washed with brine and dried over anhyd sodium sulfate. Evaporation of solvent under reduced pressure provided crude product, which was purified by silica gel column chromatography using 10% EtOAc in hexane to yield the desired compound along with **7a** (24%).

Yield: 141 mg, 32%; yellow solid; mp 188-190°C ; FTIR data (in cm^{-1}): 3282, 2972, 1660, 1593; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 8.91 (s, 1H), 8.86 (s, 1H), 7.70 (d, J = 4 Hz, 2H), 7.56 (t, J = 4 Hz, 1H), 7.48 (t, J = 8 Hz, 2H), 4.33 (q, J = 6.8 Hz, 2H), 2.75 (q, J = 8 Hz, 2H), 2.58 (m, 6H), 1.37 (t, J = 6 Hz, 3H), 1.19 (m, 9H), 1.05 (t, J = 6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ δ in ppm): 185.8, 160.6, 139.7, 134.0, 133.3, 132.8, 132.6, 131.4, 128.5, 128.1, 119.6, 116.2, 113.8, 86.2, 85.0, 60.3, 18.4, 18.2, 18.1, 15.7, 15.5, 14.4; HRMS m/z calcd. for $[M+H]^+$ $C_{28}H_{33}N_2O_3$: 445.2491 found 445.2490. UV-Vis data ($CHCl_3$), λ_{max} (in nm): 253 (4.31), 300 (4.28), 377 (4.54); Fluorescence ($CHCl_3$), λ_{max} (in nm): 446; ϕ_f : 0.002.

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Keywords: Alkynes • Biaryls • C-C coupling • Porphyrinoids • Sonogashira coupling

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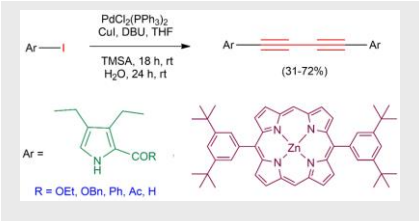
COMMUNICATION

Butadiyne bridged bipyrroles were obtained from the corresponding iodo pyrroles in one pot strategy which was subsequently applied to synthesize butadiyne bridged bisporphyrin in good yield.



Butadiyne bridged bipyrroles*

*M. V. Nanda Kishore, Pradeepta K. Panda**

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One Pot Syntheses of Butadiyne bridged Bipyrrole derivatives and Bisporphyrin