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Facile Synthesis of 9,10,19,20-Tetraarylporphycenes

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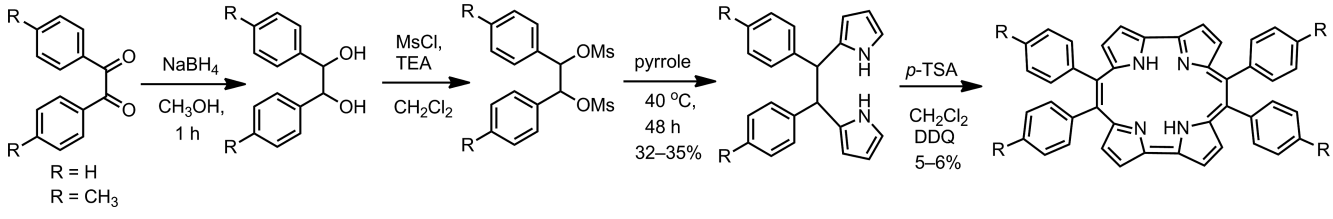
A simple route was developed for the synthesis of 9,10,19,20-tetraarylporphycenes by combining both McMurry and oxidative synthetic strategies and using readily available precursors. The desired 5,6-diaryldipyrroethenes, which were prepared in multigram quantities over two steps, were used to prepare 9,10,19,20-tetraarylporphycenes under mild acid-catalyzed conditions. As 5,6-diaryldipyrroethene precursors can easily be prepared in multigram quantities, this method is useful for the preparation of *meso*-tetrarylporphycenes that contain different aryl substituents. The molecular structures of these macrocycles were determined by HRMS analysis as well as 1D and 2D NMR studies. The tetraarylporphycenes exhibited a strong Soret band at approximately 380 nm and three Q bands in the region of 580–655 nm. The tetraarylprophycenes are reasonably fluorescent and stable under redox conditions.

Introduction

Porphycene is a tetrapyrrolic planar 18π-electron aromatic macrocycle, which consists of two 2,2′-bipyrrole subunits that are linked by two double bonds.[1] Porphycene, which was prepared by Vogel and co-workers in 1986,[2] is a constitutional isomer of porphyrin and possesses unique optical properties such as a strong absorption in the far red region of the visible spectrum,[1,3] which differentiates it from porphyrins. Because of these optical properties, porphycenes have been examined as possible photosensitizers for photodynamic therapy.[4] Porphycenes, like porphyrins, are divalent and have a high tendency to form metal complexes.[1] The synthetic approaches for porphycenes have been well established in the literature and were reviewed by Sessler and co-workers in 2008.[1] It has been shown that substituents at the β-pyrrole[5] and *meso* positions can significantly modulate the physico-chemical properties of the porphycene macrocycle. In general, porphycenes have been prepared by the reductive dimerization of diformyl-2,2′-bipyrrole under McMurry coupling conditions followed by oxidation.[2] A perusal of the literature reveals that porphycenes that contain alkyl substituents at the β-pyrrole and *meso* carbon atoms were readily prepared by following the standard McMurry coupling strategy over a sequence steps,[6] but there is no report available for the synthesis of a porphycene that contains *meso*-aryl substituents by using this strategy.

Srinivasan and co-workers[7] reported the first examples of 9,10,19,20-tetraarylporphycenes by adopting a new synthetic method (see Scheme 1). They first prepared the appropriate benzoin or benzil compounds, which were then converted into 1,2-diphenylethane-1,2-diol through a $NaBH_4$ reduction. The diol was treated with mesyl chloride (MsCl) to give the mesylated product, which was then treated with pyrrole to obtain 5,6-diaryldipyrroethane.[7] In the final step, the 5,6-diaryldipyrroethane was subjected to an acid-catalyzed oxidative coupling by treatment with *para*-toluenesulfonic acid (*p*-TSA) followed by an oxidation by treatment with 2,3-dichloro-5,6-dicyano-*para*-benzoquinone (DDQ) to yield 9,10,19,20-tetraarylporphycene in approximately 5% yield. By following this strategy, Srinivasan and co-workers[7] reported two examples of 9,10,19,20-tetraarylporphycene derivatives. There are major draw-



Scheme 1. Reported synthesis of 9,10,19,20-tetraarylporphycenes (TEA = triethylamine).

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backs, however, to this strategy. The synthesis of the key precursor 5,6-diaryldipyrroethane is one inconvenience, and the longer reaction times that are required for some reaction steps also limit the versatility of this strategy for the preparation of the desired 9,10,19,20-tetraarylporphycenes. We have developed an alternate facile approach for the synthesis of 9,10,19,20-tetraarylporphycenes that combines both McMurry and oxidative synthetic strategies and uses readily available precursors that can be easily prepared in multigram quantities. Our strategy involves three simple steps, and the method is versatile for the synthesis of the desired 9,10,19,20-tetraarylporphycenes.

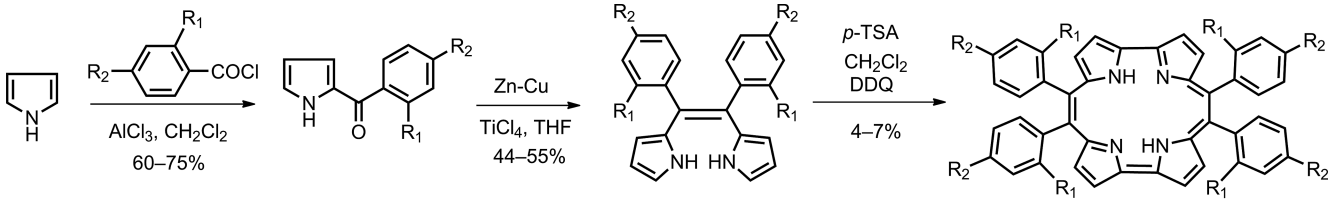
Results and Discussion

The synthesis of the desired 9,10,19,20-tetraarylporphycenes **1**–**6** was carried out in three steps by starting from commercially available pyrrole and acid chlorides as shown in Scheme 2. Pyrrole (1 equiv.) was benzoylated at the 2-position by treating it with 1 equiv. of the substituted benzoyl chloride in CH_2Cl_2 in the presence of 1.2 equiv. of $AlCl_3$ at room temperature for 4 h followed by workup and column chromatographic purification to afford benzoylated pyrroles **7**–**12** as white solids in yields of 60–75%. The 2-benzoylated pyrroles **7**–**12** were subjected to McMurry coupling conditions in the presence of Zn-Cu^I/$TiCl_4$ in tetrahydrofuran (THF), and the mixture was heated at reflux for 12 h. The progress of the reaction was followed by TLC analysis, whereupon the crude reaction mixture showed a less polar, new fluorescent spot and the disappearance of the spot from the 2-benzoylated pyrrole. The crude compounds were subjected to chromatography on a silica gel column to afford pure 5,6-diaryldipyrroethenes **13**–**18** as yellow fluorescent solids in yields of 44–54%. Dipyrroethenes **13**–**18** were characterized by HRMS and NMR spectroscopy as well as by X-ray crystallography for compounds **14** and **15**. The HRMS data for compounds **13**–**18** showed a molecular ion peak that confirmed the composition of dipyrroethenes **13**–**18**. In the ^{1}H NMR spectra of **13**–**18**, the six protons of the two pyrrole rings appeared as three sets of signals in the δ = 5.80–6.80 ppm region, and the NH proton appeared as broad singlet at approximately δ = 8.05 ppm. There were also signals that corresponded to the *meso*-aryl protons. The dipyrroethenes showed one well-defined absorption band at approximately 350 nm, which had a shoulder on the higher energy side. Compounds **13**–**18** are fluorescent in solution and in the solid state.

Single crystals of compounds **14** and **15** were obtained by slow diffusion of an *n*-hexane into a chloroform solution over a period of one week. Diaryldipyrroethenes **14** and **15** crystallized into the monoclinic space group $P2_1/c$, and their crystallographic data are summarized in the Table 1. The ORTEP plots of compounds **14** and **15** are presented in Figure 1. In these dipyrroethenes, we considered the double bond between the two pyrrole rings as the mean plane and the deviation of the two pyrrole nitrogen atoms from this mean plane as approximately 0.85 Å. In both compounds **14** and **15**, the dihedral angle between the *meso*-aryl rings and double bond of the dipyrroethene is approximately 120°, and the dihedral angle between the pyrrole rings and double bond of the dipyrroethene is approximately 125°.

Table 1. Crystallographic data for compounds **14** and **15**.

Parameters	**14**	**15**
Formula	$C_{24}H_{22}N_2$	$C_{24}H_{22}N_2O_2$
M_w	338.44	370.44
Temperature [K]	150	100
Wavelength [Å]	0.71073	0.71075
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	9.397(5)	9.340(4)
b [Å]	20.072(5)	19.040(7)
c [Å]	9.826(5)	10.970(4)
α [°]	90	90
β [°]	97.995(5)	97.836(6)
γ [°]	90	90
V [Å^3]	1835.3(14)	1932.6(13)
Z	4	4
μ [mm^{-1}]	0.072	0.082
$\rho_{calcd.}$ [g cm^{-3}]	1.225	1.273
F(000)	720.0	784.0
2θ range [°]	2.03–25.00	3.89–25.36
e data	3233	3506
R_1, wR_2 [$I > 2\sigma(I)$]	0.0491, 0.1341	0.0510, 0.1250
R_1, wR_2 (all data)	0.0551, 0.1466	0.0685, 0.1127
Goodness-of-fit	1.103	0.963
Largest diff. peak/hole [e Å^{-3}]	0.466/–0.281	0.196/–0.216



$R_1 = R_2 = H$	**7**	$R_1 = R_2 = H$	**13**	$R_1 = R_2 = H$	**1**
$R_1 = H, R_2 = CH_3$	**8**	$R_1 = H, R_2 = CH_3$	**14**	$R_1 = H, R_2 = CH_3$	**2**
$R_1 = H, R_2 = OCH_3$	**9**	$R_1 = H, R_2 = OCH_3$	**15**	$R_1 = H, R_2 = OCH_3$	**3**
$R_1 = H, R_2 = NO_2$	**10**	$R_1 = H, R_2 = NO_2$	**16**	$R_1 = H, R_2 = NO_2$	**4**
$R_1 = H, R_2 = Br$	**11**	$R_1 = H, R_2 = Br$	**17**	$R_1 = H, R_2 = Br$	**5**
$R_1 = F, R_2 = H$	**12**	$R_1 = F, R_2 = H$	**18**	$R_1 = F, R_2 = H$	**6**

Scheme 2. Alternate method for the synthesis of 9,10,19,20-tetraarylporphycenes.

The torsion angle between the two pyrrole units and the two *meso*-aryl groups is 15° and 17°, respectively. Overall the molecule is significantly distorted.

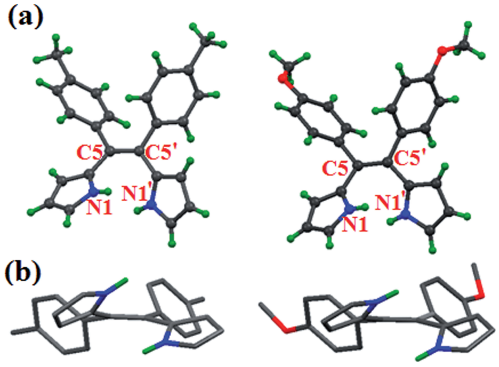


Figure 1. Single-crystal X-ray structures of compounds **14** and **15**: (a) top view and (b) side view. In the side view, hydrogen atoms are omitted for clarity.

In the final synthetic step, 5,6-diaryldipyrroethenes **13**–**18** were subjected to a condensation reaction by using *p*-TSA in CH_2Cl_2 at room temperature under nitrogen for 1.5 h followed by an oxidation by treatment with DDQ at room temperature in air for 1 h. TLC analysis showed one significant, rapidly moving red fluorescent spot under UV light, which indicated the formation of the desired macrocycles. The crude compounds were purified by chromatography on a silica gel column to afford the desired 9,10,19,20-tetraarylporphycenes **1**–**6** as purple solids in yields of 4–7%. Porphycenes **1**–**6** were readily soluble in common organic solvents, and their compositions were confirmed by HRMS analysis. The molecular structures of compounds **1**–**6** were deduced by 1D and 2D NMR spectroscopy. The signals of ^{1}H NMR spectra were identified by NOESY analysis as shown for compound **1** in Figure 2. The signals in the NMR spectrum were assigned on the basis of the integration values, coupling constants, and cross-peak correlations in the NOESY spectrum (see Figure 2). In the ^{1}H NMR spectrum, the macrocycle showed only five sets of signals in the region of δ = 7.0 to 10.0 ppm, because of the symmetric nature of the molecule, and these signals correlated with each other in NOESY spectrum. The doublets at δ = 9.43 and 8.43 ppm with a coupling constant of approximately 4.4 Hz were identified as the pyrrole protons, as these signals correlated with each other in the NOESY spectrum. The doublet at δ = 7.72 ppm with a coupling constant of 7.7 Hz and the multiplet at δ = 7.38–7.36 ppm were recognized as the *meso*-aryl protons. In the NOESY spectrum, the doublet at δ = 7.72 ppm, which we identified as the c-type *meso*-aryl protons showed an NOE correlation with the multiplet at δ = 7.38–7.36 ppm as well as with the doublet at δ = 8.43 ppm. The multiplet at δ = 7.38–7.36 ppm was identfied as the d- and e-type protons of the *meso*-aryl groups, and the doublet at δ = 8.43 ppm was recognized as the b-type pyrrole protons. The b-type pyrrole protons at δ = 8.43 ppm showed a cross-peak correlation with the doublet at δ = 9.43 ppm, which we identified as the a-type pyrrole protons. The broad signal at δ = 5.98 ppm was the result of the two inner NH protons. Thus, the macrocycle had a very simple NMR spectrum. Furthermore, porphycene **1** was also characterized by crystal structure analysis, and the structure was identical with the previously reported[7] structure of porphycene **1** (see Figures S46–S47 in Supporting Information).

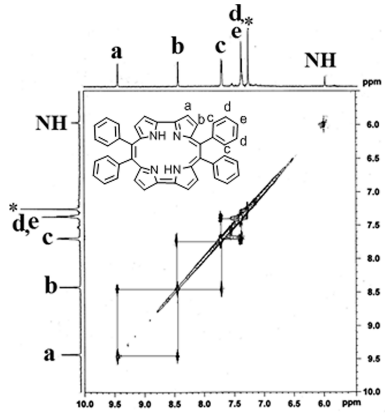


Figure 2. NOESY spectrum of compound **1**.

Absorption, Fluorescence, and Electrochemical Properties

The properties of porphycenes **1**–**6** were studied by absorption, fluorescence, and electrochemical experiments. The relevant data for the absorption and fluorescence properties of **1**–**6** in $CHCl_3$ are shown in Table 2, and the representative absorption and fluorescence spectra of porphycene **1** are shown in Figure 3. Upon inspection of Figure 3 and the data in Table 2, we found that *meso*-tetraarylporphycenes **1**–**6** generally show a strong Soret band at approximately 380 nm and three weak Q bands in the region of 580–655 nm. Porphycenes **1**–**6** did not show any significant shifts to their peak maxima upon changing the *meso*-aryl group. The fluorescence properties of porphycenes **1**–**6** were

Table 2. Photophysical data of compounds **1**–**6** (1×10^{-6} M) recorded in $CHCl_3$.

	Soret band [nm][a]	Q bands [nm][a]	λ_{em} [nm]	Φ_f	τ [ns]
1	381 (5.1)	585 (4.1), 624 (4.3), 653 (4.4)	665, 724 (sh)	0.23	3.91
2	383 (5.0)	586 (4.2), 626 (4.4), 654 (4.5)	668, 725 (sh)	0.21	3.68
3	382 (5.0)	585 (4.1), 626 (4.3), 655 (4.5)	667, 724 (sh)	0.21	3.59
4	380 (4.9)	578 (4.0), 619 (4.2), 650 (4.4)	656, 716 (sh)	0.18	3.01
5	379 (4.9)	580 (4.0), 623 (4.2), 653 (4.3)	660, 720 (sh)	0.16	2.95
6	380 (5.0)	580 (4.1), 621 (4.3), 650 (4.4)	658, 717 (sh)	0.18	3.06

[a] Values in parentheses correspond to logε.

studied by both steady-state and time-resolved fluorescence techniques. Porphycenes **1**–**6** are reasonably fluorescent with a strong fluorescence band at approximately 660 nm along with a shoulder band at approximately 720 nm. The quantum yields are dependent on the type of aryl substituent present at the *meso* position. The quantum yields of porphycenes **1**–**6** were in the range of 0.16–0.23. The fluorescence decays of porphycenes **1**–**6** were fitted to single exponential decay, and the representative fluorescence decay profile for porphycene **1** in $CHCl_3$ is shown in Figure 4. The lifetimes of the singlet state of porphycenes **1**–**6** were in the range of 2.95–3.91 ns. The electrochemical properties of porphycenes **1**–**6** were measured by cyclic voltammetry and differential pulse voltammetry at a scan rate of 50 $mV\,s^{-1}$ with tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte in CH_2Cl_2. The representative cyclic voltammogram along with the differential pulse voltammogram for porphycene **1** is shown in Figure 5, and the data are presented in Table 3. All porphycenes **1**–**6** showed one reversible oxidation, one reversible reduction, and one quasi-reversible reduction. For example, porphycene **1** showed one reversible oxidation at 1.18 V, one reversible reduction at –0.63 V, and the second quasi-reversible reduction at –0.98 V. The redox potentials were sensitive to the nature of the substituent present in the *meso*-phenyl groups. However, compared to the isomer 5,10,15,20-tetraphenylporphyrin (H_2TPP), porphycenes **1**–**6** are difficult to oxidize but much easier to reduce, which supports the electron-deficient nature of porphycenes. The HOMO–LUMO gap of porphycenes **1**–**6** were in the range of 1.81–1.87 eV, which is smaller than that of H_2TPP (2.23 eV). Thus, electrochemical studies indicate that porphycenes **1**–**6** are highly stable under redox conditions.

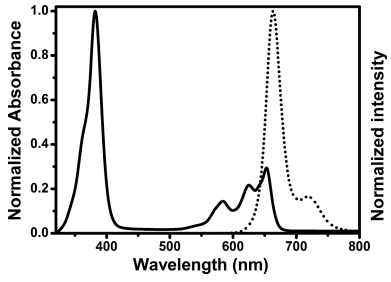


Figure 3. Comparison of normalized absorption (thick line) and emission (dotted line) spectra of tetraphenylporphycene **1** (1×10^{-6} M) in $CHCl_3$.

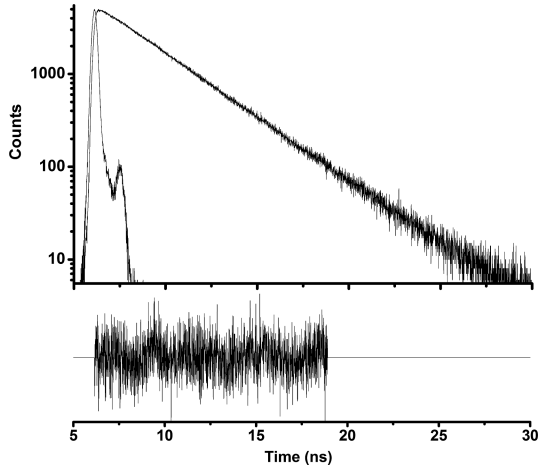


Figure 4. Fluorescence decay profile and the corresponding weighted residual distribution fit for the fluorescence decay of tetraphenylporphycene **1** in $CHCl_3$. The employed excitation wavelength was approximately 380 nm, and the emission was detected at the emission peak maxima (655–665 nm) of tetraphenylporphycene **1** in $CHCl_3$.

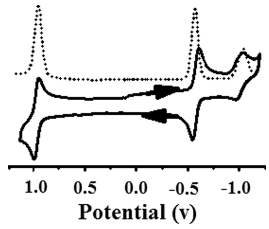


Figure 5. Overlay of cyclic voltammogram (thick line) and differential pulse voltammogram (dotted line) of compound **1** recorded in CH_2Cl_2 by using TBAP (0.1 M) as the supporting electrolyte at a scan rate of 50 $mV\,s^{-1}$.

Table 3. Electrochemical data of compounds **1**–**6** recorded in CH_2Cl_2 containing TBAP (0.1 M) as the supporting electrolyte recorded at scan rate 50 $mV\,s^{-1}$.

	Oxidation $E_{1/2}$/V vs. SCE	Reduction $E_{1/2}$/V vs. SCE		
	II	I	II	HOMO–LUMO gap
	E_{ox} [V]	E_{red} [V]	E_{red} [V]	ΔE_{red-ox} [V]
1	1.18	–0.63	–0.98	1.81
2	1.28	–0.59	–0.88	1.87
3	1.29	–0.54	–0.84	1.83
4	1.29	–0.52	–0.82	1.81
5	1.30	–0.51	–0.80	1.81
6	1.41	–0.46	–0.72	1.87
H_2TPP	1.03	–1.23	–1.55	2.26

Conclusions

In summary, we synthesized the *meso*-tetraarylporphycenes by using readily available precursors under simple reaction conditions. This straightforward method allows for the preparation of different types of *meso*-tetraarylporphycenes and is complementary to the earlier reported approach. The *meso*-tetraraylporphycenes strongly absorb and emit in the visible region and are stable under redox conditions. The *meso*-tetraarylporphycenes have tremendous potential for applications in various fields from materials to medicine, and we are currently exploring the possibility to prepare water soluble *meso*-tetraraylporphycenes.

Experimental Section

General Methods: All chemicals that were used in the synthesis were reagent grade, and solvents were dried by routine procedures immediately before use. Column chromatography was performed on silica gel (60–120 mesh). The ^1H and ^{13}C NMR spectroscopic data

were recorded by using $CDCl_3$ as the solvent and tetramethylsilane [$Si(CH_3)_4$] as the internal standard. The fluorescence quantum yields (Φ_f) were estimated from the emission and absorption spectra by using a comparative method at the excitation wavelength of 380 nm with tetraphenylporphycene[7] (Φ_f = 0.23) as the standard. Cyclic voltammetric (CV) studies were carried out by using a three-electrode configuration that consisted of glassy carbon (working electrode), platinum wire (auxiliary electrode), and saturated calomel (SCE, reference electrode) electrodes. The experiments were done in dry CH_2Cl_2 with tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte. Half-wave potentials were measured by DPV (differential pulse voltammetry) and also calculated manually by taking the average of the cathodic and anodic peak potentials. All potentials were calibrated versus a saturated calomel electrode by the addition of ferrocene (Fc) as an internal standard, taking $E_{1/2}$ (Fc/Fc^+) = 0.42 V vs. SCE.[8] The HRMS spectra were recorded by using ESI and a quadrupole analyzer.

X-ray Crystallography Method: Single crystals of suitable size for the X-ray diffractometer were selected under a microscope and mounted on the tip of a glass fiber, which was positioned on a copper pin. The X-ray crystal structure data for compounds **14** and **15** were collected with a Bruker Kappa CCD diffractometer, employing graphite-monochromated Mo-K_α radiation at 200 K and the $\theta - 2\theta$ scan mode. The space groups for compounds **14** and **15** were determined on the basis of systematic absences and intensity statistics, and the structures of compounds **14** and **15** were solved by direct methods using SIR92 or SIR97 and refined with SHELXL-97.[9] An empirical absorption correction by multi-scans was applied. All non-hydrogen atoms were refined by anisotropic displacement factors. Hydrogen atoms were placed in ideal positions and fixed by relative isotropic displacement parameters.

CCDC-990254 (for **15**) and -990255 (for **14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Method for the Synthesis of 5,6-Diaryldipyrroethenes 13–18: Activated zinc powder (35.1 mmol) and copper(I) chloride (1.16 mmol) in THF (80 mL) were combined in a three-neck round-bottomed flask, and the system was purged with nitrogen for 10 min. The mixture was cooled to 0 °C, and $TiCl_4$ (17.55 mmol) was slowly added as the temperature was maintained at 0 °C. The suspension was warmed to room temperature, stirred for 30 min, and then heated at reflux for 3 h. The mixture was once again cooled to 0 °C, and a solution of the appropriate 2-arylated pyrrole **7**–**12** (5.85 mmol) in THF (25 mL) was added slowly. The reaction mixture was heated at reflux for 12 h until the starting material was completely consumed, as monitored by TLC analysis. The reaction mixture was quenched by the addition of a 10% aqueous $NaHCO_3$ solution, and the resulting mixture was extracted with diethyl ether. The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated by using a rotary evaporator under vacuum. The crude compound was purified by chromatography on a silica gel column (petroleum ether/ethyl acetate) to afford the desired 5,6-diaryldipyrroethene **13**–**18** as a light green solid.

Compound 13: (0.94 g, 52% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.09 (br. s, 2 H, NH), 7.09–7.07 (m, 6 H, Ar), 6.93 (d, J = 7.9 Hz, 4 H, Ar), 6.72 [dd, J = 4.1 Hz, J = 1.6 Hz, 2 H, Py (pyrrole)], 6.19 (dd, J = 4.1 Hz, J = 1.6 Hz, 2 H, Py), 5.95 (dd, J = 4.0 Hz, J = 1.5 Hz, 2 H, Py) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 133.1, 131.5, 130.8, 129.6, 129.3, 128.1, 127.6, 126.7, 126.3, 111.9, 110.4, 109.8, 106.6 ppm. HRMS: calcd. for $C_{22}H_{19}N_2$ [M + 1]$^+$ 311.1543; found 311.1551. $C_{22}H_{18}N_2$ (310.40): calcd. C 85.13, H 5.85, N 9.03; found C 85.17, H 5.93, N 9.06.

Compound 14: (1.06 g, 54% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (br. s, 2 H, NH), 6.99 (d, J = 8.3 Hz, 4 H, Ar), 6.89 (d, J = 8.3 Hz, 4 H, Ar), 6.67 (dd, J = 3.8 Hz, J = 1.8 Hz, 2 H, Py), 6.17 (dd, J = 3.8 Hz, J = 1.8 Hz, 2 H, Py), 5.93 (dd, J = 3.9 Hz, J = 1.7 Hz, 2 H, Py), 2.46 (s, 6 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.1, 137.7, 136.5, 133.1, 125.6, 119.3, 112.3, 108.8, 107.3, 36.4 ppm. HRMS: calcd. for $C_{24}H_{23}N_2$ [M + 1]$^+$ 339.1856; found 339.1860. $C_{24}H_{22}N_2$ (338.45): calcd. C 85.17, H 6.55, N 8.28; found C 85.16, H 6.54, N 8.25.

Compound 15: (1.09 g, 51% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (br. s, 2 H, NH), 7.03 (d, J = 8.2 Hz, 4 H, Ar), 6.67 (dd, J = 3.9 Hz, J = 1.5 Hz, 2 H, Py), 6.65 (d, J = 8.2 Hz, 4 H, Ar), 6.15 (dd, J = 3.9 Hz, J = 1.5 Hz, 2 H, Py), 5.94 (dd, J = 3.9 Hz, J = 1.6 Hz, 2 H, Py), 3.74 (s, 6 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.2, 134.8, 133.6, 132.7, 128.4, 118.5, 113.1, 111.6, 108.9, 55.3 ppm. HRMS: calcd. for $C_{24}H_{22}N_2O_2Na$ [M + Na]$^+$ 393.1573; found 393.1578. $C_{24}H_{22}N_2O_2$ (370.45): calcd. C 77.81, H 5.99, N 7.56; found C 77.87, H 6.04, N 7.61.

Compound 16: (1.02 g, 44% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.04 (br. s, 2 H, NH), 7.05 (d, J = 7.5 Hz, 4 H, Ar), 6.89 (d, J = 7.4 Hz, 4 H, Ar), 6.59 (dd, J = 4.2 Hz, J = 1.8 Hz, 2 H, Py), 6.15 (dd, J = 4.2 Hz, J = 1.8 Hz, 2 H, Py), 5.92 (dd, J = 4.1 Hz, J = 1.6 Hz, 2 H, Py) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.57, 133.4, 131.9, 131.1, 130.2, 129.9, 129.1, 128.5, 128.3, 126.2, 120.3, 111.0 ppm. HRMS: calcd. for $C_{22}H_{17}N_4O_4$ [M + 1]$^+$ 401.1253; found 401.1249. $C_{22}H_{16}N_4O_4$ (400.39): calcd. C 66.00, H 4.03, N 13.99; found C 66.09, H 4.12, N 14.06.

Compound 17: (1.21 g, 45% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.08 (br. s, 2 H, NH), 7.13 (d, J = 7.8 Hz, 4 H, Ar), 6.95 (d, J = 7.8 Hz, 4 H, Ar), 6.69 (dd, J = 3.8 Hz, J = 1.7 Hz, 2 H, Py), 6.13 (dd, J = 3.8 Hz, J = 1.7 Hz, 2 H, Py), 5.82 (dd, J = 3.9 Hz, J = 1.8 Hz, 2 H, Py) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.2, 132.5, 132.0, 131.7, 130.9, 130.7, 126.8, 126.3, 120.1, 111.3 ppm. HRMS: calcd. for $C_{22}H_{17}N_2Br_2$ [M + 1]$^+$ 469.9811; found 469.9807. $C_{22}H_{16}Br_2N_2$ (468.19): calcd. C 56.44, H 3.44, N 5.98; found C 56.40, H 3.38, N 5.90.

Compound 18: (0.96 g, 48% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.10 (br. s, 2 H, NH), 7.45 (d, J = 8.1 Hz, 2 H, Ar), 7.33 (d, J = 8.0 Hz, 2 H, Ar), 7.24 (dd, J = 8.1 Hz, J = 1.9 Hz, 2 H, Ar), 7.04 (dd, J = 8.1 Hz, J = 1.8 Hz, 2 H, Ar), 6.70 (d, J = 4.1 Hz, 2 H, Py), 6.18 (d, J = 4.1 Hz, 2 H, Py), 5.92 (d, J = 4.0 Hz, 2 H, Py) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 104.5, 130.9, 130.2, 130.1, 128.3, 124.9, 120.2, 119.0, 118.9, 116.1, 115.9, 111.5 ppm. HRMS: calcd. for $C_{22}H_{17}N_2F_2$ [M + 1]$^+$ 348.1432; found 348.1438. $C_{22}H_{16}F_2N_2$ (346.38): calcd. C 76.29, H 4.66, N 8.09; found C 76.33, H 4.70, N 8.15.

General Procedure for the Synthesis of Tetraarylporphycenes 1–6: 5,6-Diaryldipyrroethene **13**–**18** (0.65 mmol) was dissolved in dry dichloromethane (300 mL) in a 500 mL one-neck round-bottomed flask, and the mixture was stirred under nitrogen for 15 min. The condensation reaction was initiated by the addition of a catalytic amount of *p*-TSA (0.13 mmol), and the reaction mixture was stirred at room temperature for 1.5 h under nitrogen. DDQ (0.65 mmol) was added, and the mixture was stirred at room temperature for an additional 1 h in the air. The solvent was removed under reduced pressure, and the resulting crude compound was purified by chromatography on a silica gel column (petroleum ether/ dichloromethane, 90:10) to afford the desired tetraarylporphycene **1–6** as a purple solid in a yield of 5–7%.

Compound 1: (27 mg, 7% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.43 (d, J = 4.4 Hz, 4 H, Py), 8.43 (d, J = 4.4 Hz, 4 H, Py), 7.72 (d, J = 7.7 Hz, 8 H, Ph), 7.38–7.36 (m, 12 H, Ph), 5.98 (br. s, 2 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.3, 134.7, 127.8, 126.8, 120.2 ppm. UV/Vis ($CHCl_3$): λ_{max} [log(ε/M^{-1} cm^{-1})] = 381 [5.1], 585 [4.1], 624 [4.3], 653 [4.4] nm; λ_{em} = 665, 724 (sh) nm. HRMS: calcd. for $C_{44}H_{31}N_4$ [M + 1]$^+$ 615.2543; found 615.2537. $C_{44}H_{30}N_4$ (614.75): calcd. C 85.97, H 4.92, N 9.11; found C 85.92, H 4.88, N 9.05.

Compound 2: (26 mg, 6% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.42 (d, J = 4.4 Hz, 4 H, Py), 8.44 (d, J = 4.3 Hz, 4 H, Py), 7.61 (d, J = 7.8 Hz, 8 H, Ar), 7.21 (d, J = 7.8 Hz, 8 H, Ar), 6.12 (br. s, 2 H, NH), 2.53 (s, 12 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 137.4, 134.7, 127.5, 120.2, 29.8 ppm. UV/Vis ($CHCl_3$): λ_{max} [log(ε/M^{-1} cm^{-1})] = 383 [5.0], 586 [4.2], 626 [4.4], 654 [4.5] nm; λ_{em} = 668, 725 (sh) nm. HRMS: calcd. for $C_{48}H_{39}N_4$ [M + 1]$^+$ 671.3169; found 671.3172. $C_{48}H_{38}N_4$ (670.86): calcd. C 85.94, H 5.71, N 8.35; found C 85.99, H 5.75, N 8.38.

Compound 3: (28 mg, 6% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.42 (d, J = 4.5 Hz, 4 H, Py), 8.43 (d, J = 4.5 Hz, 4 H, Py), 7.72 (d, J = 7.6 Hz, 8 H, Ar), 7.15 (d, J = 7.6 Hz, 8 H, Ar), 5.99 (br. s, 2 H, NH), 3.90 (s, 12 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7, 135.7, 135.1, 132.1, 124.8, 117.8, 55.4 ppm. UV/Vis ($CHCl_3$): λ_{max} [log(ε/M^{-1} cm^{-1})] = 382 [5.0], 585 [4.1], 624 [4.3], 655 [4.5] nm; λ_{em} = 667, 724 (sh) nm. HRMS: calcd. for $C_{48}H_{39}N_4O_4$ [M + 1]$^+$ 735.2978; found 735.2971. $C_{48}H_{38}N_4O_4$ (734.85): calcd. C 78.45, H 5.21, N 7.62; found C 78.49, H 5.26, N 7.69.

Compound 4: (26 mg, 5% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.48 (d, J = 4.1 Hz, 4 H, Py), 8.48 (d, J = 4.1 Hz, 4 H, Py), 7.61 (d, J = 8.1 Hz, 8 H, Ar), 7.14 (d, J = 8.1 Hz, 8 H, Ar), 5.82 (br. s, 2 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.3, 138.0, 134.4, 128.9, 125.5, 117.7 ppm. UV/Vis ($CHCl_3$): λ_{max} [log(ε/M^{-1} cm^{-1})] = 380 [4.9], 578 [4.0], 619 [4.2], 650 [4.4] nm; λ_{em} = 656, 716 (sh) nm. HRMS: calcd. for $C_{44}H_{27}N_8O_8$ [M + 1]$^+$ 795.1945; found 795.193. $C_{44}H_{26}N_8O_8$ (794.74): calcd. C 66.50, H 3.30, N 14.10; found C 66.42, H 3.20, N 14.07.

Compound 5: (30 mg, 5% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.43 (d, J = 3.9 Hz, 4 H, Py), 8.40 (d, J = 3.9 Hz, 4 H, Py), 7.70 (d, J = 7.8 Hz, 8 H, Ar), 7.16 (d, J = 7.9 Hz, 8 H, Ar), 5.93 (br. s, 2 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8, 139.0, 136.5, 127.7, 124.8, 123.9 ppm. UV/Vis ($CHCl_3$): λ_{max} [log(ε/M^{-1} cm^{-1})] = 379 [4.9], 580 [4.0], 623 [4.2], 653 [4.3] nm; λ_{em} = 660, 720 (sh) nm. HRMS: calcd. for $C_{44}H_{27}N_4Br_4$ [M + 1]$^+$ 930.8926; found 930.8916. $C_{44}H_{26}Br_4N_4$ (930.33): calcd. C 56.81, H 2.82, N 6.02; found C 56.90, H 2.93, N 6.10.

Compound 6: (27 mg, 6% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.48 (d, J = 4.2 Hz, 4 H, Py), 8.49 (d, J = 4.2 Hz, 4 H, Py), 7.55–7.32 (m, 12 H, Ar), 7.16–7.14 (m, 4 H, Ar), 5.82 (br. s, 2 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.4, 141.1, 135.9, 135.1, 129.2, 127.9, 127.3, 117.8 ppm. UV/Vis ($CHCl_3$): λ_{max} [log(ε/M^{-1} cm^{-1})] = 380 [5.0], 580 [4.1], 621 [4.3], 650 [4.4] nm; λ_{em} = 658, 717 (sh) nm. HRMS: calcd. for $C_{44}H_{27}N_4F_4$ [M + 1]$^+$ 687.2166; found 687.2159. $C_{44}H_{26}F_4N_4$ (686.71): calcd. C 76.96, H 3.82, N 8.16; found C 76.90, H 3.77, N 8.09.

Supporting Information (see footnote on the first page of this article): The characterization data including HR-MS, ^{1}H NMR, ^{13}C NMR for all the compounds, and spectral and electrochemical data for selected compounds.

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