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SYNTHESIS, PROPERTIES AND CRYSTAL STRUCTURES OF 2,7,12,17-TETRAARYLPORPHYCENES

Daiki Kuzuhara,[a] Haruka Nakaoka,[a] Takuya Okabe,[a] Naoki Aratani,[a] and Hiroko Yamada[a,b]

[a] Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama-cho, Ikoma 630-0192, Japan. [b] CREST, Japan Science and Technology (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Abstract – We have synthesized 2,7,12,17-tetraarylporphycenes, which have phenyl (**7a**), *p*-trifluoromethylphenyl (**7b**) or *p*-methoxyphenyl (**7c**) groups, by McMurry coupling. The crystal structures revealed that **7a** formed a herringbone-type arrangement, while **7b** formed a slip-stacked structure with π-π stacking. The reduction potentials of these porphycenes depend on the attached aryl groups: –1.02 V (vs. ferrocene/ferrocenium cation) for **7b** (Ar = p-$C_6H_4CF_3$), –1.17 V for **7a** (Ar = Ph) and –1.23 V for **7c** (Ar = p-C_6H_4OMe), which are close to that of $PC_{61}BM$ (E_{red} = –1.08 V). These porphycenes, thus, are expected to behave as n-type semiconducting materials in OTFT and OPV devices.

INTRODUCTION

Porphycene, a constitutional isomer of porphyrin, has two directly-linked bipyrrole units connected by two ethylene bridges.[1] Compared with porphyrin, porphycene is more chemically stable because of removal of the highly reactive methine carbons and has a stabilized lowest unoccupied molecular orbital (LUMO) by dissolving the degeneracy of LUMO and LUMO+1 levels.[2] Therefore, the highest occupied molecular orbital (HOMO)–LUMO difference of porphycene is smaller than that of porphyrin, which results in the intense and red-shifted visible/near infrared (NIR) absorption and NIR fluorescence of porphycene. These unique optical and electronic properties are suitable for photodynamic therapy (PDT),[3] non-linear optics[4] and protein mimic systems.[5] We have succeeded in the preparation of tetrabenzoporphycenes (TBPc) from thermal-convertible precursors of bicyclo[2.2.2]octadiene (BCOD)-fused porphycene by retro Diels-Alder reaction under heating conditions.[6] TBPc is a constitutional isomer of tetrabenzoporphyrin, which is known as an excellent organic semiconducting material for organic thin-film transistors (OTFTs) and organic photovoltaics (OPVs).[7] We have fabricated p–n type devices consisting of the TBPc as the p-layer and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) as the n-layer by a solution process and the power-conversion efficiency was 1.49%.[7a] Recently, we reported the synthesis of porphycene–diketopyrrolopyrrole conjugates which showed intense Q-bands in the NIR regions, indicating an electronic interaction between porphycene and diketopyrrolopyrrole moieties.[8] From these results, we expect that porphycenes were attractive organic functional dyes for OTFT and OPV, in which the porphycene with the low-lying LUMO level could be used as n-type semiconducting materials for OTFT and OPV devices. In particular, non-fullerene n-type materials are strongly required for OPV devices. In this context, Jux and Guldi have used porphycene derivatives used as electron acceptor in the composites of graphene oxide and nano-graphene to generate a photocurrent.[9] In the OTFT and OPV, the molecular packing and electronic properties of compounds directly influence the device performances. To date various 2,7,12,17-tetraarylporphycenes and their metal complexes have been reported,[10,11] and their photophysical properties were well investigated to be applied to PDT as photosensitizer.[12] However their crystal structures and the systematic substitution effects of aryl groups at *para*-position have been rarely investigated sufficiently. Herein, we describe the synthesis, crystal structures and electronic properties of a series of 2,7,12,17-tetraarylporphycenes with phenyl (**7a**), *p*-trifluorophenyl (**7b**) and *p*-methoxyphenyl (**7c**) groups, as candidates for new n-type semiconducting materials.

RESULTS AND DISCUSSION

2,7,12,17-Tetraphenylporphycene **7a** was prepared according to the previously reported method.[10] The synthetic route of 2,7,12,17-tetraaryporphycenes **7b** and **7c** is shown in Scheme 1. Diethyl 3-arylpyrrole-2,4-dicarboxylates **2b** and **2c** were synthesized from 4-trifluoromethylbenzaldehyde **1b** and anisaldehyde **1c** with ethyl isocyanate in 17% and 42% yields, respectively.[13] Iodination of **2b** and **2c** at the pyrrolic α-position was performed with iodine and HIO_3 in 1,2-dichloroethane under reflux conditions.[6a] In the case of **2b**, iodination reaction smoothly proceeded to give **3b** in 88% yield. When **2c** was reacted under the same conditions, the yield of **3c** was decreased to 66%, while iodination occurred at the pyrrolic α-position as well as the anisole moiety to give diiodo product **3c-I** in 17% yield as a byproduct. The anisole moiety is well known to provide iodinated products by similar iodination conditions.[14] The structure of **3c-I** was confirmed by X-ray diffraction analysis (Figure 1).

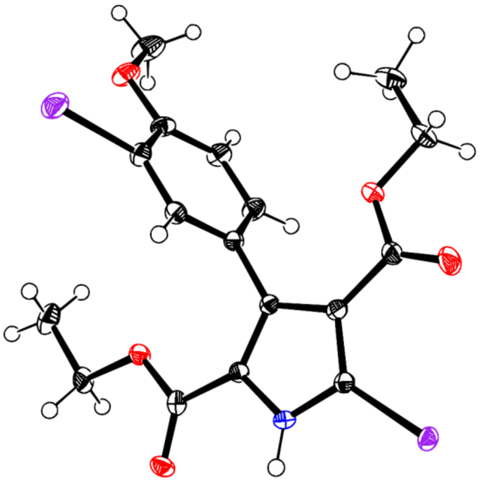
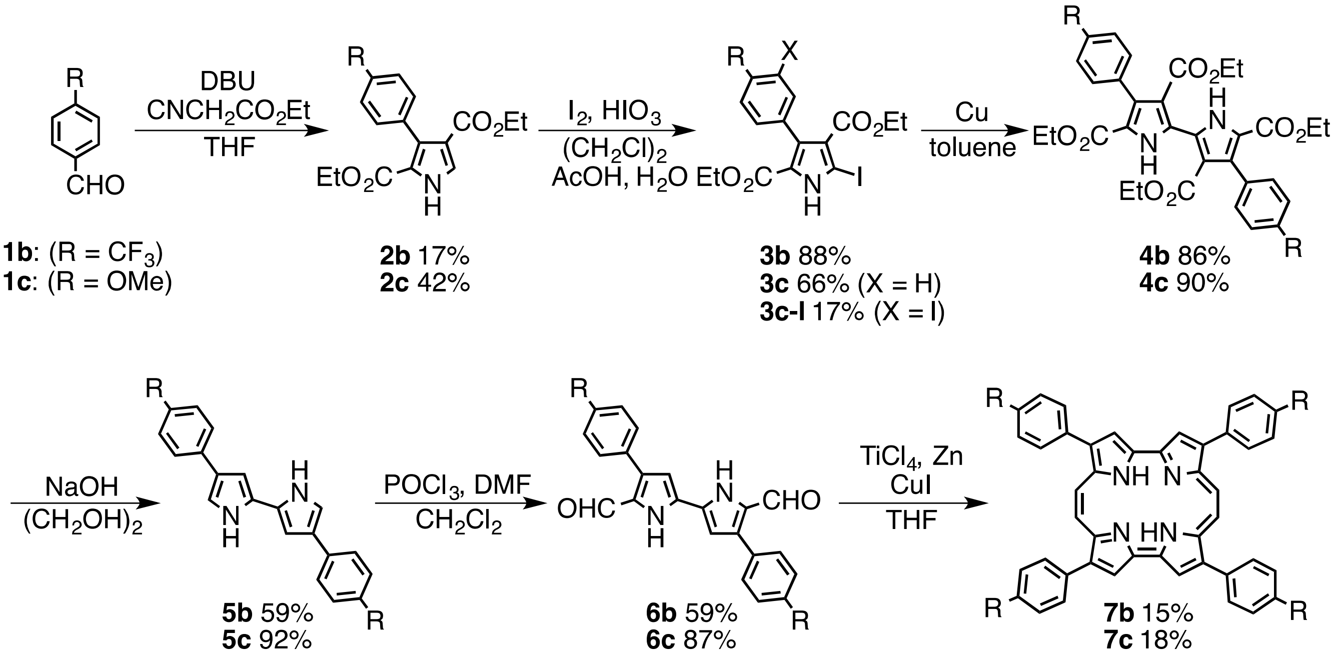


Figure 1. Crystal structure of **3c-I**. Thermal ellipsoids represent 50% probability

Subsequently, Ullmann coupling of **3b** and **3c** afforded 2,2'-bipyrroles **4b** and **4c** in 86% and 90% yields, respectively. Decarboxylation and formylation by Vilsmeier–Haack reaction gave 5,5-diformyl-2,2'-bipyrroles **6b** and **6c**, respectively. A McMurry coupling of **6b** and **6c** resulted in the formation of porphycenes **7b** and **7c** in 15% and 18% yields, respectively. These compounds were characterized by ^{1}H-NMR spectroscopy, high-resolution MS spectrometry and X-ray diffraction analysis.



Scheme 1. Synthetic scheme of porphycenes **7b** and **7c**

In the ^{1}H-NMR spectra of **7b** and **7c**, the signals of pyrrolic β-protons were observed at 9.78 and 9.63 ppm as singlet peaks, and the N-H protons were observed at 3.92 ppm and 3.77 ppm. In general, the signals of N-H protons of porphyrins appear in the range of –2 to –5 ppm due to the effect of a strong diatropic ring current of porphyrin macrocycles. Despite the same 18 π-electron structure, the N-H protons of porphycenes is drastically downfield shifted compared to those of porphyrins because the NH•••N distances in the porphycene cavities are shorter than those of porphyrins and therefore NH protons of porphycenes form stronger hydrogen-bonding interactions with neighboring nitrogen atoms.

Single crystals of **7a** and **7b** suitable for X-ray diffraction analysis were obtained by vapor slow diffusion of 2-propanol into chlorobenzene solution (Figure 2). The crystal structures of **7a** and **7b** show a highly planar macrocyclic structure of porphycene core with mean plane deviation with respect to the macrocyclic atoms of 0.04 Å for **7a** and 0.05 Å for **7b**. The N-N distances are 2.635(3) and 2.843(2) Å for **7a**, and 2.612(3), 2.608(3), 2.863(3) and 2.865(3) Å for **7c**. These distances are similar to those of 2,7,12,17-tetrapropylporphycene at 2.831 and 2.615 Å.[15] The dihedral angles between the porphycene macrocycle and attached aryl groups are 32.98° and 47.82° for **7a** and 28.3°, 33.6°, 37.9° and 45.5° for **7b**. These angles are totally different from the 5,10,15,20-tetraarylporphyrins (TPP).[16] The aryl groups of TPP are positioned almost perpendicular because of steric hindrance between aryl groups and the porphyrin macrocycle. Similarly, 9,10,19,20-tetraphenylporphycene shows the aryl groups positioned perpendicular, where dihedral angles of phenyl groups and porphycene macrocycle are 79° and 90°.[17] On the other hand, in the case of β-aryl porphyrins, the dihedral angles between the β-aryl-groups and porphyrin were reported as 46-53°.[18] The distances between phenyl-carbon and porphycene-carbons are 1.47 Å (ave.) for both **7a** and **7b** which are shorter than those of TPP and 9,10,19,20-tetraphenylporphycene (1.50 Å). These structural features indicate that despite the introduction of the aryl groups at the 2,7,12,17-positions, high planarity is retained and the aryl groups exhibit effective conjugation to porphycene macrocycles. The crystal packing of **7a** shows a herringbone type arrangement. The intermolecular distance of each porphycene planes is 3.409 Å which is slightly shorter than sum of van der Waals radii of carbon atoms. On the other hand, porphycene **7b** is packed as a slip-stack structure. We found that the change of the crystal structures of **7b** from **7a** was induced by the C–F•••F–C interactions of the trifluorobenzene moieties between neighboring molecules.[19] The alternate face-to-face distances of molecules are 3.308 Å and 3.357 Å which distances decreased from that of **7a** by the introduction of the CF_3 moieties. This means that the introduction of the substituents at the *para*-positions of the phenyl moieties could be control of the crystal structures of the porphycenes. In addition, these herringbone and slip stacked structures might introduce good semiconducting properties as OTFT and OPV to **7a** and **7b**.

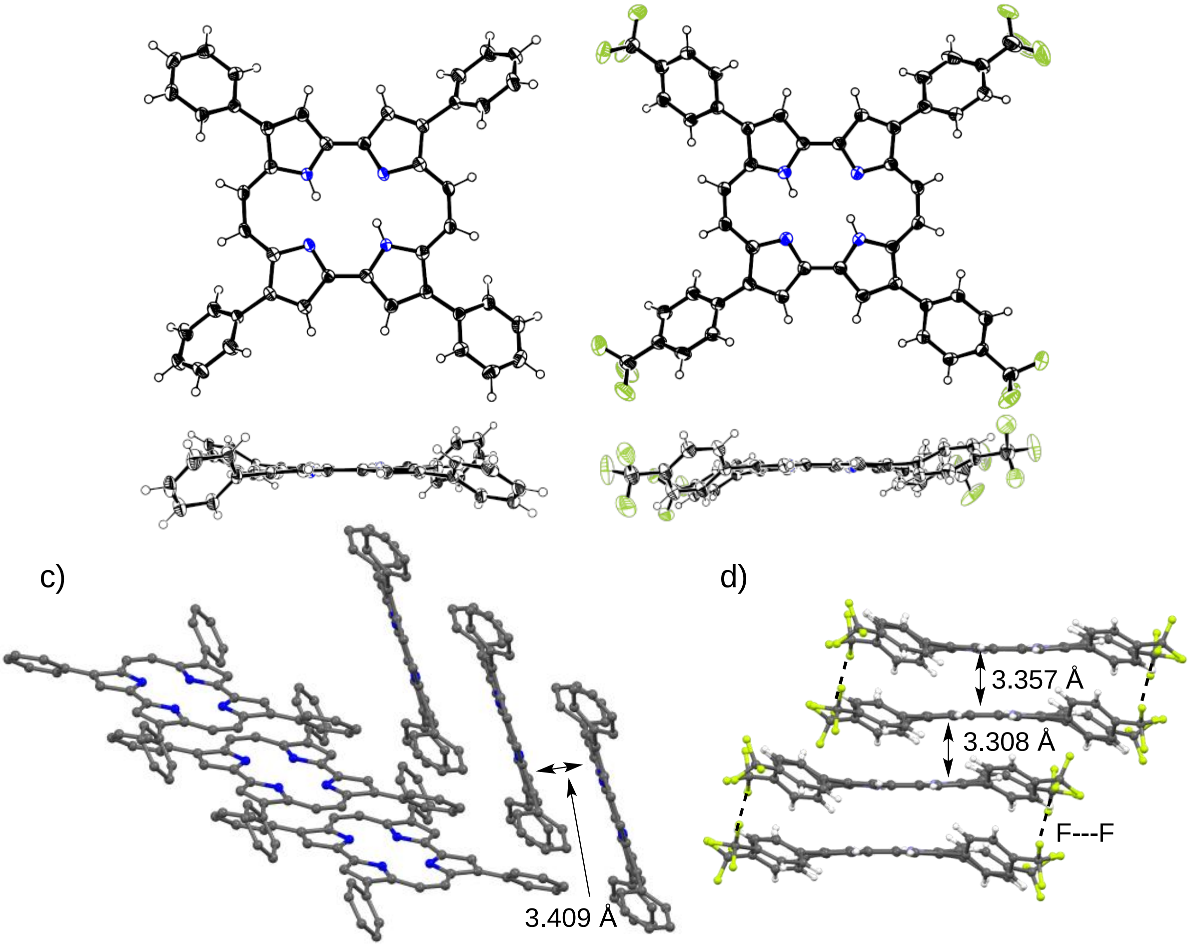


Figure 2. X-Ray crystal structures: a) top and side views of **7a**, b) top and side views of **7b**, c) packing structure of **7a** and e) packing structure of **7b**. Thermal ellipsoids represent 50% probability for a) and b). The hydrogen atoms are omitted for clarity for c).

The absorption spectra of **7a**, **7b** and **7c** in CH_2Cl_2 are shown in Figure 3. The absorbance peaks of **7a** were observed at 376 nm and 392 nm as split Soret bands, and 584, 625 and 656 nm as Q-bands. The absorption shape of **7b** was similar to **7a** and the peak tops are slightly red-shifted by 2 nm at the Soret and Q-bands. On the other hand, the Soret band of **7c** became one broad peak at 380 nm and Q-bands appear at 591, 632 and 662 nm. The fluorescence spectra of **7a** and **7b** in CH_2Cl_2 were observed at 669 and 732 nm, and 670 and 730 nm with fluorescence quantum efficiencies (Φ_{em}) of 19% and 26%, respectively. The Stokes shifts were 13 nm for **7a** and 12 nm for **7b**. On the other hand, the fluorescence of **7c** was largely quenched. The fluorescence peaks were observed at 681 and 739 nm and fluorescence quantum efficiency was only 4%. The Stokes shift of **7c** was 19 nm, which was slightly bigger than that of **7a** and **7b**. The fluorescence lifetimes of **7a**, **7b** and **7c** were measured by the time correlated single photon counting method. All compounds exhibited the single exponential decay. Fluorescence lifetimes of **7a** and **7b** were 3.38 and 4.31 ns, respectively, while the fluorescence lifetime of **7c** was decreased to 0.72

ns. These results revealed that the optical properties of **7a** and **7b** were very similar, indicating little influence of the electron-withdrawing *p*-trifluorophenyl moiety on the absorption and emission properties of porphycene. In contrast, the *p*-methoxyphenyl group clearly affected the optical properties. Nonell has reported that *meta*-tetrahydroxyphenyl-porphycene has a 2.3 ns fluorescence lifetime and 8.4% fluorescence quantum yield in THF.[20] These results indicate that fluorescence quenching of **7c** may be ascribed to introductions of the electron-rich substituents at the *para*-positions. Therefore, the possible reason of the fluorescent quenching of **7c** is the formation of the charge-transfer structures, although the substitutional effects of the electron donating groups are not clear.

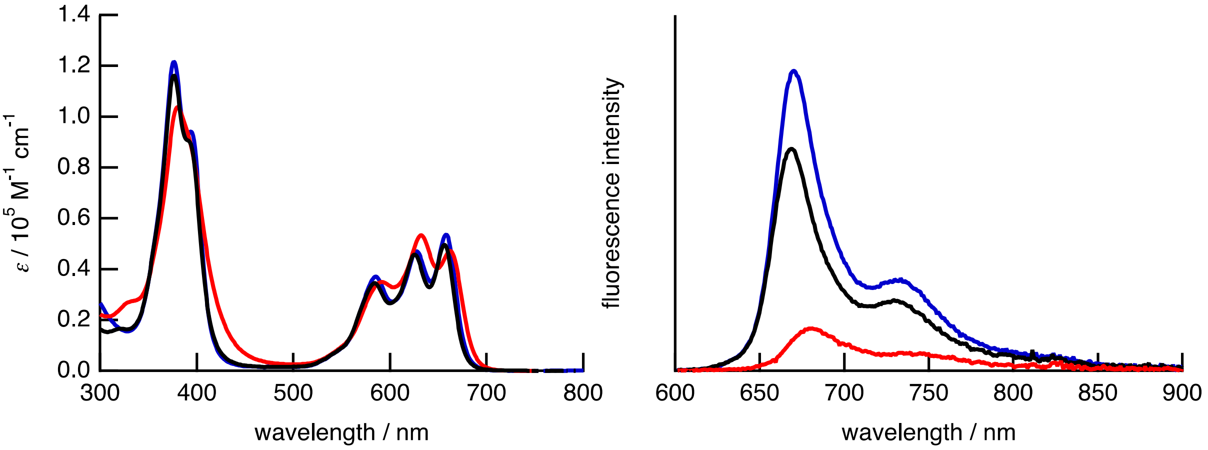


Figure 3. Absorption (left) and fluorescence (right) spectra of porphycenes **7a** (black), **7b** (blue) and **7c** (red) in CH_2Cl_2. Fluorescence spectra were excited at Soret bands.

To investigate the electrochemical properties of **7a**, **7b** and **7c**, cyclic voltammetry was measured in benzonitrile containing 0.1 M *n*Bu_4NPF_6 as electrolyte at room temperature (Figure 4). All porphycenes showed one reversible oxidation and two reversible reductions in the voltage range of -1.7 to +1.0. The first reductive potentials were negative-shifted depending on the electronic nature of the arylsubstituents: -1.02 V (vs ferrocene/ferrocenium cation) for **7b** (Ar = *p*-$C_6H_4CF_3$), -1.17 V for **7a** (Ar = Ph) and -1.23 V for **7c** (Ar = *p*-C_6H_4OMe). The oxidation potential was also shifted by the effect of the attached aryl groups. These results indicated that the electronic properties of the porphycenes could be tuned by introducing substituents on the aryl groups. In addition, these reduction potentials are comparable to the typical n-type semiconductor $PC_{61}BM$ (E_{red} = -1.08 eV).[21] The LUMO levels of **7b**, **7a** and **7c** are estimated from the reduction potentials as 3.78, 3.63 and 3.57 eV by the ferrocene standard (4.8 eV). With these characteristics, **7a** and **7b** are expected to behave as the n-type semiconducting materials for OTFT and OPV.

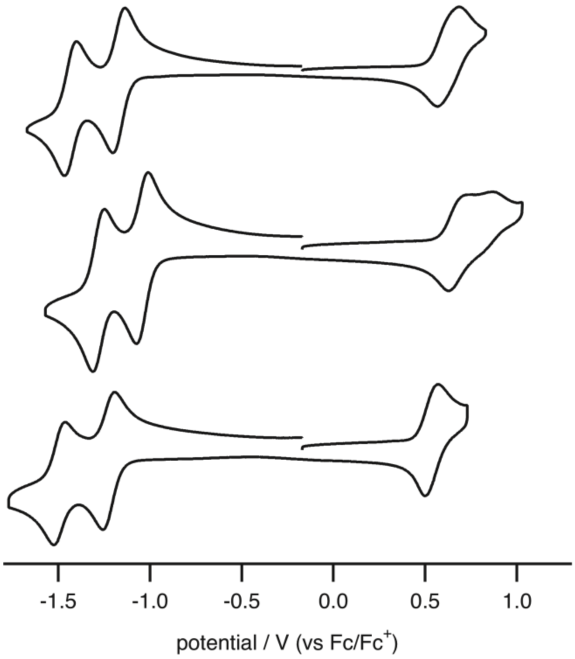


Figure 4. Cyclic voltammograms of porphycenes **7a** (top), **7b** (middle) and **7c** (bottom) in benzonitrile containing 0.1 M $n\mathrm{Bu_4NPF_6}$, scan rate 100 mV s^{-1}.

Table 1. Optical and electronic properties of porphycenes **7a**, **7b** and **7c**

	λ_{abs} / nm [a]	λ_{em} / nm [a,b]	Φ_{em} [a, b]	τ_{em} / ns [a, c]	E_{ox} / V [d]	E_{red} / V [d]	HOMO / eV [e]	LUMO / eV [e]
7a	376, 392, 584, 625, 656	669, 732	0.19	3.38	0.63	–1.17, –1.43	5.43	3.63
7b	376, 394, 585, 627, 658	670, 730	0.26	4.31	0.65	–1.02, –1.26	5.45	3.78
7c	380, 591, 632, 662	681, 739	0.04	0.72	0.54	–1.23, –1.49	5.34	3.57

[a] in $\mathrm{CH_2Cl_2}$. [b] excited at Soret bands. [c] excited at 384 nm, [d] Potential values were measured by cyclic voltammetry in benzonitrile with 0.1 M $n\mathrm{Bu_4NPF_6}$. The ferrocene/ferrocenium cation redox couple was used as the internal standard. Scan rate = 100 mV s^{-1}. [porphycene] = 1.0 mM. Working electrode: glassy carbon. Counter electrode: Pt wire. Reference electrode: $\mathrm{Ag/AgNO_3}$. [e] HOMO and LUMO energy levels were estimated from equations; HOMO = $-(4.8 + E_{\mathrm{ox}})$ and LUMO = $-(4.8 + E_{\mathrm{red}})$.

In summary, we have succeeded in the preparation of 2,7,12,17-tetraarylporphycenes **7b** and **7c** with an electron-withdrawing trifluoromethyl group and an electron-donating methoxy group, respectively. The crystal structures of **7a** and **7b** showed highly planar structures with small dihedral angles between attached aryl groups and the macrocycles. This leads to the formation of π-π stacking with intramolecular distances within the van der Waals radii. The electrochemical properties of **7a**, **7b** and **7c** indicated the low-lying LUMO levels were close to the $\mathrm{PC_{61}BM}$. These properties show the potential of the porphycenes to be applied to n-type organic electronics materials. The fabrication of OTFT and OPV devices with these porphycenes is now underway.

EXPERIMENTAL

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JNM-ECX 400 and JNM-Al 300 spectrometers using tetramethylsilane as an internal standard. ESI mass spectra were recorded on a JEOL JMS-MS T100LC spectrometer. EI mass spectra recorded on a JEOL JMS 700. UV-vis absorption spectra were recorded on a JASCO UV/VIS/NIR Spectrophotometer V-670. Fluorescence spectra and fluorescence quantum yields were obtained on a Hamamatsu Absolute PL Quantum Yield Measurement System C9920-02. CV and DPV measurements were conducted in a solution of 0.1 M nBu$_4$NPF$_6$ in dry benzonitrile at room temperature in an argon-filled cell. Scan rate was 100 mV s^{-1}. A glassy carbon electrode and a Pt wire were used as working and counter electrodes, respectively. An Ag/AgNO$_3$ electrode was used as a reference electrode, which was normalized with the half-wave potential of ferrocene/ferrocenium cation (Fc/Fc$^+$) redox couple. TLC and gravity column chromatography were performed on Art. 5554 (Merck KGaA) plates and silica gel 60N (Kanto Chemical), respectively. All solvents and chemicals were reagent-grade quality, obtained commercially, and used without further purification except as noted. For spectral measurements, spectral-grade dichloromethane was purchased from Nacalai Tesque. The dry-benzonitrile was prepared by vacuum distillation with P$_2$O$_5$. X-Ray crystallographic data were recorded at 100 K on a Rigaku CCD detector (Saturn 724) mounted on a Rigaku rotating anode X−ray generator (MicroMax−007HF) using Mo−Kα radiation from the corresponding set of confocal optics. The diffraction data were processed with CrystalClear on a Rigaku program and the structures were solved by direct methods and refined on F^2 by full−matrix least−squares using the CrystalStructure and SHELXL-97.[22] CCDC: 1016106, 1016105 and 1016104 contain supplementary crystallographic data for **3c-I**, **7a** and **7b** respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.Diethyl

Diethyl 3-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-2,4-dicarboxylate (2b)

To a solution of ethyl isocyanoacetate (10.9 mL, 100 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (14.9 mL, 100 mmol) in THF (150 mL) was added dropwise a solution of *p*-trifluoromethylbenzaldehyde (6.7 mL, 50 mmol) in THF (50 mL) at 50 ºC under an argon atmosphere. After stirring for 10 h at the same temperature, the reaction was quenched with 1 M HCl. After the removal of the solvent, the residue was extracted with EtOAc. The extract was washed with water and brine, and then dried over Na$_2$SO$_4$. The crude product was purified by silica gel column chromatography (EtOAc:hexane = 3:7). Recrystallization from CHCl$_3$/hexane gave **2b** as an off-white solid. Yield: 18% (3.1 g, 8.8 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 9.80$ (brs, 1 H), 7.60 (AA'BB', 2H), 7.60 (d, 2H, $J =$ 3.7 Hz, pyrrolic α-H), 7.44 (AA'BB', 2 H), 4.15-4.09 (q+q, 2H+2H, -CO$_2$Et), 1.11 (t, 3H, $J = 7.3$ Hz, -CO$_2$Et), 1.04 (t, 3H, $J = 7.3$ Hz, -CO$_2$Et); ^{13}C NMR (100 MHz, CDCl$_3$) $\delta = 163.70$, 160.83, 137.97, 130.78, 130.67, 129.31 (q, $J = 33$ Hz), 127.10, 124.50 (q, $J = 271$ Hz, CF$_3$), 124.00 (q, $J = 4$ Hz), 121.26, 117.25, 60.90, 60.08, 14.04, 13.83; HRMS (ESI): *m/z* = 378.0929. calcd. for $C_{17}H_{16}F_3NO_4Na$: 378.0929 $[M+Na]^+$.

Diethyl 5-iodo-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-2,4-dicarboxylate (3b)

A mixture of **2b** (3.0 g, 8.4 mmol), iodine (2.3 g, 9.3 mmol), HIO_3 (0.37 g, 2.1 mmol), AcOH (10 mL) and H_2O (1.5 mL) in 1,2-dichloroethane (25 mL) was refluxed for 10 h. After cooling to room temperature, the reaction was quenched with an aqueous $NaHSO_3$. The separated organic layer was washed with water, saturated aqueous $NaHCO_3$ and brine, and then dried over Na_2SO_4. The crude product was recrystallized from $CHCl_3$/hexane to give **3b** as a colorless needle. Yield: 88% (3.6 g, 7.4 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ = 9.93 (brs, 1 H,), 7.59 (AA'BB', 2H), 7.36 (AA'BB', 2H), 4.13 (q, 2H, J = 7.3 Hz, $-CO_2Et$), 4.05 (q, 2H, J = 7.3 Hz, $-CO_2Et$), 1.02 (t, 3H, J = 7.3 Hz, $-CO_2Et$), 0.96 (t, 3H, J = 7.3 Hz, $-CO_2Et$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.88, 159.91, 138.22, 131.73, 130.33, 129.50 (q, J = 33 Hz), 125.25, 124.42 (q, J = 271 Hz, CF_3), 124.08 (q, J = 4 Hz), 120.95, 78.03, 61.44, 60.88, 13.86, 12.94; HRMS (ESI): *m/z* = 503.9896. calcd. for $C_{17}H_{15}F_3NO_4$ Na: 503.9895 $[M+Na]^+$.

Tetraethyl 4,4'-bis(4-(trifluoromethyl)phenyl)-1*H*,1'*H*-[2,2'-bipyrrole]-3,3',5,5'-tetracarboxylate (4b)

A mixture of **3b** (3.4 g, 7.0 mmol) and copper powder (3.0 g) in toluene (20 mL) was refluxed for 12 h under an argon atmosphere. After cooling to room temperature, the precipitate was filtrated off on Celite pad and washed well with toluene. The filtrate was concentrated under a reduced pressure. The crude product was recrystallized from CH_2Cl_2/hexane to give **4b** as white solids. Yield: 90% (2.2 g, 3.2 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ = 14.40 (brs, 2H, -NH), 7.63 (AA'BB', 4H), 7.39 (AA'BB', 4H), 4.17 (q, 4H, J = 7.3 Hz, $-CO_2Et$), 4.03 (q, 4H, J = 7.3 Hz, $-CO_2Et$), 1.01 (t, 6H, J = 7.3 Hz, $-CO_2Et$), 0.73 (t, 6H, J = 7.3 Hz, $-CO_2Et$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.29, 160.15, 139.84, 132.89, 130.14, 129.43, 129.26 (q, J = 33 Hz, $-CF_3$), 124.50 (q, J = 271 Hz, CF_3), 124.14 (q, J = 4 Hz), 120.75, 113.94, 61.25, 60.40, 13.80, 13.60; HRMS (ESI): *m/z* = 731.1804. calcd. for $C_{34}H_{30}F_3N_2O_8Na$: 731.1804 $[M+Na]^+$.

4,4'-Bis(4-(trifluoromethyl)phenyl)-2,2'-bipyrrole (5b)

A mixture of **4b** (2.12 g, 3.0 mmol) and NaOH (0.6 g, 15 mmol) in ethylene glycol (35 mL) was heated to 170 ºC for 1.5 h under an argon atmosphere. After cooling to room temperature, the reaction mixture was diluted with water. The appeared precipitate was corrected by filtration and washed with water to give desired product **5b** (0.54 g) as white solids. The filtrate was extracted with $CHCl_3$ and the combined organic layer was washed with water and brine, and then dried over Na_2SO_4. After removal of the solvent, the crude product was recrystallization from CH_2Cl_2/hexane to give **5b** as gray solids. Total yield was 59% (0.74 g, 1.77 mmol). ^1H NMR (400 MHz, DMSO-d_6) δ = 11.39 (brs, 2H, -NH), 7.71 (AA'BB', 4H), 7.62 (AA'BB', 4H), 7.39 (m, 2H), 6.75 (m, 2H). ^{13}C NMR spectrum was not recorded because of poor solubility; HRMS (EI): *m/z* = 420.1061. calcd for $C_{22}H_{14}F_6N_2$: 420.1046 $[M]^+$.

4,4'-Bis(4-(trifluoromethyl)phenyl)-1*H*,1'*H*-[2,2'-bipyrrole]-5,5'-dicarbaldehyde (6b)

To a solution of bipyrrole **5b** (0.42 g, 1.0 mmol) and DMF (5.0 mL) in CH_2Cl_2 (15 mL) was slowly added $POCl_3$ (0.37 mL, 4.0 mmol) at room temperature under an argon atmosphere. The reaction mixture was refluxed for 2 h. After cooling to room temperature, aqueous NaOAc was carefully added. The resulting mixture was refluxed for another 1 h. The organic layer was separated and the solvent was concentrated under a reduced pressure. The crude product was rinsed with MeOH to give **6b** as greenish yellow solids. Yield: 93% (0.44 g, 0.93 mmol). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ = 12.61 (brs, 2H, NH-), 9.67 (s, 2H, -CHO), 8.04 (AA'BB', 4H), 7.74 (AA'BB', 4H), 7.20 (s, 2H). ^{13}C NMR spectrum was not recorded because of poor solubility; HRMS (EI): *m/z* = 476.0959. calcd for $C_{24}H_{14}F_6N_2O_2$: 476.0956 $[M]^+$.

2,7,12,17-Tetra(*p*-trifluoromethylphenyl)-porphycene (7b)

$TiCl_4$ (2.0 mL, 18 mmol) was added dropwise to a THF (75 mL) solution containing Zn dust (2.46 g) and CuCl (0.15 g, 1.5 mmol) at room temperature under an argon atmosphere, and then the mixture was refluxed for 2 h. Subsequently a solution of **6b** (357 mg, 0.75 mmol) in THF (100 mL) was added dropwise to the boiling reaction mixture. The mixture was stirred at same temperature for another 1 h. After cooling to 0 ºC, an aqueous 10% K_2CO_3 solution (200 mL) was added dropwise. The precipitate was filtrated off with Celite pad and was washed with $CHCl_3$. The combined organic layer was then dried with Na_2SO_4, and the solution was removed under a reduced pressure. The crude product was purified by alumina column chromatography ($CHCl_3$) and then silica gel column chromatography (CH_2Cl_2). Recrystallization from CH_2Cl_2/MeOH provided **7b** as a purple powder. Yield: 15% (49 mg, 0.055 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.92 (s, 4H, *meso*), 9.78 (s, 4H, β), 8.47-8.44 (AA'BB', 8H), 8.11-8.08 (AA'BB', 8H), 3.92 (brs, 2H, -NH); ^{13}C NMR spectrum was not recorded because of poor solubility; HRMS (MALDI-TOF) : *m/z* = 887.2026. calcd for $C_{48}H_{27}N_4F_{12}$: 887.2039 $[M + H]^+$.

Diethyl 3-(4-methoxyphenyl)-1*H*-pyrrole-2,4-dicarboxylate (2c)

To a solution of ethyl isocyanoacetate (10.9 mL, 100 mmol) and DBU (14.9 mL, 100 mmol) in THF (150 mL) was added dropwise a solution of 4-anisaldehyde **1c** (6.0 mL, 49.6 mmol) in THF (50 mL) at 60 ºC under an argon atmosphere. After stirring for 4 h at the same temperature, the reaction was quenched with 1 M HCl (100 mL). After removal of the solvent, the residue was extracted with EtOAc. The extract was washed with 1 M HCl, water and brine, and then dried over Na_2SO_4. After removal of the solvent, the crude product was purified by silica gel column chromatography (CH_2Cl_2) to give **2c** as yellow viscous oil. Yield: 33% (5.19 g, 16.4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.05 (brs, 1H, -NH), 7.54 (d, 1H, *J* = 3.1 Hz, pyrrolic α-H), 7.28 (AA'BB', 2H), 6.99 (AA'BB', 2H), 4.18-4.12 (q+q, 2H+2H, $-CO_2Et$), 3.83 (s, 3H, -OMe), 1.17 (t, 3H, *J* = 7.3 Hz, $-CO_2Et$), 1.10 (t, 3H, *J* = 7.3 Hz, $-CO_2Et$); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.14, 161.31, 158.89, 132.44, 131.53, 127.38, 125.89, 120.91, 116.87, 112.54, 60.64, 59.87, 55.28, 14.26, 14.07; HRMS (ESI): *m/z* = 340.11609. calcd. for $C_{17}H_{19}NO_5Na$: 340.11724 $[M+Na]^+$.

Diethyl 5-iodo-3-(4-methoxyphenyl)-1*H*-pyrrole-2,4-dicarboxylate (3c)

A solution of **2c** (5.60 g, 17.7 mmol), iodine (4.50 g, 17.7 mmol), HIO_3 (0.82 g, 4.65 mmol), AcOH (23 mL) and H_2O (3.0 mL) in 1,2-dichloroethane (56 mL) was refluxed for 18 h. After cooling to room temperature, the reaction was quenched with aqueous $NaHSO_3$. The separated organic layer was washed with water, saturated aqueous $NaHCO_3$ and brine, and then dried over Na_2SO_4. The solution was removed under a reduced pressure. The crude product was purified by silica gel column chromatography (CH_2Cl_2). As a result, the crude product was isolated to **3c** and **3c-II**. Finally, **2c** and **2c-I** were recrystallized from $CHCl_3$/hexane, respectively.

3c: Yield: 62% (4.85 g, 10.9 mmol); ^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.88 (brs, 1H, -NH), 7.09 (AA’BB’, 2H), 6.86 (AA’BB’, 2H), 4.00 (q, 2H, J = 7.3 Hz, -CO_2Et), 3.92 (q, 2H, J = 7.3 Hz, -CO_2Et), 3.76 (s, 3H, -OCH_3), 1.1 (t, 3H, J = 7.3 Hz, -CO_2Et), 0.92 (t, 3H, J = 7.3 Hz, -CO_2Et); ^{13}C NMR (100 MHz, DMSO-d_6) δ =163.58, 159.77, 158.80, 132.95, 131.61, 126.68, 124.61, 120.85, 112.82, 81.94, 60.27, 59.89, 55.56, 14.39, 14.22; HRMS (ESI): m/z = 466.01273. calcd. for $C_{17}H_{18}NO_5Na$: 466.0.1230 $[M+Na]^+$.

3c-I: yield: 17% (1.76 g, 3.1 mmol), ^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.97 (brs, 1H, -NH-), 7.57 (m, 1H), 7.17 (m, 1H), 6.94 (m, 1H), 4.06 (q, 2H, J = 7.3 Hz, -CO_2Et), 3.98 (q, 2H, J = 7.3 Hz, -CO_2Et), 3.84 (s, 3H, -OMe), 1.07 (t, 3H, J = 7.3 Hz, -CO_2Et), 0.99 (t, 3H, J = 7.3 Hz, -CO_2Et); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 163.37, 159.70, 157.26, 140.71, 132.04, 131.19, 128.79, 124.81, 120.48, 110.40, 84.60, 82.48, 60.41, 59.96, 56.91, 14.45, 14.31; HRMS (ESI): m/z = 591.90938. calcd. for $C_{17}H_{17}I_2NO_5Na$: 591.91051 $[M+Na]^+$. CCDC No.

Tetraethyl 4,4'-bis(4-methoxyphenyl)-1*H*,1'*H*-[2,2'-bipyrrole]-3,3',5,5'-tetracarboxylate (4c)

A mixture of **3c** (4.51 g, 10.2 mmol) and Cu (4.33 g) in toluene (21 mL) was refluxed for 20 h under an argon atmosphere. The precipitate was filtered off on Celite pad and washed with CH_2Cl_2. The filtrate was concentrated under a reduced pressure. The crude product was purified by silica gel column chromatography (CH_2Cl_2) and recrystallization from CH_2Cl_2/MeOH to give **4c** as white solids. Yield: 90% (2.90 g, 4.59 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 14.00 (brs, 2H, -NH), 7.17 (AA’BB’, 4H), 6.89 (AA’BB’, 4H), 4.15 (q, 4H, J = 7.3 Hz, -CO_2Et), 4.04 (q, 4H, J = 7.3 Hz, -CO_2Et), 3.83 (s, 6H, -OMe), 1.14 (t, 6H, J = 7.3 Hz, -CO_2Et), 0.82 (t, 6H, J = 7.3 Hz, -CO_2Et); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 168.22, 160.63, 159.25, 134.34, 131.32, 129.38, 127.99, 120.77, 114.51, 112.85, 61.54, 60.87, 55.64, 14.18, 13.48; HRMS (ESI): m/z = 655.22676. calcd. for $C_{34}H_{36}N_2O_{10}Na$: 655.22544 $[M+Na]^+$.

4,4'-Bis(4-methoxyphenyl)-2,2'-bipyrrole (5c)

A mixture of **4c** (2.53 g, 4.0 mmol) and NaOH (1.04 g, 26.0 mmol) in ethylene glycol (52 mL) was heated at 170 ºC for 2 h under an argon atmosphere. The reaction mixture was diluted with cold water. The appeared precipitate was filtrated and washed with water, hexane and MeOH. The residue was dried in vacuo with P_2O_5 to give product as gray solids. This product was used for the next step without further purification. Yield: 92% (1.28 g, 3.7 mmol). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ = 11.00 (brs, 2H, -NH), 7.41 (AA'BB', 4H), 7.06 (m, 2H), 6.87 (AA'BB', 4H), 6.54 (m, 2H), 3.75 (s, 6H, -OMe); ^{13}C NMR (400 MHz, DMSO-*d*$_6$) δ = 156.84, 128.55, 126.67, 125.24, 123.60, 113.92, 113.54, 100.23, 54.89; HRMS (ESI) *m/z* = 345.16030. calcd for $C_{22}H_{21}N_2O_2$: 345.16061 [M+H]$^+$.

4,4'-Bis(4-methoxyphenyl)-1*H*,1'*H*-[2,2'-bipyrrole]-5,5'-dicarbaldehyde (6c)

To a solution of **5c** (1.20 g, 3.5 mmol) in DMF (50 mL) was slowly added $POCl_3$ (1.6 mL, 17 mmol) at 0 °C under an argon atmosphere. The reaction mixture was refluxed for 2 h. After cooling to room temperature, aqueous NaOAc (4.0 g in 54 mL) was carefully added. The mixture was refluxed for another 1 h. The solution was poured into cold water and then the appeared precipitate was filtrated and rinsed with water, hexane and MeOH. The residue was dried in vacuo with P_2O_5 to give **6c** as yellowish green solids. Yield: 87% (1.21 g, 3.0 mmol). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ = 12.34 (brs, 2H, -NH), 9.57 (s, 2H, -CHO), 7.53 (AA'BB', 4H), 7.12 (s, 2H), 7.05 (AA'BB', 4H), 3.81 (s, 6H, -OMe); ^{13}C NMR (400 MHz, DMSO-*d*$_6$) δ = 178.42, 158.97, 136.22, 130.05, 129.93, 128.73, 125.47, 114.21, 109.92, 55.10; HRMS (ESI): *m/z* = 401.15013. calcd for $C_{24}H_{21}N_2O_4$: 401.15010 [M+H]$^+$.

2,7,12,17-Tetra(*p*-methoxyphenyl)-porphycene (7c)

$TiCl_4$ (2.80 mL, 25 mmol) was added dropwise to a THF (100 mL) solution containing Zn dust (3.33 g) and CuCl (0.20 g, 2.0 mmol) at room temperature under an argon atmosphere, and then the mixture was refluxed for 3 h. Subsequently a solution of **6c** (373 mg, 0.93 mmol) in THF (150 mL) was added dropwise to the boiling reaction mixture. The mixture was stirred at same temperature for another 1 h. After cooling to 0 ºC, an aqueous 10% K_2CO_3 solution (120 mL) was added dropwise. The precipitate was filtrated off on Celite pad and washed with CH_2Cl_2. The combined organic layer was then dried with Na_2SO_4, and the solution was removed under reduced pressure. The crude product was purified by alumina column chromatography (CH_2Cl_2) and then silica gel column chromatography (hexane/CH_2Cl_2 = 9:1 to 1:1). Recrystallization from $CHCl_3$/MeOH provided **7c** as purple powders. Yield: 15% (51 mg, 0.07 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.90 (s, 4H), 9.63 (s, 4H) 8.28 (AA'BB', 8H), 7.36 (AA'BB', 8H), 4.06 (s, 12H, -OMe), 3.77 (brs, 2H, -NH); ^{13}C NMR spectrum was not recorded because of poor solubility; HRMS (ESI): *m/z* = 757.27907. calcd for $C_{48}H_{38}N_4O_4Na$: 757.27948 [M+Na]$^+$.

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