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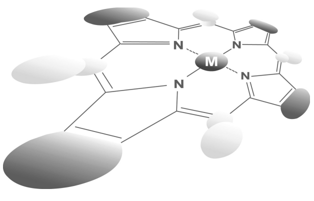

Alkynyl corroles: synthesis by Sonogashira coupling reaction and the physicochemical properties

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ABSTRACT: Alkynyl corroles were synthesized from iodidphenyl corrole precursor by using Sonogashira coupling reaction with or without the presence of copper(I) iodide co-catalyst. The alkynyl group on corrole macrocycle has a significant effect on the photophysical and electrochemical properties of free-base and metal corrole derivatives.

KEYWORDS: corrole, Sonogashira coupling reaction, fluorescence, electrochemistry.

INTRODUCTION

Corroles are one *meso*-carbon shorter analogs of porphyrin. The first synthesis of corroles may be traced back to the 1960s and for more than 30 years, the elaborate and time-consuming preparation of corroles had presented a formidable obstacle in the study of corroles. This situation was not changed until 1999 when the direct synthesis of *meso*-triarylcorroles [1, 2] and the rational two-step synthesis of A_2B-type *meso*-substituted corroles [3] were discovered. Nowadays, a number of well-established synthetic protocols are available for corroles, and an increasing amount of effort is devoted to the study of their properties and applications [4–7].

Sonogashira coupling reaction [8] of terminal acetylenes with aryl or vinyl halides provides a powerful tool for C–C bond formation. Despite the wide reporting of studies [9–12] on preparation of new porphyrins by using this reaction, examples of corroles bearing alkynyl groups prepared by Sonogashira coupling reaction are rare. So far, the only example for the synthesis of alkynyl corroles by Sonogashira coupling reaction was reported by Gryko and co-workers quite recently [13]. Herein, we wish to report the synthesis of several new alkynyl corroles by using Sonogashira reaction with iodided free-base corrole and its metal (Cu and Mn) complexes as precursors (Table 1). The fluorescence and electrochemical properties of synthesized alkynyl corroles were also examined.

RESULTS AND DISCUSSION

Synthesis

Sonogashira coupling reaction is generally co-catalyzed by CuI with an amine as base and a phosphine as ligand for palladium catalyst [16, 17]. In this work, we chose $Pd_2(dba)_3$ as initial catalyst as it is air-stable and shows good results in alkynyl porphyrin preparation [11]. The dative ligand throughout the investigation was consistently triphenylphospine, since it is relatively cheap, easy to handle, non-toxic and air-stable. Firstly, we use copper and manganese iodidphenylcorroles (**1b** and **1c**) as reactants. As shown in Table 1, when Sonogashira reaction is co-catalyzed by CuI, the reaction of the copper corrole **1b** and manganese corrole **1c** with 2 equiv. of phenylacetylene resulted in formation of **2b** and **2c** with an isolated yield of 73.4% and 76.2%, respectively (Table 1, entries 1, 2). The addition of copper

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◊SPP full member in good standing

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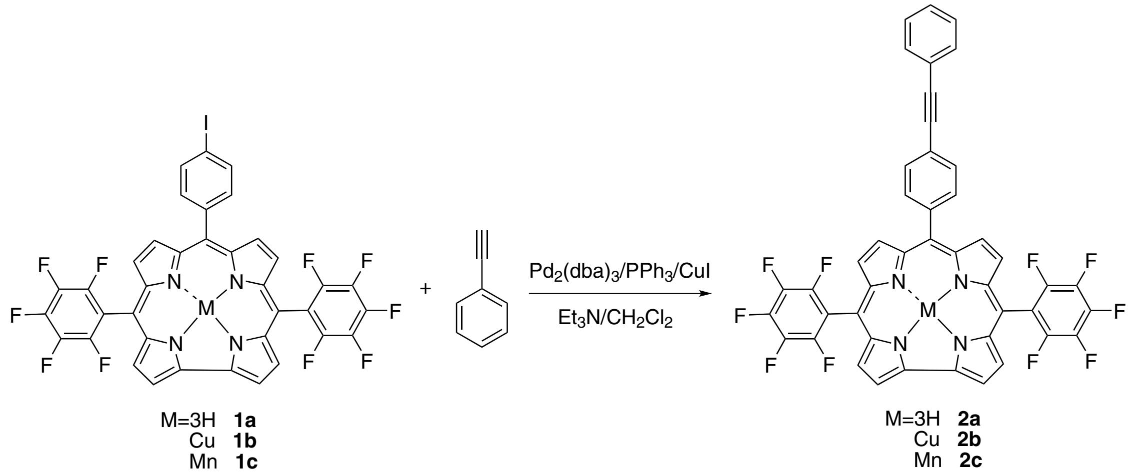
Table 1. Synthesis of alkynyl corrole derivatives[a]

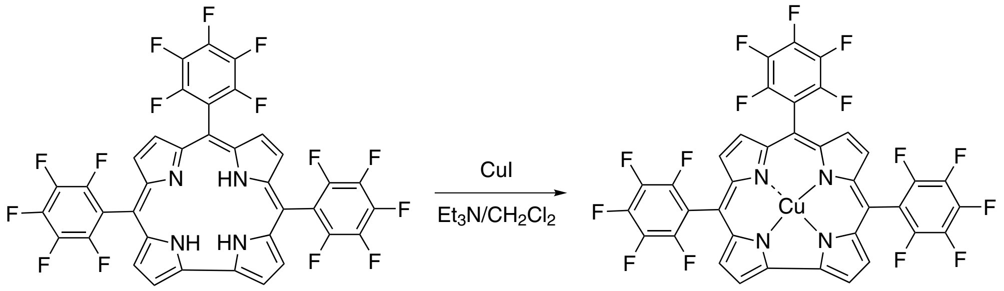


	Substrate	Catalyst	CuI, mol.%	Product	Yield, %[b]
1	**1b**	$Pd_2(dba)_3$	10	**2b**	73.4
2	**1c**	$Pd_2(dba)_3$	10	**2c**	76.2
3	**1b**	$Pd_2(dba)_3$	—	**2b**	70.5
4	**1c**	$Pd_2(dba)_3$	—	**2c**	71.0
5	**1a**	$Pd_2(dba)_3$	—	**2a**	54.8
6	**1a**	$Pd_2(dba)_3$	10	**2a**	58.0
				2b	5.0
7	**1a**	$Pd_2(dba)_3$	100	**2b**	62.5
				1b	3.0
8	**1b**	—	100	—	—
9	**1b**	—	—	—	—
10[c]	**1a**	$Pd_2(dba)_3$	—	**2a**	96
11[c]	**1a**	$Pd(OAc)_2$	—	**2a**	92
12[c]	**1a**	$PdCl_2$	—	**2a**	94
13[d]	**1a**	$PdCl_2(PPh)_3$	—	**2a**	97

[a] Conditions: catalyst (10 mol.%) and CuI (0–100 mol.%), PPh_3 (1 equiv.), iodidphenylcorrole (0.2 mmol), phenylacetylene (2 equiv.), Et_3N (30 mL), DCM (60 mL), rt, nitrogen, 16 h. [b] Isolated yield. [c] The reaction was carried out at 60 °C for 4 h. [d] The reaction was carried out at reflux for 4 h in the absence of PPh_3.

salts as co-catalysts in typical Sonogashira reactions may cause difficulty in recovering reagent (alkyne), making the reaction less environmental friendly [8]. Sonogashira reactions without CuI have been developed [18, 19]. In our experiments, when the reaction were performed in the absence of CuI, the alkynylation could also go on smoothly to give an isolated yield of **2b** in 70.5% and **2c** in 71% (Table 1, entries 3, 4).

The functionalization of free-base corroles is more challenging due to their intriguing and erratic reactivity, such as the observations in bromination [20], hydroformylation of corrole [21] and the reaction of corrole with CI_4 [22]. The Sonogashira reaction of metal-free corroles offers another way of preparing free-base corrole derivatives. In the absence of CuI, free-base corrole **1a** reacted with phenylacetylene to give **2a** in a lower yield (54.8%) than that of corresponding metal corrole homologous reactants (Table 1, entry 5). When the reaction was carried out in the presence of co-catalyst CuI, the isolated yield of free-base **2a** increased slightly to 58.0% (Table 1, entry 6). Interestingly, copper corrole **2b** could also be isolated with a yield of 5% under these conditions. This result indicated that some of the copper ions may have inserted into the N_4 coordination core of corrole in the reaction. To address this issue, the reaction was performed with an increased amount of CuI up to 100 mol.%. It turned out the yield of copper corrole **2b** increased to 62.5% (Table 1, entry 7), and no free-base corrole **2a**



Scheme 1. Reaction of H_3TPFC and copper(I) iodide

could be isolated. In this case, copper corrole **1b** could be isolated with a yield of 3%. Since copper can be efficiently removed from corroles by reductive demetalation [23–26], the insertion of copper into corrole is not a significant problem when using typical Sonogashira reaction for the preparation of alkynyl corroles. To test the reactivity between free-base corrole and CuI, 5,10,15-tris(pentafluorophenyl)corrole (H_3TPFC) was reacted with 2 equiv. of CuI in CH_2Cl_2/Et_3N (V/V, 2/1) at room temperature for 1 h, and CuTPFC was obtained with a yield of 97%. This represents a new method for the preparation of copper corrole (Scheme 1). Since copper corrole is generally prepared by reaction of Cu(II) salt (such as copper(II) acetate and copper(II) dichloride) and corrole in DMF or pyridine [27–29]. It is noteworthy that the reaction of H_3TPFC and CuI did not occur without Et_3N after 24 h. Furthermore, Sonogashira reaction of corroles cannot go on without $Pd_2(dba)_3$ catalyst (Table 1, entries 8–9). When the reaction was performed at the elevated temperature (60 °C) for 4 h, the yield of **2a** increased sharply (Table 1, entry 10). Excellent yields could also be obtained with different palladium salts as catalyst (Table 1, entries 11–13).

From the above observations, metal corrole is a better precursor than free-base corrole in Sonogashira coupling reaction at room temperature, with the former giving a significantly higher isolated yield of target alkynyl corrole ; the different metal corroles (Cu and Mn) give similar yields. When the reaction was carried out at 60 °C, free-base corrole **2a** was obtained with the best yield. This temperature is suitable for Sonogashira coupling reaction of iodidphenylcorrole and phenylacetylene. There is no big difference in the catalytic activity of different palladium salts. Also, free-base corrole can react with CuI to give copper corrole in the presence of triethylamine in dichloromethane.

Photophysical properties

UV-vis spectra. Figure 1 shows the UV-vis spectra of the free-base corrole **1a** and **2a**, and metal corrole **1b**, **1c**, **2b** and **2c** in toluene. All investigated corroles exhibited typical UV-vis spectra of free-base, copper(III) or manganese(III) corrole. The Soret bands of **1a** and **2a** are located at 420 and 425 nm, respectively. A red shift of about 5 nm was observed in the alkynation of **1a** to **2a**. The Soret bands of the Cu and Mn-complexes **1b**, **2b**, **1c** and **2c** are located around 411 nm (± 1 nm). Soret bands of these metal corroles blue-shifted significantly compared to free-base **1a** and **2a**.

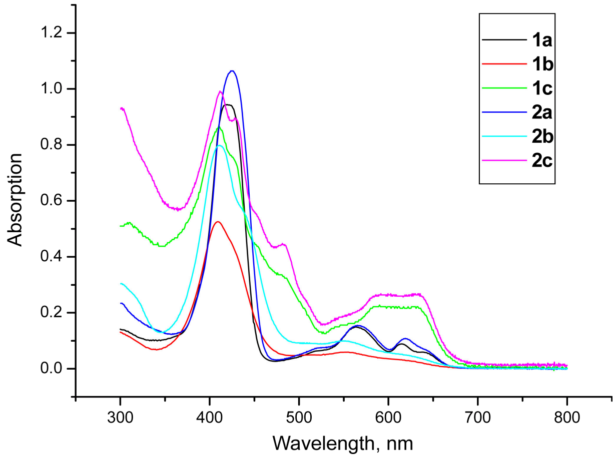


Fig. 1. UV-vis spectra of corrole in toluene

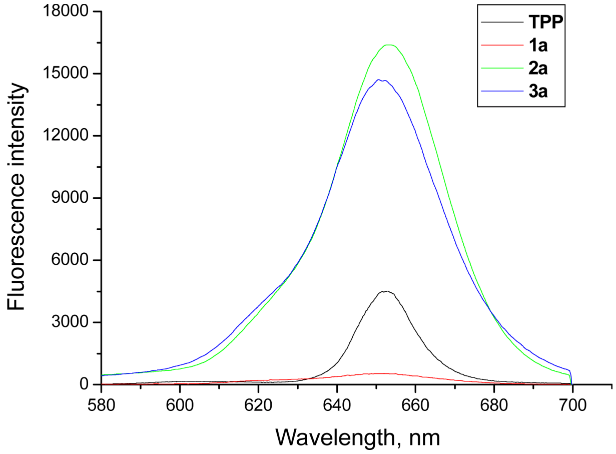


Fig. 2. Fluorescence spectra of corroles in toluene at room temperature (λ_{ex} = 560 nm, 1.0×10^{-5} M)

Fluorescence spectra. The steady-state fluorescence spectra of corroles **1a**, **2a** and **3a** in toluene at room temperature are shown in Fig. 2. Transient fluorescence spectra were recorded by the method described in the Experimental section, and the transient fluorescence spectra of these free-base corroles are shown in Fig. 3. Fluorescence quantum yields were determined using TPP as a standard (Φ_{fl} = 0.11) [30]. The fluorescence emission maxima

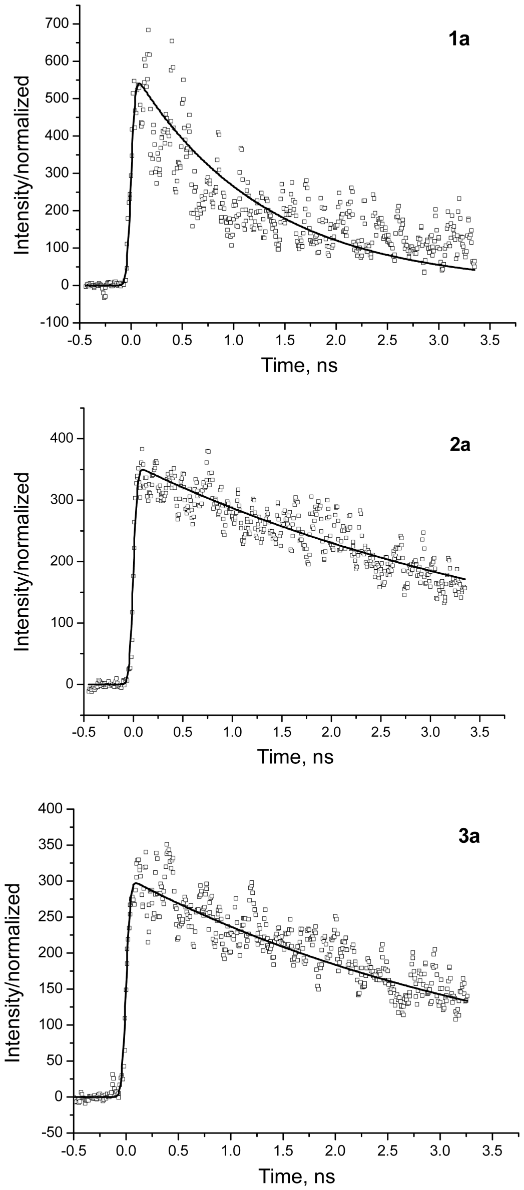
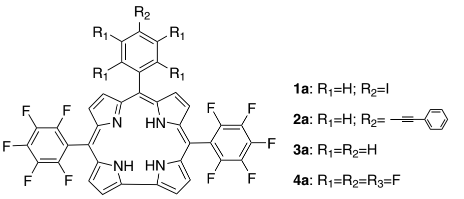


Fig. 3. Fluorescence decay curve of corroles in toluene

Table 2. Fluorescence data of corroles **1a**, **2a**, **3a** and **4a** at 295 K



Corroles		Solvent	λ_{ex}, nm	λ_{max}, nm	Φ_{fl}[a]	τ, ns	Reference
1	**1a**	toluene	560	647	0.005	1.27[b]	this work
2	**2a**	toluene	560	654	0.132	4.55[b]	this work
3	**3a**	toluene	560	653	0.106	3.94[b]	this work
4	**4a**	toluene	550	645, 707	0.13	4.8, 4.3[c]	32
		CH_2Cl_2	407	643, 700	0.14	3.7, 1.1	33

[a] Tetraphenylporphyrin was used as a standard (Φ_{fl} = 0.11). [b] Excitation at 420 nm. [c] Excitation at 373 nm.

(λ_{max}), quantum yield (Φ_{fl}) and lifetime (τ) are summarized in Table 2. No emission was observed for metal corroles **1b**, **1c**, **2b** and **2c** due to the suppression by the central metal ions. For the purpose of discussion, the emission spectra of 10-phenyl-5,15-dis(pentafluorophenyl) corrole (**3a**) and tetraphenylporphyrin (TPP) were also measured. When excited by 560 nm wavelength light, fluorescence intensity of **2a** and **3a** is several times stronger than that of **1a,** and the maximum emission shifts to lower energy by 7 and 6 nm, respectively (Fig. 2). **1a** is a weak emitter, with Φ_{fl} = 0.005 and lifetime of 1.27 ns because of the heavy-atom effect caused by iodide [31]. Therefore, a close analog corrole **3a** was used as a reference to evaluate the alkynation effect on the fluorescence property of synthesized **2a** here. It could be seen that the fluorescence quantum yield of **2a** (0.132) is obviously larger than that of **3a** (0.106). Fluorescence lifetime of **2a** (4.55 ns) is also longer than that of **3a** (3.94 ns). The Φ_{fl} and τ values for **2a** and **4a** [32] in toluene are similar. 5,10,15-tris(pentafluorophenyl)corrole (**4a)** exhibited a lower fluorescence lifetime (3.7 ns, [33]) in CH_2Cl_2 than in toluene with the similar fluorescence quantum yield.

Electrochemical properties

Cyclic voltammograms of free-base corrole (**1a** and **2a**), copper corroles (**1b** and **2b**) and manganese corroles (**1c** and **2c**) are shown in Fig. 4, and their redox potentials are shown in Table 3. The first comprehensive study on the electrochemistry of *meso*-substituted free-base corroles was carried out in PhCN [34]. In this paper, cyclic voltammetry (CV) of free-base corrole **1a** and **2a** were performed in CH_3CN because of their electrochemical lability in dichloromethane. The CV of **1a** in CH_3CN consists of one irreversible reduction (at E_{pc} = -0.24 V) and four oxidations processes between -0.5 and +1.7 V (*vs.* SCE). The first and fourth oxidations located at peak potentials of 0.03 and 1.39 V are irreversible (scan rate: 0.1 V/s). Two additional reversible oxidations located at $E_{1/2}$ = 0.50 and 0.86 V are observed for this compound. The CV of **2a** in CH_3CN only displays one reversible reduction (at $E_{1/2}$ = -0.88 V) and one reversible oxidation (at $E_{1/2}$ = 0.31 V) between -1.4 and +0.6 V (*vs.* SCE).

Complex **1b** displays three redox processes at $E_{1/2}$ = -1.02, 0.03 and 1.04 V *vs.* SCE. The reversible one-electron reduction at $E_{1/2}$ = -1.02 V is metal-centered (Cu(II)/Cu(III)) and the first reversible oxidation can be confidently assigned to be corrole-centered [35]. Except for two reversible redox processes at $E_{1/2}$ = 0.06 and 0.97 V (Table 2), **2b** undergoes an irreversible reduction at E_{pc} = -1.11 V and an irreversible oxidation at E_{pa} = 1.53 V. No evidence of dimerization is observed upon the electrochemical oxidation. This is different from the case of (OEC)Cu [36]. Due

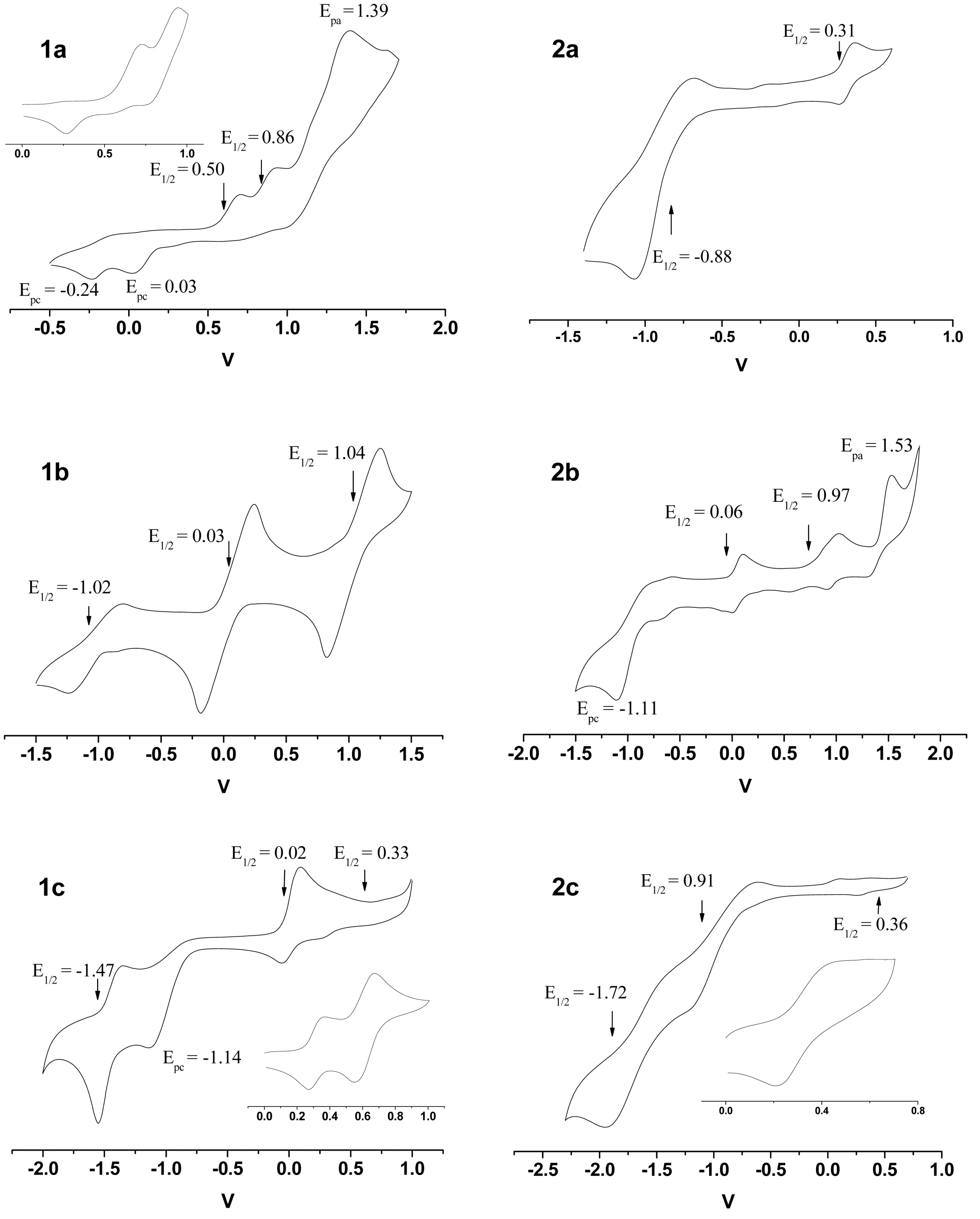


Fig. 4. Cyclic voltammograms (CVs) of corroles **1a**, **2a**, **1b**, **2b**, **1c** and **2c** (0.1 M TBAPF$_6$, SCE as reference electrode, glass carbon disc electrode as working electrode; scan rate 0.1 V/s)

to the formation of [(OEC)Cu]$_2$ dimer, the first oxidation of (OEC)Cu involved two stepwise abstractions of one electron from each macrocycle, or CE mechanism for the electrochemistry of (OEC)Cu.

Manganese corrole complex **1c** undergoes a reversible reduction at $E_{1/2}$ = -1.47 V, irreversible reduction at E_{pc} = -1.14 V and two reversible oxidations at $E_{1/2}$ = 0.02 and 0.33 V. While complex **2c** undergoes a reversible reduction at $E_{1/2}$ = -1.72 V, one quasi-reversible reduction at $E_{1/2}$ = -0.91 V and a single reversible oxidation at $E_{1/2}$ = 0.36 V. Based on the previous electrochemical study of manganese corroles [37, 38], the reversible oxidation at $E_{1/2}$ = 0.02 for **1c** and $E_{1/2}$ = 0.36 V for **2c** may be assigned to Mn(III)/Mn(IV) redox couple. Thus, a 340 mV

Table 3. Redox potential data of corrole complexes

Metal ion	Compound	Solvent	$E_{1/2}{}^a$/V *vs.* SCE	
			Reduction	Oxidation
none	**1a**	CH_3CN	-0.24^b	0.03^b, 0.50, 0.86, 1.39^c
none	**2a**	CH_3CN	-0.88	0.31
Cu	**1b**	CH_2Cl_2	-1.02	0.03, 1.04
	2b	CH_2Cl_2	-1.11^b	0.06, 0.97, 1.53^c
Mn	**1c**	CH_2Cl_2	-1.47, -1.14^b	0.02, 0.33
	2c	CH_2Cl_2	-1.72, -0.91^d	0.36

^{a} $E_{1/2} = (E_{pa} + E_{pc})/2$, SCE as reference, scan rate = 0.1 V/s. ^{b} E_{pc}. ^{c} E_{pa} for a scan rate of 0.1 V/s. ^{d} $E_{1/2}$ for one quasi-reversible reduction.

positive shift of Mn(III)/Mn(IV) couple from **1c** to **2c** was observed. This indicates the alkynyl group on the *meso*-phenyl of corrole may exert an electron-withdrawing effect on the corrole macrocycle.

EXPERIMENTAL

General

Reagents (Sigma-Aldrich and Alfa Aesar) were of synthetic grade and used without further purification. Triethylamine (Et_3N) and dichloromethane (CH_2Cl_2) were distilled from CaH_2 under argon. Pyrrole was freshly distilled before use. Tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) was purchased from Sigma Chemical Co. And dried under vacuum at 40 °C for at least one week prior to use.

Preparative thin-layer chromatography was carried out on silica gel plates loaded with Merck silica gel 60 GF254. Column chromatography was performed on Merck 60 silica gel (300–400 mesh). ^1H NMR and ^{19}F NMR spectra were recorded on Bruker Avance DRX (400 MHz or 300 MHz) spectrometers. UV-vis spectra were measured on a Hitachi U-3010 spectrophotometer. Mass spectra (FAB mode) were recorded on a VG Analytical spectrometer in the positive-ion mode using *m*-nitrobenzyl alcohol (Aldrich) as a matrix. Absorption spectra of all of the samples were measured by a PerkinElmer Lambda 850 UV-vis spectrometer. Fluorescence spectra were recorded by a Combined Fluorescence Lifetime and Steady State Spectrometer (FLS920). The fluorescence decay curves were measured by a time-resolved fluorescence spectroscopic experimental setup. A Nd:YAG laser (EKSPLA PL2143) and an OPG system (EKSPLA PG401SH/DFG2-10) generated the laser pulse (420 nm, 10 Hz) with a full width at half maximum (FWHM) of 22 ps as a light source. The fluorescence was collected with a pair of lenses with big caliber. After passing through a monochromator, it was recorded by a streak camera (Hamamatsu C1587) and a CCD (Hamamatsu C4742-95). The fluorescence lifetime can be determined with a 30 ps resolution by the deconvolution procedure. All measurements were carried out at room temperature.

Cyclic voltammetry was carried out with Auto LAB PGSTAT 30. A three-electrode system was used and consisted of a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE). The SCE electrode was separated from the bulk of the solution by a fritted-glass bridge of low porosity that contained the solvent/supporting electrolyte mixture. Half-wave potentials were calculated as $E_{1/2} = (E_{pa} + E_{pc})/2$ and are referenced to SCE.

General Sonogashira coupling procedure

Corrole (0.2 mmol), CuI (0–100 mol.%), $Pd_2(dba)_3$ (10 mol.%), 1 equiv. of PPh_3 and Et_3N (30 mL) were mixed in DCM (60 mL). The reaction mixture was saturated with nitrogen and 2 equiv. of phenylacetylene were added. After stirring 16 h at room temperature, solvent was removed under reduced pressure and the reaction mixture was purified by preparative TLC on silica gel eluted with *n*-hexane/CH_2Cl_2 (3/1 to 1/1) to yield the products.

5-(pentafluorophenyl)dipyrromethane was prepared according to previously published methods, spectral properties were consistent with literature data [14]. The free-base corroles (**1a** and **3a**) were synthesized according to the published general procedures [15].

Preparation of 10-(4-iodophenyl)-5,15-bis(pentafluorophenyl)corrole (1a). (isolated yield: 12%). ^1H NMR (400 MHz; $CDCl_3$): δ_H, ppm 7.89–7.91 (2H, m, Ph), 8.08–8.10 (2H, m, Ph), 8.55–8.56 (2H, m, pyrrole-*H*), 8.66–8.71 (4H, m, pyrrole-*H*), 9.10–9.11 (2H, m, pyrrole-*H*). ^{19}F NMR (376.498 MHz; $CDCl_3$): δ_F, ppm -137.84 (4F, m, Ph), -152.63 (2F, m, Ph), -161.63–161.81 (4F, m, Ph). UV-vis (toluene): λ_{max}, nm ($\varepsilon \times 10^3$ $M^{-1}.cm^{-1}$) 420 (0.944), 564.0 (0.149), 615 (0.089), 639 (0.06). MS (FAB): *m/z* 832 (calcd. for $[M + H]^+$ 832.43).

Preparation of copper complex of 10-(4-iodophenyl)-5,15-bis(pentafluorophenyl)corrole (1b). An approximate three-fold excess of copper(II) acetate hydrate (145 mg, 0.73 mmol) was added to a solution of **1a** (200 mg, 0.24 mmol) in 10 mL methanol in one portion. TLC examinations (silica gel; *n*-hexane/CH_2Cl_2, 2:1) revealed that the starting material was fully consumed at room temperature within 2 h. The solvents were evaporated and the product was purified by chromatography on silica gel with *n*-hexane/CH_2Cl_2 (3:1) as eluent. 161 mg **1b** was obtained (isolated yield: 75%).

^{1}H NMR (400 MHz; $CDCl_3$): δ_H, ppm 7.16–7.20 (4H, m, Ph), 7.29–7.31 (2H, m, pyrrole-*H*), 7.39–7.40 (2H, m, pyrrole-*H*), 7.80–7.82 (2H, m, pyrrole-*H*), 7.93–7.94 (2H, m, pyrrole-*H*). ^{19}F NMR (376.498 MHz; $CDCl_3$): δ_F, ppm -136.96–137.01 (4F, m, Ph), -152.15–152.26 (2F, m, Ph), -160.69–160.79 (4F, m, Ph). UV-vis (toluene): λ_{max}, nm ($\varepsilon \times 10^3$ M^{-1}.cm^{-1}) 410 (0.525), 553 (0.06). MS (FAB): *m/z* 892 (calcd. for $[M + H]^+$ 892.95).

Preparation of manganese complex of 10-(4-iodophenyl)-5,15-bis(pentafluorophenyl)corrole (1c). An approximate three-fold excess of manganese(II) acetate tetrahydrate (175 mg, 0.72 mmol) was added to a solution of **1a** (200 mg, 0.24 mmol) in 10 mL methanol in one portion. TLC examinations (silica gel; *n*-hexane/CH_2Cl_2, 2:1) revealed that the starting material was fully consumed at room temperature within 1 h. The solvents were evaporated and the product was purified by chromatography on silica gel with CH_2Cl_2 as eluent. 149 mg **1b** was obtained (isolated yield: 70.2%). ^{19}F NMR (376.498 MHz; $CDCl_3$): δ_F, ppm -172.03 (4F, m, Ph), -178.19–179.17 (6F, m, Ph). UV-vis (toluene): λ_{max}, nm ($\varepsilon \times 10^3$ M^{-1}.cm^{-1}) 411 (0.13), 482 (0.041), 584 633 (0.023). MS (FAB): *m/z* 884 (calcd. for $[M + H]^+$ 884.34).

10-(4-(2-phenylethynyl)phenyl)-5,15-bis(pentafluorophenyl)corrole (2a). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H, ppm 7.39–7.42 (3H, m, Ph), 7.44–7.45 (2H, m, Ph), 7.65–7.68 (2H, m, Ph), 7.95 (2H, m, Ph), 8.16 (2H, m, pyrrole-*H*), 8.56 (2H, m, pyrrole-*H*), 8.73 (2H, m, pyrole-*H*), 9.11 (2H, m, pyrrole-*H*). ^{19}F NMR (376.498 MHz; $CDCl_3$): δ_F, ppm -138.02–138.43 (4F, m, Ph), -150.38–150.91 (2F, m, Ph), -160.51–161.48 (4F, m, Ph). UV-vis (toluene): λ_{max}, nm ($\varepsilon \times 10^3$ M^{-1}.cm^{-1}) 425 (1.064), 565.5 (0.155), 619 (0.108), 641 (0.069). MS (FAB): *m/z* 807 (calcd. for $[M + H]^+$ 806.65).

Copper complex of 10-(4-(2-phenylethynyl)phenyl)-5,15-bis(pentafluorophenyl)corrole (2b). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H, ppm 7.21 (4H, m, Ph), 7.35–7.36 (3H, m, Ph), 7.405–7.413 (2H, m, Ph), 7.55–7.58 (4H, m, pyrrole-*H*), 7.623–7.642 (2H, m, pyrrole-*H*), 7.933 (2H, m, pyrrole-*H*). ^{19}F NMR (376.498 MHz; $CDCl_3$): δ_F, ppm -135.376–135.433 (4F, m, Ph), -150.626–150.774 (2F, m, Ph), -159.151–159.307 (4F, m, Ph). UV-vis (toluene): λ_{max}, nm ($\varepsilon \times 10^3$ M^{-1}.cm^{-1}) 411 (0.798), 551.5 (0.1). MS (FAB): *m/z* 866.09 (calcd. for $[M + H]^+$ 867.17).

Manganese complex of 10-(4-(2-phenylethynyl)phenyl)-5,15-bis(pentafluorophenyl)corrole (2c). ^{19}F NMR (376.498 MHz; $CDCl_3$): δ_F, ppm -172.21 (4F, m, Ph), -178.55 (6F, m, Ph). UV-vis (toluene): λ_{max}, nm ($\sum \times 10^3$ M^{-1}.cm^{-1}) 411.5 (0.248) 428.5 (0.224) 484 (0.111), 591.5 637.5 (0.065). MS (FAB): *m/z* 859 (calcd. for $[M + H]^+$ 858.57).

10-phenyl-5,15-bis(pentafluorophenyl)corrole (3a). (isolated yield: 13%). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H, ppm 7.75 (3H, m, Ph), 8.16 (2H, m, Ph), 8.56 (2H, m, pyrrole-*H*), 8.69 (4H, m, pyrrole-*H*), 9.11 (2H, m, pyrrole-*H*). ^{19}F NMR (376.498 MHz; $CDCl_3$): δ_F, ppm -138.3 (4F, m, Ph), -153.2 (2F, m, Ph), -162.1 (4F, m, Ph). UV-vis (toluene): λ_{max}, nm ($\varepsilon \times 10^3$ M^{-1}.cm^{-1}) 418 (0.86), 568 (0.18) , 644 (0.12). MS (FAB): *m/z* 706 (calcd. for $[M + H]^+$ 706.58).

CONCLUSION

In summary, we have reported a general method for the alkynylation of corroles *via* Sonogashira reaction. The reaction proceeds smoothly with an isolated yield from moderate to excellent. When using free-base corrole as precursor, the reaction product was always the corresponding alkynyl copper(III) corrole in the presence of excess of CuI co-catalyst. It was also found that copper corrole may be prepared by the reaction of free-base corrole and CuI in CH_2Cl_2 at room temperature with the addition of Et_3N. This reveals a new method for the preparation of copper corrole complex. Our preliminary results also show the alkynyl group on corrole macrocycle has a significant effect on the photophysical and electrochemical properties of free-base and metal corrole derivatives.

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