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ARTICLE

Structure–Performance Relationship in Copper Phthalocyanine-Based Supercapacitor Electrodes: Influence of Substituent Geometry from Molecular Design to Electrochemical FunctionŞirin Siyahjani-Gültekin^{a*}, Berivan Arin Öztürmen^b, Damla Şahin^a, Gülşah Yılmaz^a, Bahar Tosun Ercan^a, Burak Gültekin^a, Zekeriya Biyiklioglu^{b*}Received 00th January 20xx,
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This work investigates how substituent position governs the structure–performance relationship of copper phthalocyanine (CuPc) derivatives used as supercapacitor electrodes. Two positional isomers bearing the same (3,4,5-trimethoxybenzyl)oxy substituent, namely the peripheral derivative (TMe-Cu) and the non-peripheral derivative (n-TMe-Cu), were synthesized and characterized by spectroscopic and structural techniques. Electrochemical evaluation in 1 M H₂SO₄ using cyclic voltammetry, galvanostatic charge-discharge, electrochemical impedance spectroscopy, and scan-rate-dependent kinetic analyses revealed a pronounced performance advantage for n-TMe-Cu, which delivered a specific capacitance of up to 360 F g⁻¹ at 1 A g⁻¹ and retained 80% of its initial capacitance after 5000 cycles. Dunn analysis showed that n-TMe-Cu exhibits a substantially higher surface-controlled contribution than TMe-Cu, indicating that a larger fraction of charge storage proceeds through rapidly accessible interfacial pathways. In conjunction with the observed morphological differences between the two electrodes, these results suggest that non-peripheral substitution promotes a more electrochemically accessible electrode architecture and more favourable charge-storage kinetics. Overall, this study demonstrates that substituent geometry is a key molecular design parameter for regulating electrochemical utilization and rate performance in CuPc-based organic electrode materials.

Introduction

Among various energy storage technologies, supercapacitors stand out due to their remarkably high-power density, rapid charge-discharge capability, and extended cycle life, making them promising candidates for next-generation energy storage applications¹. Consequently, their utilization is continually expanding into diverse fields, including electric and hybrid vehicles, buses, trams, uninterruptible power supplies (UPS), temporary memory backup systems in computers, energy harvesting devices, solar energy systems, and wind turbines^{2,3}.

The fundamental challenge in advancing supercapacitor technology is the development of effective electrode materials. Among various candidates, metal phthalocyanines (MPcs), organic semiconductors comprising four isoindole units coordinated around a central metal ion, are particularly noteworthy^{4,5}. Their planar conjugated structure promotes efficient electron transport through π - π interactions, while strong adsorption ensures robust adherence to electrode surfaces. Additionally, the presence of 18-delocalized electrons in their macrocyclic structure facilitates charge transport and molecular stacking, further enhancing electrochemical

performance. MPcs demonstrate excellent thermal and chemical stability^{4,6}, enabling their application under challenging conditions such as elevated temperatures and highly acidic or basic environments.

They can exist in covalent or electrovalent forms, with covalent MPcs exhibiting higher stability, capable of sublimation in a vacuum environment at 400–500°C without structural decomposition^{7,8}. Strong bonds between the metal centre and phthalocyanine ring, combined with aromatic stabilization, confer chemical resilience, resulting in minimal structural changes upon exposure to inorganic acids, except nitric acid (HNO₃). Some MPcs with electrovalent character, containing alkali or alkaline metals, readily dissociate their metal ions upon exposure to acidic or aqueous media. However, copper-based MPcs employed in this study exhibit covalent bonding character, providing greater chemical stability under similar conditions^{5,7}.

The electronic properties and thus the electrochemical performance of MPcs significantly depend on the type of metal at their center. Divalent MPcs such as NiPc and CuPc exhibit relatively low intrinsic conductivity ($\sim 10^{-12}$ S cm⁻¹)⁹, necessitating their integration with conductive carbon materials, including carbon nanotubes, reduced graphene oxide (rGO), or porous carbons, to enhance their performance in practical applications¹⁰.

In this study, CuPc was functionalized with a (3,4,5-trimethoxybenzyl)oxy substituent to investigate how substituent position, rather than substituent identity, affects electrochemical behaviour in supercapacitor electrodes. Two positional isomers, the

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peripheral (TMe-Cu) and non-peripheral (n-TMe-Cu) derivatives, were employed as a structurally controlled pair to clarify how molecular geometry influences electrode organization and charge-storage characteristics under identical testing conditions. While the electron-rich methoxy groups were expected to modulate the electronic structure and redox response of the CuPc framework, the positional arrangement of the substituent was anticipated to influence intermolecular packing, electrode microstructure, and the accessibility of electroactive domains. Structural, electrochemical, and kinetic analyses were therefore correlated to determine how peripheral and non-peripheral substitution patterns give rise to differences in interfacial charge-storage pathways, rate capability, and overall electrochemical utilization. The findings highlight substituent geometry as an important molecular design parameter for CuPc-based organic supercapacitor electrodes.

Experimental

Materials and methods

The synthesis procedure of 3-[(3,4,5-Trimethoxybenzyl)oxy]phthalonitrile (n-TMe-CN):

TMe-OH (1 g, 5.05 mmol) was dissolved in 15 mL anhydrous DMF. 3-Nitrophthalonitrile (872 mg, 5.05 mmol) was added. Then, dry K_2CO_3 (2.08 g, 15.15 mmol) was added in equal portions for 2 hours and was stirred at 60 °C for four days. Finally, the mixture was poured into iced water. **n-TMe-CN** was purified by using column chromatography on aluminium oxide with $CHCl_3$ as solvent. Yield: 450 mg (28%) m.p.: 170-171 °C. IR (ATR) ν/cm^{-1} : 3075 (Ar-H), 2941-2839 (Aliph. C-H), 2227 (C≡N), 1594, 1580, 1512, 1470, 1422, 1379, 1288, 1243, 1185, 1154, 1070, 1041, 993, 818, 733, 657, 626, 595. 1H -NMR (400 MHz, DMSO- d_6), (δ): 7.85 (t, 1H, Ar-H), 7.73 (d, 1H, Ar-H), 7.67 (d, 1H, Ar-H), 6.80 (s, 2H, Ar-H), 5.27 (s, 2H, $-CH_2-O$), 3.76 (s, 6H, $-O-CH_3$), 3.65 (s, 3H, $-O-CH_3$). ^{13}C -NMR (100 MHz, DMSO- d_6), (δ): 161.12, 153.44, 137.79, 136.25, 131.31, 126.44, 119.54, 116.21, 115.84, 114.18, 105.59, 103.80, 71.59, 60.45, 56.31. MS (ESI), (m/z): 347.02 [M+Na] $^+$.

The synthesis procedure of peripherally and nonperipherally tetra-[(3,4,5-trimethoxybenzyl)oxy] group substituted copper(II) phthalocyanines (TMe-Cu, n-TMe-Cu)

TMe-CN (100 mg, 0.3 mmol) and n-TMe-CN (100 mg, 0.3 mmol), $CuCl_2$ (20 mg, 0.15 mmol), 1-pentanol (2 mL) and DBU (5 drops) was heated at 165 °C for 1 day. The product was precipitated with n-hexane. Then, TMe-Cu and n-TMe-Cu were purified by column chromatography on aluminium oxide by using $CHCl_3$ as solvent.

Copper(II) phthalocyanine (TMe-Cu)

Yield: 75 mg (72%), m.p. > 250 °C. IR (ATR), ν/cm^{-1} : 3071 (Ar-H), 2925-2846 (Aliph. C-H), 1590, 1504, 1454, 1419, 1374, 1329, 1224, 1118, 1088, 1055, 1000, 818, 744, 680. UV-Vis ($CHCl_3$) λ_{max} nm (log ϵ): 684 (4.93), 624 (4.54), 340 (4.73). MALDI-TOF-MS m/z: 1360.135 [M] $^+$.

Copper(II) phthalocyanine (n-TMe-Cu)

Yield: 48 mg, 47% m.p. > 250 °C. IR (ATR) ν/cm^{-1} : 3061 (Ar-H), 2930-2831 (Aliph. C-H), 1588, 1501, 1454, 1417, 1328, 1230, 1121, 1084, 1005, 798, 739. UV-Vis ($CHCl_3$) λ_{max} nm (log ϵ): 710 (5.01), 646 (4.47), 327 (4.72). MALDI-TOF-MS m/z: 1360.135 [M] $^+$.

Electrode Preparation

Three different components were used when preparing the material for the electrodes: Pc derivatives, carbon black (CB) as an additive to increase electrical conductivity and the surface area¹¹, and PVDF-HFP as a binder.

The electrode base materials (TMeO-CuPc and n-TMeO-CuPc), carbon black (CB) and PVDF-HFP were mixed with acetone to obtain a homogeneous paste in a weight ratio of 80:15:5, respectively. The resulting paste was coated on a flexible graphite sheet used as a current collector and the electrodes were kept in a vacuum oven at 100 °C. The active electrode material covering an area of 1 cm² on each current collector is approximately 1 mg.

Electrochemical characterization

The electrochemical performance of the electrodes was tested with a three-electrode system. TMeO-CuPc, n-TMeO-CuPc, Ag/AgCl as reference electrode and Pt wire as counter electrode were used as working electrodes. All measurements were performed using 1M H_2SO_4 electrolyte.

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) for the supercapacitors were performed on a CHI660E electrochemical workstation. Specific capacitance, energy and power densities were calculated from the measurements.

The gravimetric capacitance of SC cells was determined using the Galvanostatic Charge-Discharge (GCD) technique at various current densities. The gravimetric capacitance (C_s , Fg^{-1}) obtained from GCD analysis was calculated for the three-electrode system using the following equation¹².

$$C_s = \frac{I\Delta t}{m\Delta V} \text{ (Eq-1)}$$

Where I is the constant current (A), m is the mass of the electrode material (g), Δt is the discharge time (s) and ΔV is the voltage change during the discharge process.

Electrochemical Impedance Spectroscopy (EIS) measurement was performed in the frequency range of 10 mHz-100 kHz to investigate the charge transfer between the electrode and electrolyte interface and ion diffusion across the electrode. The calculation of the total capacitance in the SC cell by EIS analysis is determined by the following formula¹³.

$$C = -\frac{1}{2\pi fZ''} \text{ (Eq-2)}$$

Here, Z'' represents the imaginary component of the impedance, while f represents the frequency in Hz of the applied AC signal.

Cyclic voltammetry (CV) studies on SCs provide information on charge storage properties at electrode-electrolyte interfaces for different scan rates. The rectangular shape observed in CV profiles refers to the capacitive behaviour of the cells, and the consistent maintenance of this shape at high scan rates indicates the high-rate capability of the cells. The following equation was used to calculate capacitance values from CV¹⁴.



$$C_s = \frac{\int IVdV}{2mvk} \text{ (Eq-3)}$$

Where m is the mass of the electrode material (g), $\frac{\int IVdV}{2mvk}$ is the charge area under the CV curve, v is the potential window (V) and k is the scan rate (Vs^{-1}).

The energy density (E , $Whkg^{-1}$) and power density (P , Wkg^{-1}) for the SC cell were calculated using the following equations:

$$\frac{E}{0.5} = \frac{C_s(\Delta V)^2}{2t} \text{ (Eq-4)}$$

$$P = \frac{E}{t} \times 3600 \text{ (Eq-5)}$$

Where C_s is the specific capacitance of the supercapacitor cell, V is the voltage change during the discharge process after the IR drop in the GCD curve and t is the discharge time.

Experimental

Synthesis and characterization of Copper(II) phthalocyanines

The synthesis of peripherally and nonperipherally tetra-[(3,4,5-trimethoxybenzyl)oxy] group substituted copper(II) phthalocyanines (TMe-Cu and n-TMe-Cu) is visualized in Figure 1.

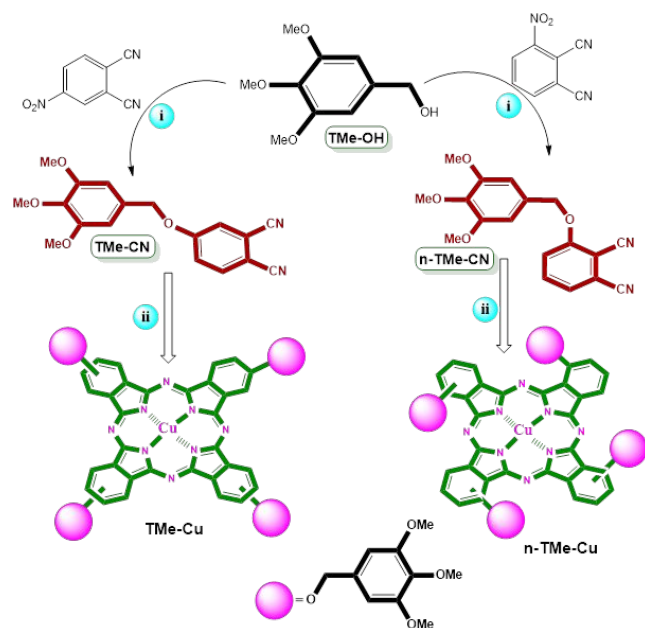


Fig 1. The synthesis of TMe-Cu, n-TMe-Cu. (i) K_2CO_3 , $60^\circ C$, DMF. (ii) $CuCl_2$, 1-pentanol, DBU, $165^\circ C$.

4-(3,4,5-Trimethoxybenzyl)phthalonitrile (TMe-CN) was synthesized according to the literature. In the IR spectrum of n-TMe-CN, $C\equiv N$ stretching vibration was shown at 2227 cm^{-1} . In the 1H -NMR spectrum of the n-TMe-CN, aromatic protons appeared between 7.85–6.80 ppm. Also, $-CH_2-O$ and $-O-CH_3$ protons were shown at 5.27, (3.76, 3.65). ppm, respectively. In the ^{13}C -NMR spectrum of n-TMe-CN, aromatic carbons were shown in the range

of 161.12–103.80 ppm, aliphatic carbons in the range of 71.59–56.31 ppm. The mass spectra of n-TMe-CN showed molecular ion peak at m/z 347.02 as $[M+Na]^+$. In the IR spectrum of TMe-Cu and n-TMe-Cu, the absence of the $C\equiv N$ stretching vibrations at 2228 cm^{-1} , 2227 cm^{-1} supported the metallo phthalocyanines formation. 1H -NMR and ^{13}C -NMR measurement of TMe-Cu and n-TMe-Cu were excluded because of their paramagnetic properties¹⁵. The TMe-Cu and n-TMe-Cu MALDI-TOF MS spectra at m/z 1360.13 as $[M]^+$ (TMe-Cu) (Fig. 2a), 1360.13 as $[M]^+$ (n-TMe-Cu) (Fig. 2b) showed

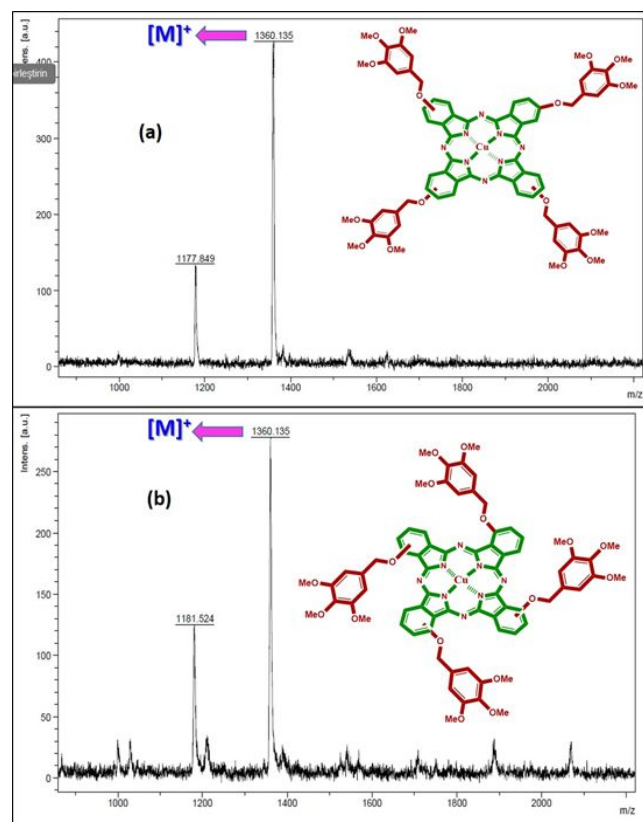


Fig. 2. MALDI-TOF MS spectrum of (a) TMe-Cu, (b) n-TMe-Cu.

molecular ion peaks.

The UV-visible spectra of TMe-Cu and n-TMe-Cu were recorded in $CHCl_3$ (Fig. 3). As shown in Figure 3, TMe-Cu and n-TMe-Cu, exhibited characteristic Q band absorptions at 684 nm and 710 nm, respectively which were attributed to the $\pi-\pi^*$ transition of the

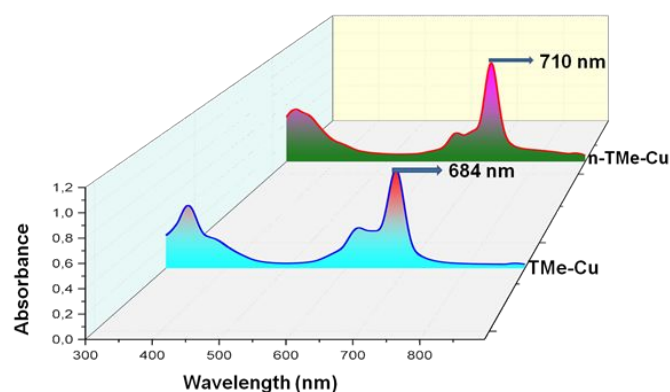


Fig. 3. UV-Vis spectra of TMe-Cu, n-TMe-Cu in $CHCl_3$.



phthalocyanine ring⁷. The other bands (B) in UV region for TMe-Cu and n-TMe-Cu were shown at 340 nm and 327 nm, respectively due to transition from the deeper π -levels to the LUMO.

FT-IR spectroscopy was utilized to examine the chemical structure and substitution patterns of the synthesized phthalocyanine (Pc) derivatives (Fig. 4a). The characteristic vibrational peaks related to Pc macrocycles appear distinctly within the spectral region. Specifically, peaks observed around 1605–1610 cm^{-1} correspond to aromatic C=C stretching vibrations of the phthalocyanine ring. Additionally, prominent absorption bands around 1480–1490 cm^{-1} can be attributed to aromatic C–N stretching vibrations typical of metal-coordinated phthalocyanines^{14,16}. The bands in the 1240–1280 cm^{-1} region are associated with the aromatic ether (Ar–O–C) stretching vibrations originating from the (3,4,5-trimethoxybenzyl)oxy substituents⁶. Furthermore, the methoxygroups (–OCH₃) give rise to sharp and characteristic bands near 1025–1040 cm^{-1} due to C–O stretching vibrations¹⁷.

A comparative evaluation between peripheral and non-peripheral derivatives reveals notable spectral shifts and intensity variations. In non-peripheral derivative (n-TMe-Cu), the vibration peaks appear slightly broader and shifted, indicating distortion in symmetry and enhanced intermolecular interactions due to increased steric hindrance. For instance, the non-peripheral n-TMe-Cu exhibits broadened bands around 1275 cm^{-1} and 1485 cm^{-1} compared to its peripheral counterpart TMe-Cu, suggesting greater disorder or intermolecular stacking differences.

The structural ordering and crystallinity of the Pc derivatives were further elucidated by XRD analysis (Fig. 4b). XRD diffractograms demonstrate characteristic broad peaks typically observed in

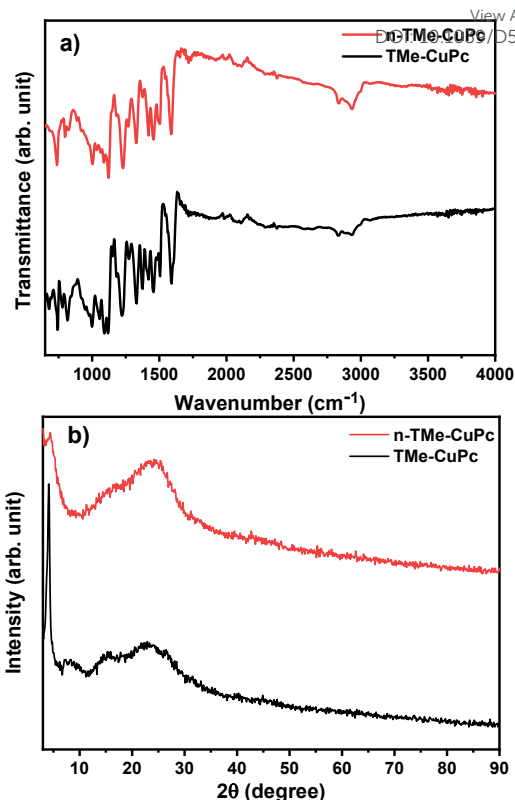


Fig. 4. (a) FTIR spectra of TMe-CuPc and n-TMe-CuPc, (b) XRD patterns of TMe-CuPc and n-TMe-CuPc.

molecularly aggregated, semi-crystalline phthalocyanines around

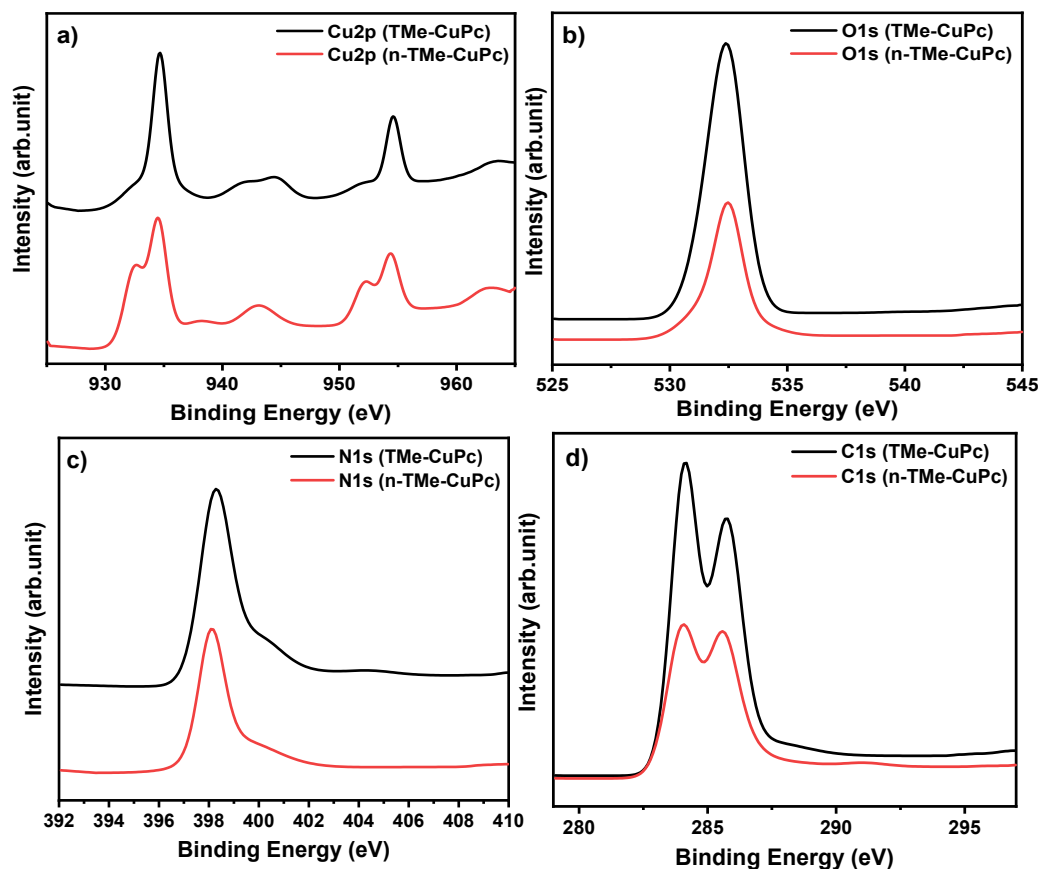


Fig. 5. XPS analyses of TMe-CuPc and n-TMe-CuPc a) Cu 2p, b) O1s, c) N1s, d) C1s



20–30° and 40–45°. Notably, the TMe-Cu derivative exhibits a pronounced and relatively sharp diffraction peak below 5°, indicative of substantial molecular packing or self-assembly into ordered structures at the supramolecular scale¹⁸. Such a distinct feature is less pronounced in non-peripheral analogues, where steric hindrance likely disrupts efficient π - π stacking. This finding correlates well with previously reported studies, where peripheral substituents significantly improved crystallinity due to more favourable molecular alignment⁷.

XPS was employed to investigate the elemental composition and chemical environment of the peripheral (TMe-Cu) and non-peripheral (n-TMe-Cu) copper phthalocyanine (CuPc) derivatives (Fig. 5). The analysis focused primarily on the Cu 2p region to evaluate the oxidation state and coordination environment of the central copper ion (Fig. 5a).

The high-resolution Cu 2p spectra of both derivatives exhibit prominent Cu 2p_{3/2} peaks located around 934.2 eV and Cu 2p_{1/2} peaks near 953.8 eV, which are consistent with the presence of Cu(II) in a square-planar phthalocyanine coordination environment¹⁹. Additionally, the presence of satellite peaks in the 941–945 eV region confirms the d⁹ electronic configuration typical of Cu²⁺ species²⁰.

A comparison between the two substitution patterns reveals clear and meaningful differences. The Cu 2p_{3/2} peak of n-TMe-Cu appears slightly shifted to a higher binding energy (~934.5 eV) compared to TMe-Cu (~934.2 eV), indicating a relatively more electron-deficient environment around the copper center in the non-peripheral derivative. This shift can be attributed to the increased steric hindrance and local asymmetry induced by non-peripheral substitution, which may reduce delocalization around the metal center and increase the localization of positive charge²⁰. In contrast, TMe-Cu shows narrower peak widths and a slightly more symmetric Cu 2p profile, consistent with a more ordered molecular arrangement and stronger electronic delocalization afforded by the peripheral substituents²¹.

Furthermore, the intensity ratio between the main Cu 2p_{3/2} peak and its corresponding satellite features is slightly higher in n-TMe-Cu, suggesting a more pronounced shake-up effect and potentially

greater contribution from localized d-d transitions. This observation supports the hypothesis that non-peripheral substitution introduces more heterogeneous electronic environments, which could enhance redox activity and facilitate pseudocapacitive behavior, as corroborated by CV and GCD analyses. Obtained results confirm that both derivatives retain Cu(II) oxidation states, however, they exhibited different behaviours in terms of electronic environment, molecular symmetry, and delocalization characteristics, which in turn influence their electrochemical performance.

In addition to copper, the high-resolution XPS spectra for oxygen (O 1s), nitrogen (N 1s), and carbon (C 1s) provide further insight into the chemical environment of the macrocyclic framework and substituent groups (Fig. 5b,c,d). The N 1s region exhibits a primary peak near 399.5 eV, attributed to the isoindole nitrogen atoms in the phthalocyanine core, which is consistent across both derivatives²⁰. A slight shoulder at higher binding energy (~401 eV) in n-TMe-Cu may reflect more heterogeneous hydrogen bonding or protonation effects, potentially due to increased structural disorder.

The C 1s spectra display characteristic components at ~284.6 eV (C-C/C=C), ~286.1 eV (C-O), and ~288.5 eV (O-C=O). Notably, the intensity of the C-O peak is higher in non-TMe-Cu, consistent with enhanced exposure of the (3,4,5-trimethoxybenzyl)oxy group and potentially leads greater electrolyte accessibility. The O1s region shows peaks around 531.5–533.0 eV, corresponding to contributions from methoxy groups and possibly causes adsorbed water or oxygen species. Slight shifts to higher binding energy in the non-peripheral derivative again indicate a more electron-deficient local environment and support the interpretation of greater redox reactivity, however, differ clearly in terms of electronic environment, molecular symmetry, and delocalization, which in turn influence their electrochemical performance.

Morphological Characterization (SEM) of electrodes

SEM micrographs (Fig. 6) reveal distinct surface textures for the electrodes prepared with two isomers at 20kX and 50kX. The electrode based on the peripheral derivative (TMe-Cu) exhibits a rough and heterogeneous texture composed of loosely connected aggregates, with visible gap regions and local discontinuities across

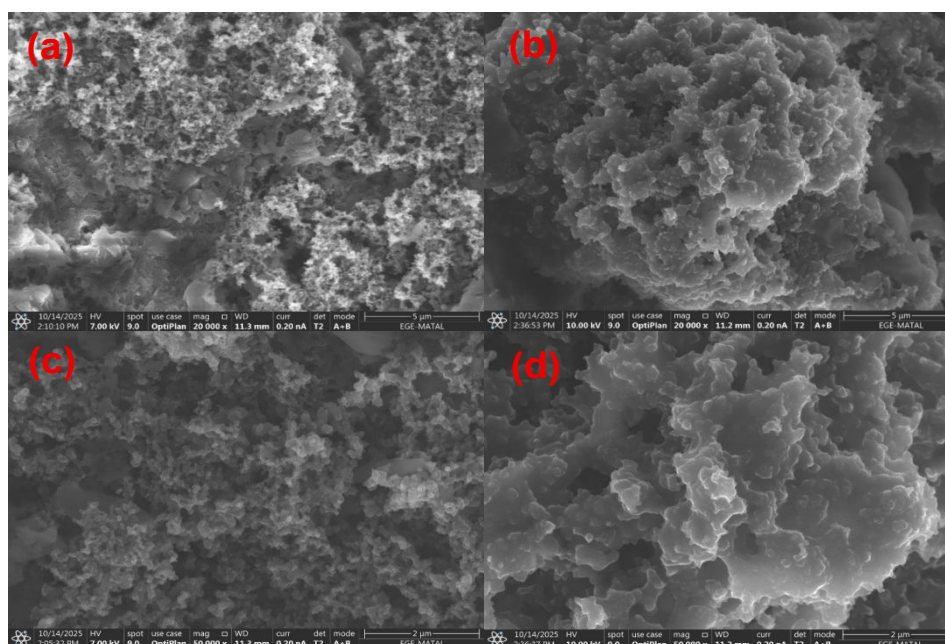


Fig. 6. SEM analyses: (a) 20kX and (c) 50kX image of TMe-CuPc ; (b) 20kX and (d) 50kX image of n-TMe-CuPc.



the surface (Fig. 6a,c). In contrast, the non-peripheral derivative (n-TMe-Cu) forms a more continuous nanogranular film with compact granular domains and tighter interparticle contacts (Fig. 6b,d). At the examined magnifications, the superior electrochemical performance of n-TMe-Cu does not appear to arise from a more pronounced macroporous structure, but rather from improved grain connectivity and better local film continuity. This morphological contrast suggests that the dominant difference lies not in the abundance of large open pores, but in how the grains pack, organize, and maintain interparticle contact within the electrode layer. Such differences are expected to influence interfacial electrochemical processes by modulating the accessibility of electroactive domains and the continuity of local ion/electron transport pathways. In this respect, the more coherent nanogranular texture of n-TMe-Cu is consistent with the higher surface-controlled contribution obtained from the kinetic analysis, whereas the rougher and more discontinuous morphology of TMe-Cu is more likely to contain transport-limited regions^{22,23}.

Electrochemical Characterization of electrodes

Electrochemical performance of copper-based Pc derivatives as electrode materials was evaluated separately using a standard three-electrode configuration in 1 M H₂SO₄ aqueous electrolyte. The working electrodes were prepared by casting a composite paste containing 80 wt% phthalocyanine derivative, 15 wt% conductive carbon black, and 5 wt% PVDF-HFP as binder onto a conductive substrate, resulting in an effective area of 1 cm². These composition ratios were optimized based on our prior experience with Pc-based electrode materials¹¹.

At a scan rate of 50 mV s⁻¹, gravimetric capacitance values calculated from the CV curves show a pronounced contrast

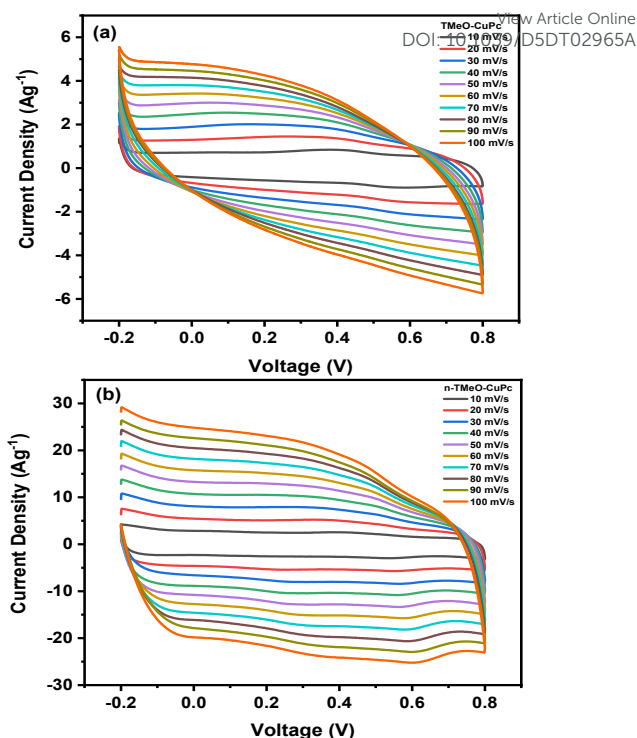


Fig. 7. CV curves of (a) TMeO-CuPc, (b) n-TMeO-CuPc at scan rates (10–100 mV s⁻¹).

between the two derivatives (Fig. 7a,b): n-TMe-Cu delivers 442.84 F g⁻¹, whereas TMe-Cu exhibits 79.82 F g⁻¹. This difference indicates that non-peripheral substitution enables a larger fraction of electroactive sites to participate under the applied timescale, yielding higher charge storage per unit mass in the same electrolyte

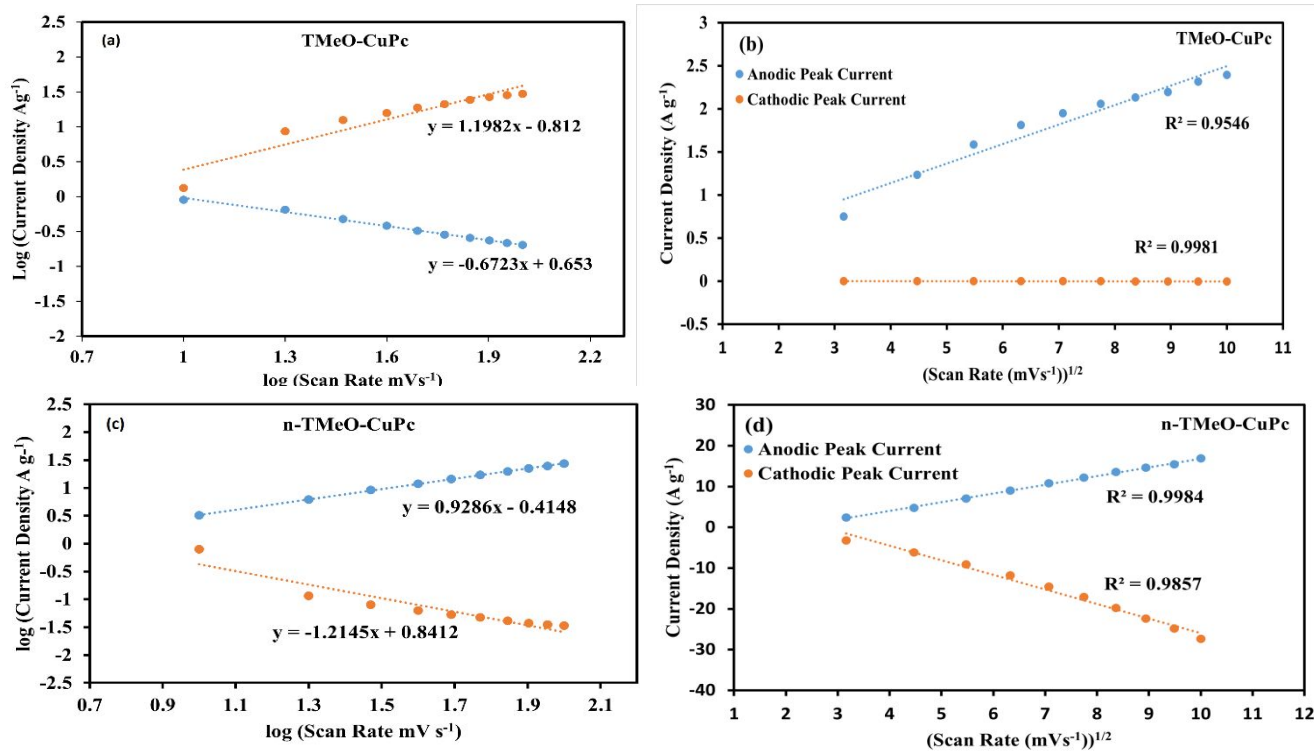


Fig. 8. Logarithm relationship between anodic peak current and scan rate (a) for TMeO-CuPc, (c) for n-TMeO-CuPc, Randles–Sevcik plot (linear curve of anodic and cathodic current density vs. square root of the scan rate) (b) for TMeO-CuPc, (d) for n-TMeO-CuPc.



and configuration²⁴.

The scan-rate-dependent CVs (Fig. 7) provide additional kinetic insight beyond the single-scan comparison. As the scan rate increases from 10 to 100 mV s⁻¹, both electrodes show the expected increase in current response. However, their profile evolution differs markedly. For n-TMe-Cu, the voltammograms retain a broad, quasi-rectangular envelope with persistent Faradaic distortion across the range, suggesting that a substantial portion of charge storage remains accessible within the shortened timescale and is governed by fast interfacial processes. In contrast, the TMe-Cu electrode shows a more pronounced distortion of the CV shape at higher scan rates, consistent with stronger polarization and a greater contribution from kinetically less accessible domains. At 50 mV s⁻¹, the capacitance derived from CV reaches 442.84 F g⁻¹ for n-TMe-Cu, compared with 79.82 F g⁻¹ for TMe-Cu, confirming the substantially higher electrochemical utilization of the non-peripheral derivative under identical conditions.

To further quantify charge-storage kinetics, the dependence of current (*i*) on scan rate (*v*) was analysed using the power-law relationship²⁵.

$$i(v) = av^b \text{ (Eq-6)}$$

Here, the exponent *b* provides a qualitative indicator of the kinetic regime: values close to 0.5 are characteristic of diffusion-limited processes, whereas values close to 1 indicate predominantly surface-controlled behaviour.²⁶ The *b* values extracted at 0.5 V are presented in Figure 8a and Figure 8c and indicate that both electrodes exhibit largely surface-controlled kinetics, with n-TMe-Cu displaying a pronounced surface-controlled contribution, consistent with pseudocapacitive-like behaviour²⁶.

As a complementary assessment, Randles–Sevcik-type analysis was employed by examining the relationship between redox current and

$v^{1/2}$ (Fig. 8b,d). TMe-Cu shows clear linearity primarily for the anodic branch ($R^2 = 0.9546$), while the cathodic branch deviates from ideal diffusion scaling, indicating mixed kinetics. In contrast, n-TMe-Cu shows strong linearity for both anodic and cathodic branches ($R^2 = 0.9984$ and 0.9857 , respectively), suggesting that diffusion-related transport contributes measurably to the overall response. Notably, this diffusion-related contribution can coexist with fast surface-controlled charge storage, consistent with the broad CV envelopes and the high capacitance observed for n-TMe-Cu.

To quantify the relative contributions of surface-controlled and diffusion-controlled charge storage, the Dunn method was applied²⁶:

$$i_{total} = i_{capacitive} + i_{diffusion} \text{ (Eq-7)}$$

$$\frac{i(v)}{v^{1/2}} = k_1 v^{1/2} + k_2 \text{ (Eq-8)}$$

where $k_1 v$ corresponds to surface-controlled contributions and $k_2 v^{1/2}$ represents diffusion-limited contributions. Importantly, the surface-controlled (capacitive) term in the Dunn formalism is not restricted to pure electric double-layer charging; it also includes fast surface-confined Faradaic (pseudocapacitive) processes that scale linearly with scan rate. As shown in Figure 9, n-TMe-Cu exhibits a consistently larger surface-controlled contribution than TMe-Cu across the entire scan-rate range. At 50 mV s⁻¹, the surface-controlled fraction reaches 83.5% for n-TMe-Cu, whereas TMe-Cu displays 49.2%. Across 10–100 mV s⁻¹, this contribution increases from 71.4% to 95.5% for n-TMe-Cu, while it rises from 31.7% to 68.6% for TMe-Cu. These results indicate that non-peripheral substitution enables a larger fraction of electroactive domains to

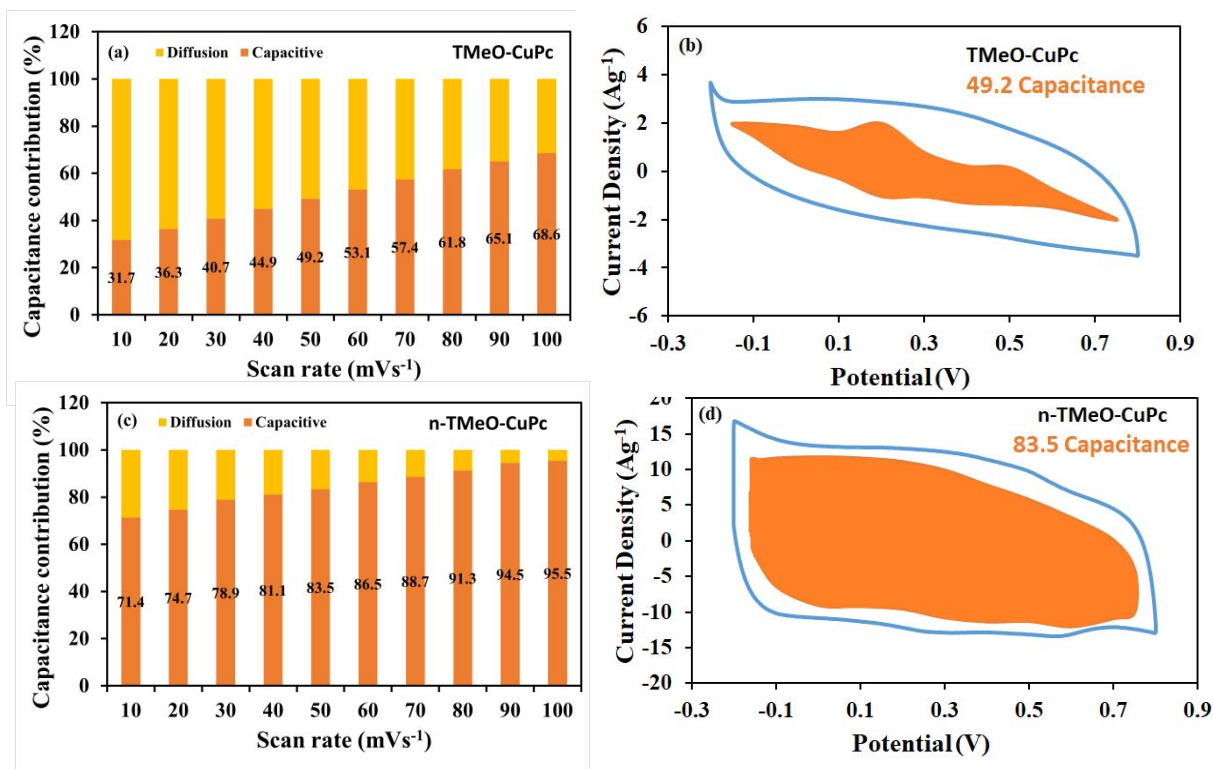


Fig. 9. Variation of capacitive and diffusion charge distributions ratio at different scan rates (a) of TMe-CuPc, (c) of n-TMe-CuPc, (b) capacitive contribution of TMe-CuPc electrode at a scan rate of 50 mV s⁻¹ (d) capacitive contribution of n-TMe-CuPc electrode at a scan rate of 50 mV s⁻¹.



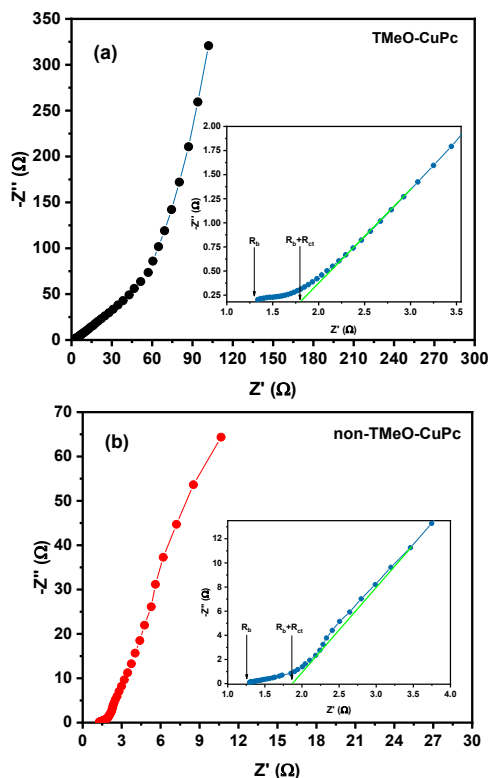


Fig. 10. Nyquist impedance spectra of the CuPc-based electrodes recorded in 1 M H_2SO_4 using a three-electrode configuration: (a) TMeO-CuPc and (b) n-TMeO-CuPc. For TMeO-CuPc, the high-frequency intercept corresponds to an R_b of 1.30 Ω and the arc diameter gives an R_{ct} of 0.50 Ω . For n-TMeO-CuPc, R_b is 1.25 Ω and R_{ct} is 0.60 Ω based on the same graphical evaluation. Insets highlight the high-frequency region

participate through rapidly accessible interfacial pathways within the CV timescale. In contrast, the peripheral derivative shows a greater relative contribution from transport-limited regions,

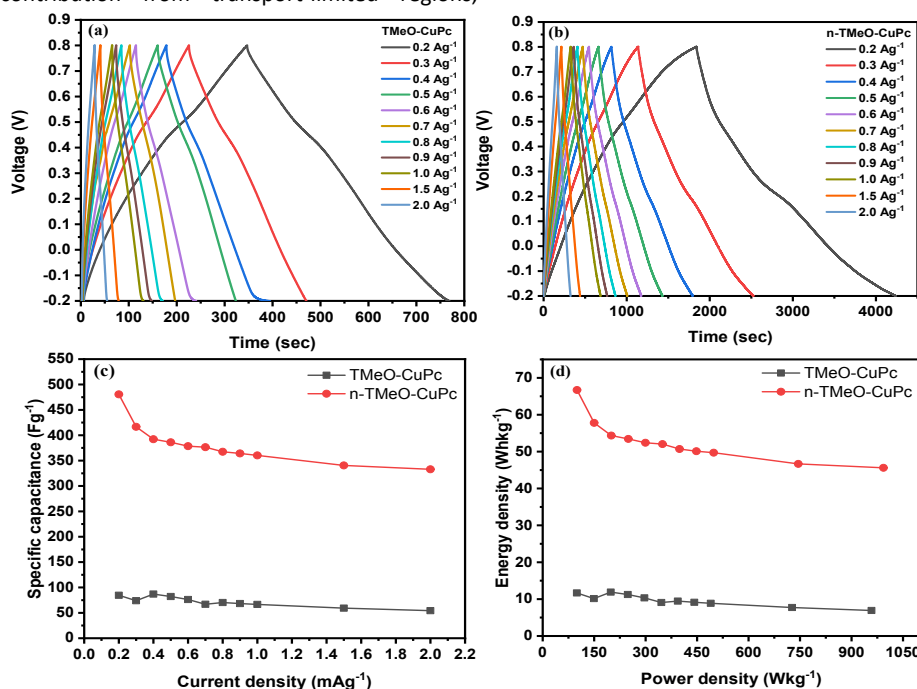


Fig. 11. CDC curve of (a) TMeO-CuPc, (b) n-TMeO-CuPc different current densities, (c) Specific capacity at a function of different current densities (0.2–2.0 Ag^{-1}) (calculated from CDC curve), (d) Comparison of energy density and power density calculated from CDC curves of TMeO-CuPc and n-TMeO-CuPc at various current distributions (Ragone plot).

particularly at lower scan rates. Combined with the SEM observations, the kinetic analysis indicates that the improved electrochemical performance of n-TMeO-Cu arises primarily from a more favourable electrode microstructure, which promotes interfacial accessibility and more efficient charge-storage kinetics, rather than from a simple increase in macroporosity.

Electrochemical impedance spectroscopy (EIS) measurements were performed to evaluate the interfacial charge-transfer and transport characteristics of the CuPc-based electrodes (Fig. 10a,b). The Nyquist plots exhibit a clear high-frequency intercept on the real axis corresponding to the solution/bulk resistance, followed by a high-to-mid frequency interfacial response associated with charge-transfer and ion-transport processes in the electrode layer²⁷. For clarity, the high-frequency region is shown as an inset in Figure 10. The TMeO-CuPc electrode exhibits an R_b value of 1.34 Ω , an R_{ct} value of 0.46 Ω , whereas the corresponding values for n-TMeO-CuPc are 1.29 Ω and 0.59 Ω , respectively. These results indicate that the two electrodes display comparable ohmic and interfacial resistance values, and therefore the superior electrochemical performance of n-TMeO-CuPc cannot be ascribed simply to a reduction in charge-transfer resistance.

More importantly, differences become evident in the overall impedance response and low-frequency behaviour, which reflect ion transport and electrochemical accessibility within the electrode architecture. In this respect, the EIS results are consistent with the scan-rate-dependent CV and Dunn analyses, indicating that the non-peripheral derivative enables more effective electrochemical utilization of accessible charge-storage domains despite not exhibiting a lower R_{ct} value. Accordingly, the performance advantage of n-TMeO-CuPc is more reasonably attributed to a more favourable electrode microstructure and interfacial accessibility than to a simple decrease in interfacial resistance^{28,29}.

The charge–discharge behaviour of CuPc-based electrodes was further examined using galvanostatic charge–discharge (GCD)



measurements over a wide range of current densities (Fig. 11a,b), which provides insight into rate capability and charge-storage dynamics of the peripheral (TMeO-CuPc) and non-peripheral (n-TMeO-CuPc) derivatives.

Across all current densities (0.2–2.0 A g⁻¹), n-TMeO-CuPc exhibits substantially longer discharge times than TMeO-CuPc, in agreement with its higher charge-storage capacity. At 1 A g⁻¹, n-TMeO-CuPc

substitution enhances effective electrochemical utilization and rate capability, rather than relying on a markedly reduced interfacial resistance.

The cycling stability of the electrodes was evaluated by galvanostatic charge–discharge measurements for 5000 cycles at a relatively high current density of 2 A g⁻¹ under ambient atmosphere (Fig. 12). The n-TMeO-CuPc electrode delivers an initial specific capacitance of 358.3 F g⁻¹ and maintains 286.3 F g⁻¹ after prolonged operation, corresponding to 80% capacitance retention. A comparable retention ratio is observed for TMeO-CuPc, which sustains 44.4 F g⁻¹ from an initial value of 60 F g⁻¹. These results demonstrate that both electrodes exhibit robust capacitive behaviour even at high current load and without any special environmental control, while the non-peripherally substituted n-TMeO-CuPc (80%) consistently provides several-fold higher capacitance than its peripheral analogue, confirming its clear advantage for practical supercapacitor applications. As summarized in Table S1, the present CuPc system performs competitively relative to representative phthalocyanine-based supercapacitor electrodes, while providing a clearer molecular-level structure–property correlation than most composite or device-oriented architectures. The n-TMeO-Cu electrode delivers 360 F g⁻¹ at 1 A g⁻¹ with 80% capacitance retention after 5000 cycles, placing it above several previously reported CuPc- and MPc-based electrodes evaluated under comparable three-electrode conditions. While some rGO- or CNT-containing hybrid systems achieve higher absolute capacitance or device-level energy density, those enhancements are often coupled to additional contributions from conductive scaffolds and composite-engineering effects. By contrast, the present work evaluates a structurally controlled pair of positional isomers within the same CuPc framework, allowing the influence of substituent geometry on electrode microstructure, interfacial accessibility, and charge-storage kinetics to be identified more directly. The results therefore highlight that the importance of this system lies not only in its electrochemical performance, but also in demonstrating how non-peripheral substitution can translate into a more coherent electrode morphology and a larger surface-controlled contribution to capacitive charge storage.^{33–35}

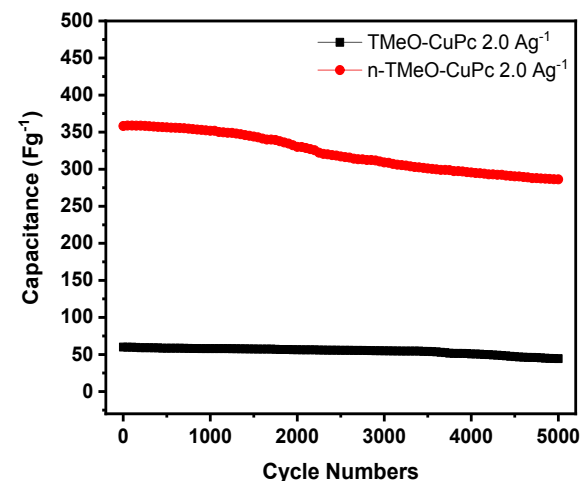


Fig. 12. Cycling stability of the CuPc-based electrodes evaluated by galvanostatic charge–discharge (GCD) at a current density of 2 A g⁻¹ over 5000 cycles in 1 M H₂SO₄ using a three-electrode configuration: (a) peripheral derivative (TMeO-CuPc) and (b) non-peripheral derivative (non-TMeO-CuPc). The plots show the capacitance retention as a function of cycle number, highlighting the long-term charge–discharge durability under repeated high-rate cycling.

delivers a specific capacitance of 360 F g⁻¹, whereas TMeO-CuPc provides 67 F g⁻¹. With increasing current density, the capacitance decreases for both electrodes, reflecting the expected limitation of ion access and active-site utilization as the timescale becomes shorter; however, n-TMeO-CuPc maintains markedly higher capacitance across the entire range and retains over 333 F g⁻¹ even at 2 A g⁻¹ (Fig. 11c). This behaviour indicates superior rate capability of the non-peripheral derivative, consistent with a larger fraction of electrochemically accessible charge-storage sites and a more favourable kinetic balance under fast cycling conditions³⁰. Literature on molecularly engineered phthalocyanine electrodes similarly emphasizes that electrode-level accessibility and utilization of redox-active domains strongly govern high-rate performance, particularly when transport limitations become pronounced³¹. The GCD profiles also suggest distinct charge-storage characteristics. While TMeO-CuPc shows more nearly linear charge–discharge traces typical of predominantly capacitive behaviour, n-TMeO-CuPc displays more pronounced deviation from ideal linearity, consistent with additional pseudocapacitive/faradaic contributions superimposed on double-layer charging³². Ragone analysis further highlights the performance gap: n-TMeO-CuPc achieves substantially higher energy density (up to 67 Wh kg⁻¹ at a power density of 99.97 A g⁻¹) than TMeO-CuPc (<15 Wh kg⁻¹) while maintaining higher energy output at elevated power demands (99.66 A g⁻¹) (Fig. 11d). Overall, the GCD results corroborate the CV and kinetic analyses by demonstrating that non-peripheral

Conclusions

In this work, two structurally distinct copper phthalocyanine derivatives, peripherally substituted (TMeO-CuPc) and non-peripherally substituted (n-TMeO-CuPc), were synthesized using a (3,4,5-trimethoxybenzyl)oxy functional group and systematically evaluated as supercapacitor electrode materials. Structural characterization by MALDI-TOF MS, FT-IR, UV–vis, XRD, and XPS analyses confirmed the expected substitution-dependent differences in molecular ordering. Electrochemical evaluation by cyclic voltammetry, galvanostatic charge–discharge, electrochemical impedance spectroscopy, and scan-rate-dependent kinetic analyses revealed a pronounced performance advantage for n-TMeO-Cu, which delivered a specific capacitance of up to 360 F g⁻¹ at 1 A g⁻¹ and retained 80% of its initial capacitance after 5000 charge–discharge cycles. Kinetic analysis showed that n-TMe-



Cu exhibits a consistently higher surface-controlled contribution than TMe-Cu, indicating that a larger fraction of charge storage proceeds through rapidly accessible interfacial pathways. When interpreted together with the SEM observations, these findings suggest that the superior performance of the non-peripheral derivative is associated not with a simple increase in macroporosity or a lower charge-transfer resistance, but with a more favourable electrode microstructure that improves interfacial accessibility and electrochemical utilization. Overall, the results demonstrate that substituent position plays a decisive role in regulating electrode organization, charge-storage kinetics, and rate capability in CuPc-based electrodes. This work therefore identifies substituent geometry as an effective molecular design parameter for the development of high-performance organic supercapacitor materials.

Author contributions

SSG: conceptualization, methodology, formal analysis, investigation, and writing- the original draft. BAÖ: methodology, visualization, investigation, formal analysis, and writing-the original draft. DŞ: investigation, visualization, writing-editing. GY: formal analysis, visualization, writing-editing, BTE: Formal analysis, methodology, writing-reviewing, editing. BG: resources, methodology, writing, review, editing, supervision. ZB:resources, conceptualization, writing-reviewing, editing, supervision. All authors have read and agreed to the submitted version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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- The data supporting this article have been included as part of the Supplementary Information.

