Development of Functional Vanillin-Based Biomaterials from Lignin Biomass for Economic Value Addition

Postdoctoral Fellowship 3P Tahun 2026

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Abstract

Vanillin offers a versatile molecular platform for developing functional organic materials with potential applications in sustainable energy technologies. This study integrates the synthesis, structural characterization, computational investigation, and electrochemical evaluation of vanillin derivatives and phenylcalix[4]resorcinarenes. Two O-alkylated vanillin derivatives were synthesized with yields of 91–93%, followed by the preparation of eleven functionalized phenylcalix[4]resorcinarenes, including two newly synthesized compounds. Molecular structures were characterized using NMR, HRMS, and complementary spectroscopic techniques. Single-crystal X-ray diffraction confirmed their molecular geometries and solid-state arrangements, while Hirshfeld surface and energy framework analyses revealed intermolecular interactions governing crystal packing. Density functional theory provided further insights into the electronic properties of vanillin derivatives. Cyclic voltammetry demonstrated substituent-dependent electrochemical responses, with anodic currents ranging from 40.21 to 131.66 μA. These findings highlight the influence of molecular functionalization on structural, supramolecular, and electrochemical properties, providing a foundation for further exploration of vanillin-based organic materials in sustainable energy applications and electrochemical energy storage systems.

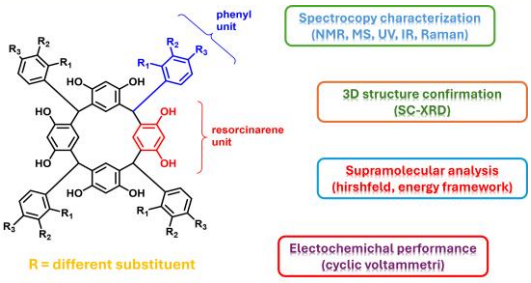
Keyword: Phenylcalix[4]resorcinarenes; SCXRD; Electrochemical Properties; Sustainable Energy Materials.

Introduction

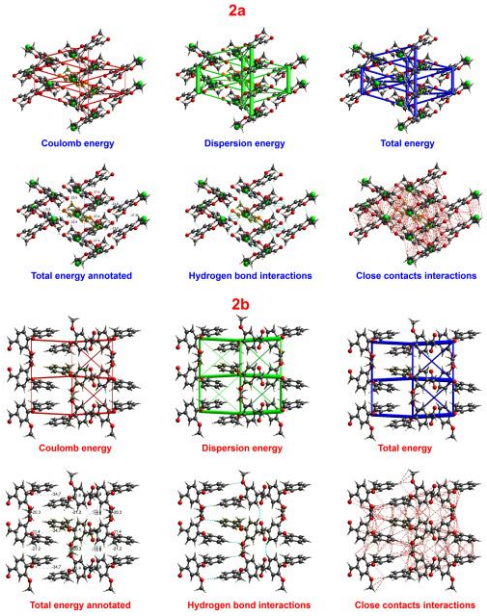
The growing demand for sustainable energy technologies has encouraged the exploration of lignocellulosic biomass as a renewable source of functional organic materials. Vanillin, an aromatic compound obtainable from lignin, offers a versatile molecular platform due to its hydroxyl, methoxy, and aldehyde functionalities. Chemical modification through O-alkylation enables structural diversification, while condensation with resorcinol produces phenylcalix[4]resorcinarenes, macrocyclic compounds with tunable molecular architectures and physicochemical properties. Peripheral functionalization can influence electronic distribution, molecular conformation, intermolecular interactions, and electrochemical behavior, making these compounds interesting candidates for energy-related material development. Understanding these structure–property relationships requires integrated experimental and computational approaches. Spectroscopic characterization, single-crystal X-ray diffraction, Hirshfeld surface analysis, and density functional theory provide insights into molecular structures, electronic properties, and supramolecular organization. Furthermore, cyclic voltammetry enables evaluation of electrochemical responses associated with structural modifications. Together, these approaches establish a foundation for exploring vanillin-based molecular systems as functional organic materials with potential applications in sustainable energy technologies and future electrochemical energy storage research.

Research Method

Vanillin was subjected to O-alkylation using 1-bromo-3-chloropropane and benzyl bromide in the presence of K_2CO_3 and DMSO at room temperature for 24 h. Subsequently, eleven phenylcalix[4]resorcinarene derivatives were synthesized through acid-catalyzed condensation of resorcinol with selected aromatic aldehydes under reflux in ethanol for 24 h. The synthesized compounds were characterized using ^1H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry (HRMS), UV–Vis, ATR-IR, and Raman spectroscopy to establish their molecular identities and functional groups. Single-crystal X-ray diffraction (SC-XRD) was performed on selected compounds to determine molecular geometries, conformations, and crystallographic arrangements. Hirshfeld surface analysis and intermolecular energy framework calculations were conducted using CrystalExplorer to investigate supramolecular interactions and crystal packing. Density functional theory (DFT) calculations at the B3LYP/6-31++G(d,p) level were employed to evaluate the electronic properties of O-alkylated vanillin derivatives. Finally, cyclic voltammetry (CV) was performed to examine the electrochemical responses of phenylcalix[4]resorcinarenes and assess the influence of peripheral functionalization on their electrochemical behavior and properties.



Picture 1. Molecular framework of functionalized phenylcalix[4]resorcinarenes and their characterization strategies.



Picture 2. Figure 5. Energy framework analysis for **2a** and **2b**.

Discussion & Result

O-Alkylation of vanillin successfully afforded two derivatives (2a and 2b) in 93% and 91% yields, respectively. Subsequent condensation reactions produced eleven phenylcalix[4]resorcinarenes in 81–91% yields, including two newly synthesized derivatives. Spectroscopic analyses confirmed their molecular structures, while single-crystal X-ray diffraction revealed distinct molecular geometries and crystal packing arrangements. Hirshfeld surface and energy framework analyses identified hydrogen bonding and dispersion interactions as important contributors to crystal stabilization. The functionalized macrocycle 4 adopted a chair conformation, with H···H (46.2%) and O···H/H···O (21.1%) contacts dominating its intermolecular interactions. Density functional theory provided insights into the electronic distributions and reactivity of O-alkylated vanillin derivatives. Cyclic voltammetry demonstrated substituent-dependent electrochemical responses, with compound 2 exhibiting the highest anodic current (131.66 μA) and compound 6 the lowest (40.21 μA). Peripheral functionalization also reduced current density by 7.6% between compounds 1 and 4, highlighting structure-dependent electrochemical behavior relevant to future investigations of organic energy materials and storage applications.

Conclusion

- Two O-alkylated vanillin derivatives were successfully synthesized with high yields of 91–93%.
- Eleven functionalized phenylcalix[4]resorcinarenes, including two novel derivatives, were synthesized with yields ranging from 81% to 91%.
- Spectroscopic analyses using NMR, HRMS, UV–Vis, ATR-IR, and Raman confirmed the molecular structures of the synthesized compounds.
- Single-crystal X-ray diffraction revealed molecular geometries, conformational characteristics, and crystal packing arrangements.
- Hirshfeld surface analysis identified hydrogen bonding and van der Waals contacts as important intermolecular interactions.
- Energy framework calculations highlighted the significant contribution of dispersion interactions to crystal stabilization.
- DFT calculations provided insights into the electronic structures and chemical reactivity of O-alkylated vanillin derivatives.
- Cyclic voltammetry revealed substituent-dependent electrochemical responses, with anodic currents ranging from 40.21 to 131.66 μA.
- Peripheral functionalization influenced electrochemical behavior, including a 7.6% decrease in current density between macrocyclic compounds 1 and 4.
- Overall, these findings establish important structure–property relationships and support further investigation of vanillin-based macrocycles as potential functional materials for sustainable energy applications.