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ABSTRACT:

Metal Phthalocyanines for Energy Technologies: From Sustainable Synthesis to CO₂-to-Methanol Electrocatalysis

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Phthalocyanines have long represented a benchmark class of functional molecular materials for energy technologies owing to their exceptional chemical robustness and highly tunable electronic properties [1]. Among them, cobalt phthalocyanines (CoPcs) represent the only class of molecular electrocatalysts reported to date to promote the electrochemical conversion of CO₂ to methanol [2], one of the most challenging CO₂ reduction processes because of its complex multi-electron/multi-proton nature and the severe selectivity limitations imposed by competing reaction pathways.

This contribution discusses how sustainable synthetic methodologies and molecular functionalization can be leveraged to access high-performance CoPc systems for selective CO₂-to-methanol electrocatalysis, with particular emphasis on environmentally conscious reaction media for accessing both unsubstituted and functionalized CoPcs [3].

Notably, a tetrabutoxy-substituted CoPc derivative exhibits Faradaic efficiencies exceeding 40% toward methanol formation together with enhanced operational stability compared to unsubstituted CoPc. Advanced spectroscopic, structural, and surface investigations provide insight into the role of peripheral butoxy substitution in determining catalyst organization and electronic properties, highlighting the critical role of peripheral molecular engineering in electrocatalytic performance.

[1] A. Kumar, V.K. Vashistha and D.K. Das, *Coord. Chem. Rev.*, 431, 213678 (2021).

[2] Y. Wu, Z. Jiang, X. Lu, Y. Liang and H. Wang, *Nature*, 575, 639–642 (2019).

[3] G. Zanotti, F. Palmeri, V. Raglione, A. Khodadadi, C. Tabaries, J. Capitolis, M. Prevot, L. Piccolo, M. Zendejdel, R. Flammini and G. Contini, *Chem. Eur. J.*, 0:e02264 (2025).