Finanziato dall'Unione europea NextGenerationEU | Ministero dell'Università e della Ricerca | Italiadomani Piano Nazionale di Ripresa e Resilienza | NEST Network for Energy Sustainable Transition

ALLEGATO B

PE00000021
"PNRR MUR - M4C2 – NEST - Extended Partnership Network 4 Energy Sustainable Transition"

SPOKE N. 4

CUP D33C22001330002

Research proposal

Innovation for novel membranes for electrolyzers

CLEAN-MEM - Clean Monomers for Electrolyzer Membranes

- Name of the PIs' host institution for the project: University of Camerino
- Name of the Principal Investigators (PIs): Prof. Alessandro Palmieri and Prof. Marino Petrini
- Proposal duration in months: 12

ROLE IN THE PROJECT	*NAME*	*SURNAME*	*INSTITUTION/ DEPARTMENT*	*QUALIFICATION*	*YOUNG (under 40 al 31.12.2023)*	*F/M*
Principal Investigator	*Alessandro*	*Palmieri*	*University of Camerino / School of Science and Technology / Chemistry Division*	*Associate Professor*		*M*
co-Principal Investigator (PI)	*Marino*	*Petrini*	*University of Camerino / School of Science and Technology / Chemistry Division*	*Full Professor*		*M*

ABSTRACT

The CLEAN-MEM project, within a concise one-year framework, is dedicated to the monomer production process for creating novel, fluorine-free membrane electrode assemblies (MEAs) for water electrolyzers, a critical component in green hydrogen (H_2) production. In alignment with the European Green Deal's objectives for a sustainable future, this initiative focuses on the synthesis of innovative Polymers of Intrinsic Microporosity (PIMs) featuring benzimidazole (BI) groups. These efforts aim to replace current high-cost, less sustainable options with a greener, more efficient alternative. The project's core activities span the targeted synthesis of novel monomers, their subsequent polymerization to fabricate advanced PIM-PBI membranes, and the integration of these membranes into MEAs for performance evaluation in electrolyzers. Key milestones set for the project include achieving high purity and yield in monomer synthesis, successful prototype membrane production, and demonstrating improved performance and durability in electrolyzer tests. Deliverables are focused on detailed reports of monomer synthesis processes, prototype development, and comprehensive performance testing outcomes, alongside optimization strategies for future scalability. The project's KPIs emphasize the critical aspects of monomer production—purity, yield, cost-effectiveness, and environmental sustainability. By concentrating on the foundational step of monomer production, CLEAN-MEM aims to significantly contribute to the scalability and adoption of environmentally sustainable materials for the green hydrogen economy, thereby supporting Europe's ambitious climate and energy goals.

RESEARCH PROPOSAL
Sections (a) and (b) should not exceed 4 pages. References do not count towards the page limits.

Section a. State-of-the-art and objectives

The European Green Deal (EGD) seeks to make Europe resource-efficient, competitive, and emission-free by 2050; to achieve this, Europe must shift to renewables while maintaining stability in energy, mobility, and industrial systems. Industrial manufacturing, transportation and energy production must update their technologies to exploit renewable energy sources and waste products while reducing CO_2 emissions. H_2 from renewable sources, or green-H_2 (gH_2), will play a crucial role in decarbonization as a renewable energy storage solution. Creating new industrial and production processes at the European level is necessary to achieve the energy transition and meet the goals of the EGD.

Technologies for H_2 production (water electrolyzers, WEs) is based on electrochemistry and employ ion exchange membranes (IEMs). Commercial IEMs are based on fluorine, which is a critical raw material (CRW), and are characterized by high cost, limited operating temperature range, performance decay and limited durability [1]. Combining the advantages of Polymers of Intrinsic Microporosity (PIMs) which have interconnected subnanometer-sized micropores in their structure, with ionisable functional groups that provide excellent mechanical properties and thermochemical stability, can result in high-performance, environmentally sustainable electrochemical energy devices. Examples include benzimidazoles (BIs) groups in the case of proton exchange membranes (PEMs). In this framework, **CLEAN-MEM** aims at proposing novel monomers to produce PIMs containing functional monomer units. These monomers will be polymerized by our partners in order to fabricate MEAs to be used in WE.

Currently, commercially available IEMs for low-temperature operation in WEs are based on Perfluorinated Sulfonic Acid (PFSA). This is a random copolymer composed of polytetrafluoroethylene (PTFE) and sidechains with SO_3H groups, known for their remarkable ion conductivity and chemical-mechanical stability [2]. However, membranes are the weakest component for long-term performance in WEs [4]. Performance decay and reduced durability are due to membrane fouling or degradation from mechanical, thermal, and chemical or electrochemical factors. Non-PFSA IEMs will help address these issues [5]. The subnanometersized micropores in PIM membranes, generated by rigid and contorted backbones, create confined channels for fast and selective transport of molecules and ions [6]. PIM membranes are typically designed for non-aqueous electrolytes due to hydrophobic chain segments, but hydrophilic IEMs are needed for energy devices. One approach is to chemically incorporating hydrophilic functionalities (-COOH, -NH_2) or charged moieties in the original monomers. An aromatic group such as BI (benzimidazole) can be easily incorporated into the rigid PIM backbone to make it hydrophilic through protonation. BI polymers are a promising alternative to PFSA IEMs, offering lower cost, satisfactory chemical and mechanical stability, and high operation temperature [7]. Efficient proton transfer in polybenzimidazole (PBI), via nitrogen atoms, is typically mediated by phosphoric acid (PA) [8]. High PA retention enable WEs operation under a wide range of temperature (–20 °C to 200 °C) without external humidification [9].

In order to develop innovative fluorine-free MEAs for energy devices characterized by reduced cost and increased environmental sustainability, all the components, namely i) PIM-based membranes monomers need to be synthetized and optimized, as detailed below. For all the components, specific objectives will be reached in the framework of **CLEAN-MEM**, as summarized in Table 1.

Table 1 CLEAN-MEM Objectives

Objectives	Parameters
Fabrication tetrafunctional ammines and bifunctional hydroxide	At least 4 functional rigid tetramines for PIM production At least 4 functional rigid dihydoxy for PIM production Purity: Achieve a minimum of 85% purity for the synthesized tetramine, as determined by High-Performance Liquid Chromatography (HPLC) analysis. This high level of purity is essential to minimize the impact of impurities on the properties of the resulting polyimides. Yield: Target a synthetic yield of at least 70% from the initial reagents to the final tetramine product, based on molar quantities. This objective is set to ensure an efficient conversion of starting materials into the desired product, reducing waste and costs. Selectivity: Ensure that the synthesis process favors the production of the desired tetramine isomer, with a selectivity goal of over 90%. This is particularly important if the tetramine has isomers that could negatively affect the properties of the final polyimides. Scalability: Develop a synthesis route that is scalable, with the ability to be replicated on a pilot scale (e.g., 100 kg batches) without significant loss in yield or purity. This ensures that the laboratory-scale synthesis is viable for industrial production. Environmental Impact: Minimize the environmental impact of the synthesis process by targeting a reduction in hazardous solvent use and waste production. Aim for a process that uses green chemistry principles, such as solvent recycling or the use of safer solvents.

Section b. Methodology

The methodology of the **CLEAN-MEM** project focuses on the synthesis and optimization of monomers to produce polymeric membranes for WEs. These membranes aim to overcome the limitations of current commercial IEMs by utilizing PIMs and incorporating BI groups for improved performance and sustainability. The approach is divided into two main strategies:

Synthesis of monomer precursor for highly rigid PIMs containing BI groups in the main-chain: This involves the development of novel monomers that will lead to the creation of microporous PBI structures. These monomers are designed to enhance the rigidity and contortion of the PBI chain, thereby generating intrinsic microporosity which is crucial for the effective transport of ions within the membrane. The synthesis process targets the production of PIM-PBIs with optimal mechanical properties and thermochemical stability, suitable for high-performance applications in energy devices.

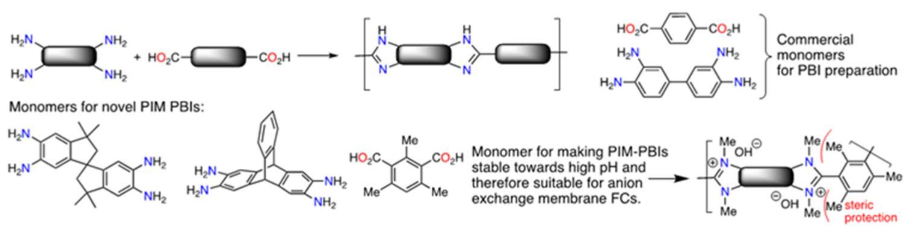

Figure 1: Synthesis of PIMN-PBIs and co polymers from produced monomers

Synthesis of PIMs with pendant BI units: Leveraging state-of-the-art (SoA) techniques in polymer chemistry, this strategy focuses on incorporating BI-containing polymers that exhibit high proton conductivity. By employing super-acid mediated reactions and xanthene ring-forming methodologies, a fully fused-ring PIM-BI with pendant BI groups is synthesized. This innovative approach aims at producing membranes that not only meet the required conductivity and stability standards but also address the environmental and cost concerns associated with current IEMs**.**

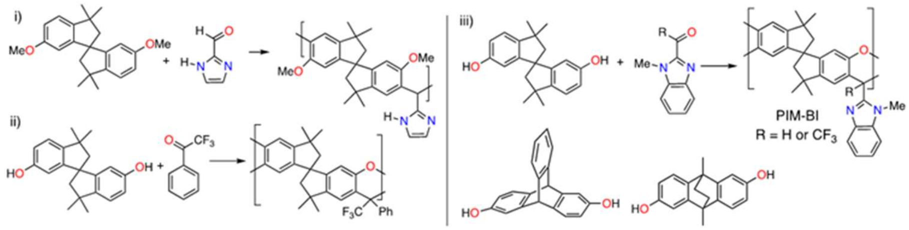

Figure2: Reaction of polymerization to produce microporous PBI from monomer produced

Both strategies are underpinned by rigorous experimental protocols that include the synthesis of monomers, polymerization to produce microporous structures, and thorough characterization of the resulting membranes. These efforts are directed towards achieving the **CLEAN-MEM** project's objectives of reducing the environmental impact of membrane production, lowering costs, and enhancing the performance of electrolyzers for sustainable energy solutions.

In conclusion, the **CLEAN-MEM** project's methodology is not only focused on the innovative synthesis of monomers and the development of advanced PIMs but also emphasizes the importance of a collaborative and iterative process. There will be constant interaction with our partnering laboratory, which specializes in the synthesis of polymers from these monomers. This laboratory will also be responsible for fabricating membrane electrode assemblies (MEAs) and testing them for their performance in WEs.

This collaborative approach ensures that feedback from the performance testing phase informs subsequent synthesis and optimization efforts. Such a feedback loop is crucial for identifying and addressing potential challenges in membrane performance, durability, and efficiency in real-world applications. By integrating synthesis, testing, and optimization processes, the **CLEAN-MEM** project aims to rapidly advance the development of high-performance, environmentally sustainable membranes for WEs. This concerted effort is expected to contribute significantly to the achievement of the European Green Deal objectives by facilitating the transition to renewable energy sources and reducing the carbon footprint of industrial processes.

Section c. Available instrumentations and resources

The research them has access to a very furnished library, meeting rooms and computer rooms. Moreover, it can access to a wide selection of chemicals as well as to an extraordinary number of equipment such as the FLOWLAB platform by Uniqsis, microwave reactors by Biotage, a variety of lamps dedicated to photochemical reactions, the H-MINI CUBE Plus to perform hydrogenation under flow chemical condition, NMR spectrometers, numerous Mass Spectrometer an extensive HPLC and GC facilities, microanalysis and infrared FT-IR spectrometers.

Section d. GANTT Diagram for a Year-Long Project

The GANTT diagram for the one-year **CLEAN-MEM** project would be structured as follows:

	1	2	3	4	5	6	7	8	9	10	11	12
Research and Initial Development Phase	■	■										
Accelerated Synthesis and Fabrication Phase			■	■	M1, D1							
Rapid Characterization and Initial Testing Phase						■	M2,D2					
Optimization and Feedback Integration Phase								■	M3	■	■	■
Final Evaluation, Reporting, and Dissemination Phase												M4, D3

Research and Initial Development Phase (Months 1-2): A focused period for literature review, design of novel monomers, and initiation of small-scale synthesis trials. This phase will be more compact, emphasizing the rapid identification of promising monomer candidates.

Accelerated Synthesis and Fabrication Phase (Months 3-5): Intense activity to synthesize the identified monomers, followed by fast feedback from the polymerization group for PIM fabrication. This phase will require efficient parallel processing and teamwork to meet the condensed timeline.

Rapid Characterization and Initial Testing Phase (Months 6-7) (by partner group): Shortened comprehensive testing of the synthesized PIMs, focusing on essential properties like mechanical strength, thermochemical stability, and ion transport. Initial tests in simulated electrolyzer conditions will also begin in this phase.

Optimization and Feedback Integration Phase (Months 8-12): A swift iterative feedback loop with testing partners to refine the monomer and polymer synthesis processes based on preliminary electrolyzer test outcomes.

Final Evaluation, Reporting, and Dissemination Phase (Month 12): Compilation and analysis of all project data, preparation of comprehensive final reports, and planning for the dissemination of findings to stakeholders and the scientific community.

Revised Section e. Milestones, Deliverables, and KPIs

Milestones

- **M1** Rapid Monomer Synthesis and PIM Fabrication: Completion of the synthesis and fabrication phases within the first five months with desired outcomes.
- **M2** Initial Positive Performance Feedback: Achieving promising laboratory test results for ion transport and stability by month 7.
- **M3** Optimized Prototype Ready for Pilot-scale Production: Development of an optimized prototype for pilot production by month 9.
- **M4** Achieved Target Performance in Real-World Testing: Meeting or surpassing target performance metrics in water electrolyzer tests by month 12.

Deliverables

D1 Synthesis and Fabrication Report: A document detailing the accelerated synthesis and fabrication process of monomers and PIMs.

D2 Initial Testing Report: Results from early-stage performance testing, highlighting potential areas for optimization.

D3 Final Project Documentation: A comprehensive report summarizing the project's outcomes, including research findings, synthesis methods, optimization strategies, and recommendations for future development**.**

KPIs

- Efficiency in Synthesis and Fabrication: Achieving streamlined synthesis and fabrication processes within the first half of the project timeline.
- Performance Metrics Achievement: Demonstrating key performance improvements in durability and ion conductivity in comparison with current benchmarks.
- Cost and Environmental Impact Reduction: Significantly lowering production costs and demonstrating a reduction in environmental impact through greener synthesis methods and reduced hazardous waste production.

Annexes: Curriculum vitae research team

Appendice dell'Allegato B

Curriculum vitae PI (max. 5 pages)

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PERSONAL INFORMATION

Palmieri Alessandro

ORCID: 0000-0001-6599-3937; Research ID: G-3741-2018; Scopus Author ID: 57219972565

URL for web site: https://docenti.unicam.it/pdett.aspx?ids=N&tv=d&UteId=543&ru=PA
https://sites.google.com/unicam.it/alessandro-palmieri/home-page

- **EDUCATION**

2007 PhD in Chemical Sciences
Department of Chemistry, University of Camerino, Italy
PhD Supervisor: Prof. Roberto Ballini

2002 Master's degree in Chemistry
Department of Chemistry, University of Camerino, Italy

- **CURRENT POSITION(S)**

2014 – Associate Professor
Department of Chemistry, University of Camerino, Italy

- **PREVIOUS POSITIONS**

2014 Postdoctoral Fellow
Department of Chemistry, University of Camerino, Italy

2010 – 2013 Assistant professor
Department of Chemistry, University of Camerino, Italy

2008 Visiting Postdoctoral Fellow in the Prof. Steven V. Ley research group (6 months)
Department of Chemistry, University of Cambridge (UK).

2007 – 2010 Postdoctoral Fellow
Department of Chemistry, University of Camerino, Italy

- **FELLOWSHIPS AND AWARDS**

2002 – 2004 Postgraduate scholarship
Department of Chemistry, University of Camerino, Italy

2011 ***Giacomo Ciamician» medal.*** The award is given to scholars under 35 years of age, by the Organic Chemistry Division of the Italian Chemical Society (SCI) for original researches in the field of organic chemistry.

2007 ***«Vincenzo Caglioti» prize for chemistry.*** The prize is for Italian or foreign scholars under 35 years of age, who have carried out research in a sector of Chemistry. The prize is an initiative of the "Accademia Nazionale dei Lincei", with the contribution of Fondazione «Guido Donegani» and the "Accademia Nazionale delle Scienze".

- **SUPERVISION OF GRADUATE STUDENTS AND POSTDOCTORAL FELLOWS (if applicable)**

2003 – 2024 Number of Postdocs / PhD / Master / Bachelor Students: 1 / 5 / 14 / 13
Department of Chemistry, University of Camerino, Italy

- **ORGANISATION OF SCIENTIFIC MEETINGS (if applicable)**

2023 *Member of the organizing* committee of "XIV Edition of the International School of Organometallic Chemistry, EuCheMS" 7-11 September, Camerino (I). (Number of participants: ~ 140)

2022 *Member of the organizing* committee of "2nd Virtual Symposium for Young Organic Chemists, SCI-ViSYOChem 2022" 24-27 October. (Number of participants: ~ 70)

2021 *Member of the organizing* committee of "XIII Edition of the International School of Organometallic Chemistry, EuCheMS" 1-3 September, online edition. (Number of participants: ~ 130)

2020 *Member of the organizing* committee of "1st Virtual Symposium for Young Organic Chemists, SCI-ViSYOChem 2020" 3-6 November. (Number of participants: ~ 120)

2019 *Member of the organizing* committee of "XII Edition of the International School of Organometallic Chemistry, EuCheMS" 31 August - 4 September, Camerino (I). (Number of participants: ~ 150)

2017 *Member of the organizing* committee of "XI Edition of the International School of Organometallic Chemistry, EuCheMS" 2-6 September, San Benedetto del Tronto (I). (Number of participants: ~ 200)

2010 *Member of the organizing committee of* "XXXIII Convegno Nazionale della Divisione di Chimica Organica della S.C.I." 12-16 September, San Benedetto del Tronto (I). (Number of participants: ~ 300)

2006 *Member of the organizing committee of* "XXV TUMA Convegno Interregionale della S.C.I." 29 June - 1 July, Camerino (I). (Number of participants: ~ 130)

- **INSTITUTIONAL RESPONSIBILITIES**

2024 – Past-President of the *Marche Section* of the Italian Chemical Society

2021 – 2023 President of the *Marche Section* of the Italian Chemical Society

2020 – Delegate for the "International Mobility and ERASMUS"
Department of Chemistry, University of Camerino, Italy

2014 – Member of the PhD council in *Chemical and Pharmaceutical Sciences and Biotechnology*
Department of Chemistry, University of Camerino, Italy

2014 –2020 Coordinator of the PhD curriculum in Chemical Sciences
Department of Chemistry, University of Camerino, Italy

2010 – 2013 Officer for mentoring of students in Chemical Sciences
Department of Chemistry, University of Camerino, Italy

- **REVIEWING ACTIVITIES**

2024 PhD Thesis Reviewer / University of Milan (I)
2023 Member of the Final Exam Commission for PhD in RESEARCH METHODS IN SCIENCE AND TECHNOLOGY / University of Urbino (I)
2023 PhD Thesis Reviewer / University of Parma (I)
2023 Member of the Commission for a position of RTD-A / University of Torino (I)
2019 PhD Thesis Reviewer / University of Perugia (I)

- **MEMBERSHIPS OF SCIENTIFIC SOCIETIES**

2002 – Member, Italian Chemical Society

- **MAJOR COLLABORATIONS**

    - Prof. Stefano Protti, Photochemistry, Chemistry Department, University of Pavia (I)
    - Prof. Davide Ravelli, Photochemistry, Chemistry Department, University of Pavia (I)
    - Prof. Luigi Vaccaro, Solid Supported Reagents, Department of Chemistry, Biology and Biotechnology, University of Perugia (I)
    - Prof. Vito Capriati, Deep eutectic Solvents, Department of Pharmacy and Pharmaceutical Science, University of Bari (I)
    - Prof. Giovanni Maestri, One-pot reactions, Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma (I)

Appendix: All current grants and on-going and submitted grant applications <u>of the PI</u> (Funding ID)

<u>Mandatory information</u> (does not count towards page limits)

Current grants (Please indicate "No funding" when applicable):

Project Title	*Funding source*	*Amount (Euros)*	*Period*	*Role of the PI*	*Relation to current proposal*
P2022HSF3R Xylonite:the new season of Xylochemistry	MUR PRIN 2022 bando PNRR	€ 51.610,00	30/11/2023 30/11/2025	RU - Coordination and research (5 months)	No relation with the current proposal

Appendice dell'Allegato B

Curriculum vitae CO-PI (max. 5 pages)

[Please follow the template below as much as possible (it may however be amended if necessary).]

PERSONAL INFORMATION

Petrini Marino
ORCID:0000-0002-4941-5878; Researcher ID (ISI): G-8899-2011; Author ID (Scopus): 7101613821

URL for web site: https://docenti.unicam.it/pdett.aspx?ids=N&tv=d&UteId=66&ru=PO.

- **EDUCATION**

1980 Master degree (Laurea) in Chemistry
Department of Chemistry, University of Camerino, Italy.

- **CURRENT POSITION(S)**

2005 – Full Professor
Department of Chemistry, University of Camerino, Italy.

- **PREVIOUS POSITIONS**

1992 – 2005 Associate Professor
Department of Chemistry, University of Camerino, Italy.
1983 – 1992 Assistant Professor
Department of Chemistry, University of Camerino, Italy.

- **FELLOWSHIPS AND AWARDS**

1987 – 1988 CNR Fellowship, Department of Chemistry, University of Montreal, Quebec, Canada.
1981 – 1983 ANSALDO Scholarship, Chemistry Institute, University of Camerino, Italy

- **SUPERVISION OF GRADUATE STUDENTS AND POSTDOCTORAL FELLOWS (if applicable)**

1992 – 2024 Number of Postdocs/ PhD/ Master Students: 1/5/25
Department of Chemistry, University of Camerino, Italy.

- **ORGANISATION OF SCIENTIFIC MEETINGS (if applicable)**

2023 *Member of the organizing* committee of "XIV Edition of the International School of Organometallic Chemistry, EuCheMS" 7-11 September, Camerino (I). (Number of participants: ~ 140)
2021 *Member of the organizing* committee of "XIII Edition of the International School of Organometallic Chemistry, EuCheMS" 1-3 September, Camerino (I). Web Edition. (Number of participants: ~ 110).

2019 *Member of the organizing* committee of "XII Edition of the International School of Organometallic Chemistry, EuCheMS" 31.8-4 September, Camerino (I). (Number of participants: ~ 130)

2017 *Member of the organizing* committee of "XI Edition of the International School of Organometallic Chemistry, EuCheMS" 2-6 September, San Benedetto del Tronto (I). (Number of participants: ~ 200)

2010 *Member of the organizing committee of* "XXXIII Convegno Nazionale della Divisione di Chimica Organica della S.C.I." 12-16 September, San Benedetto del Tronto (I). (Number of participants: ~ 300)

- **INSTITUTIONAL RESPONSIBILITIES (if applicable)**

2023 – 2024 Head, Chemistry Division of the School of Science and Technology, University of Camerino, Italy.
2013 – 2017 Head, School of Science and Technology, University of Camerino, Italy.
2011 – 2013 Rector's Delegate for European Technological Platforms.
2008 – 2010 Head, Department of Chemical Sciences, University of Camerino, Italy.
2000 – 2004 Member Academic Senate, University of Camerino, Italy.

- **REVIEWING ACTIVITIES (if applicable)**

2020 – 2022 Review Panel Member for the Evaluation of the Research Quality of Chemical Sciences, Italian Government.
2010 Member International Advisory Board, 9th International Symposium on Carbanion Chemistry – 20-24 July, Firenze, Italy.

- **MEMBERSHIPS OF SCIENTIFIC SOCIETIES (if applicable)**

1981 – 2024 Member, Italian Chemical Society

- **MAJOR COLLABORATIONS (if applicable)**

  - Prof. Luca Bernardi, Asymmetric Synthesis, Department of Industrial Chemistry, University of Bologna, Italy
  - Prof. Paolo Melchiorre, Asymmetric Synthesis, Department of Industrial Chemistry, University of Bologna, Italy.

Appendix: All current grants and on-going and submitted grant applications of the Co PI (Funding ID)

Mandatory information (does not count towards page limits)

Current grants (Please indicate "No funding" when applicable):

Project Title	*Funding source*	*Amount (Euros)*	*Period*	*Role of the PI*	*Relation to current proposal*
No funding					