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Dynamic Covalent Bonds as Tool for Tunable Liquid Crystals

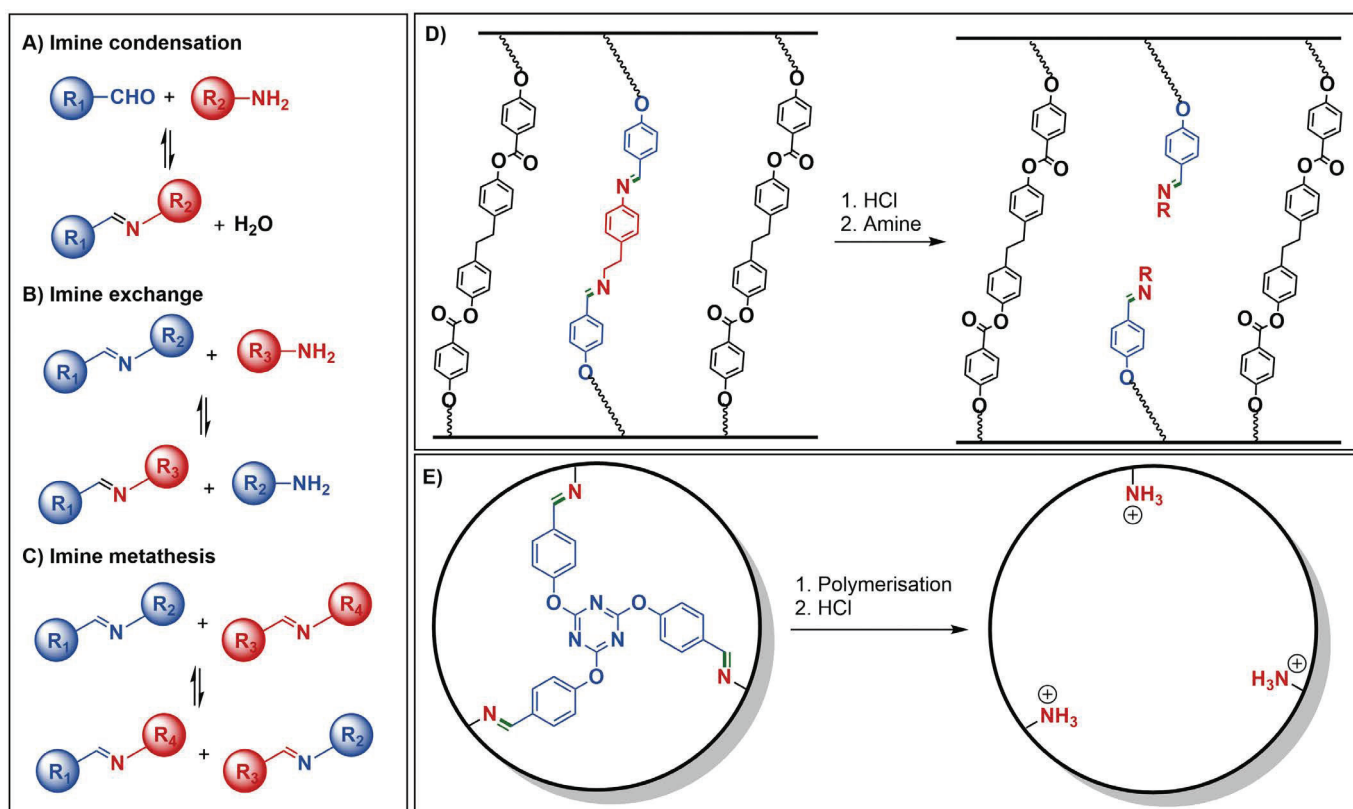


Fig. 1: Schematic view of dynamic imine reactions: A) Condensation, B) exchange and C) metathesis; D) Schematic representation of LCEs based on dynamic imine bonds by Mulder *et al* [16]. E) Schematic representation of columnar LCEs based on dynamic imine bonds by Sijbesma and coworkers [17].

Dynamic covalent bonds (DCBs) or dynamic covalent chemistry (DCC) have evolved into a promising tool for the development of functional materials such as polymers [1], gels [2] or liquid crystals [3] since they combine the error-correction capability and adaptivity of intermolecular forces with the robustness of the covalent bond. The underlying reactions for DCC need to form reversibly covalent bonds and allow free exchange of the molecular entities under thermodynamic control at equilibrium [4-6]. In the recent years, significant progress has been made in utilizing the dynamic character of esters, amides, boronic es-

ters, imines, disulfides, or the reversible character of Diels-Alder reactions to design polymeric materials [7, 8].

However, the use of DCBs in the design of low-molecular weight liquid crystals is poorly understood and most of the studies are based on the modification of liquid crystalline elastomers (LCE) [8, 9], which hold promising application potential in the field of shape-responsive materials, artificial muscles, biomimetics, tissue engineering and self-growing polymers [10, 11].

A commonly used bonding motif for the preparation of adaptable materials are imines [12, 13]. The reversibility of the imine bond provides self-healing capability and recyclability (Fig. 1A), while imine exchange (Fig. 1B) and metathesis (Fig. 1C) allows for tuning of the materials properties by exchanging the molecular building blocks. The versatile imine bond was already utilized for the development of LCEs and adaptive low molecular weight liquid crystals. They led to a variety of possible applications in different fields. Through the dynamics of

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the imine bond LCE networks get the ability to be rearranged by reactions of the imine groups, which enables post modification, shape-responsiveness and self-healing properties. Furthermore, some proof-of-concept studies showed the potential of imine-based systems as a new type of reactive mesogens to form recyclable LCEs and adaptive low molecular weight liquid crystals with possible applications in sensing [14, 15].

An example for a LCE based on dynamic imine bonds was reported by Mulder *et al.* [16]. They co-polymerized a bisimine monomer with a mesogenic monomer to form a smectic liquid crystalline nanoporous polymer network (Fig. 1 D). Treatment with an acid allowed selective cleavage of the imine bonds which yielded a contraction of the polymeric material. The subsequent treatment with a solution of different amines followed by reduction allowed post-modification of the pore size and functionalization of the porous networks, which may be applied for the controlled uptake and release of pollutants or drugs.

A related system was reported by Sijbesma and coworkers, which used a triazine-based reactive mesogen to form columnar hexagonal LC phases in the polymeric material (Fig. 1E) [17]. The hydrolysis of the imine bonds yielded a cationic nanoporous polymer with anilinium groups at the pore walls. The authors were able to show size selective uptake of aldehydes and transformed the anilinium groups to azides. In addition, they were able to enlarge the pore sizes by hydrolysis of ester groups to obtain anionic nanoporous networks, which showed selective uptake of cationic dyes.

Reports on low-molecular weight liquid crystals making use of DCC are rarely found. In 1982, Rinaldi *et al.* doped the imine based liquid crystal *N*-(4-Methoxybenzylidene)-4-butylaniline (**MBBA**) with the chiral amine **1** and found that transimination with **MBBA** yields the chiral imine **2** with a significantly higher ability to transfer chirality into the LC host system (measured by the helical twisting power, HTP β , Fig. 2A) [18]. Later they used the amine exchange for the determination of the absolute configuration of amines and aminoalcohols [19]. In 2001, Feringa and van Delden followed a related approach to tune the HTP of chiral amines and alcohols by imine condensation or esterification in LC host **E7** [20, 21].

In 2006, Lehn and coworker reported the exchange of **MBBA** and **EBBA** with a series of amines and found a direct impact of the electric field on the equilibrium of the amine exchange [22]. The authors state that the adaption of dynamic mixtures by physical effectors opens new directions in the design of functional materials.

In 2022 Giese and coworkers introduced a concept for the design of adaptive liquid crystalline materials based on the dynamics of imine bonds (Fig. 2B) [15]. Therefore, they performed a detailed structure-property relationship study for imine based low-molecular LCs and their *in situ* post-synthetic modification. This approach made it possible to tune the liquid crystalline behavior and emission properties of the materials by making use of imine condensation, exchange and metathesis reactions. For example the two imins **Im-1** and **Im-2**, which show isotropic phase behaviour underwent a metathesis reaction to form **Im-3** and **Im-4**. The mixture of all four imines showed a nematic mesophase. In further studies Giese and coworkers used the amine exchange between **Im-5** and **Am-1** for fluorescence tuning. The mixture with the products **Im-6** and **Am-2** combined the orange fluorescence of **Im-5** with the temperature activated fluorescence of **Im-6** to create a material suitable for thermo-patterning [23]. Based on this approach Martinez *et al.* treated aldehyde **Ald-1** with a series of amines (**a-e**) to achieve isothermal phase transitions driven by DCC via *in-situ* imine condensation (Fig. 2D) [24].

The given examples demonstrate the versatile potential of DCC in the design and modification of liquid crystalline materials. Especially with respect to low-molecular weight mesogens only little is known about the impact of the dynamics on the LC properties, which may be attributed to the initial assumption that the lability of imine-based mesogens exclude these materials from application. In the light of the novel developments in the field of DCBs, however, imine-based LCs may experience a renaissance for the design of responsive and adaptable liquid crystalline materials combining the error-correction capability and adaptivity of supramolecular chemistry with the robustness of the covalent bond. The need for recyclable and adaptable materials combined with new processing technologies such as additive manufacturing opens the route for variety of

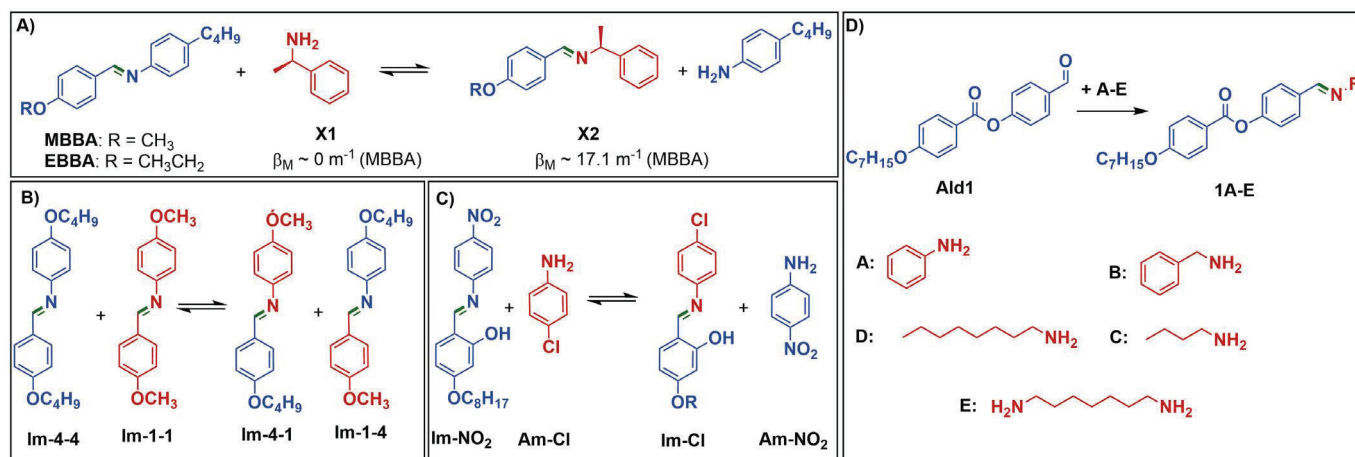


Fig. 2: Schematic view of dynamic imine reactions in low molecular liquid crystals Rinaldi *et al.* (A), Giese and coworkers (B/C) [15, 23] and Martinez *et al.* (D) [24].

new application fields for the next generation of materials (e.g. for 4D printing).

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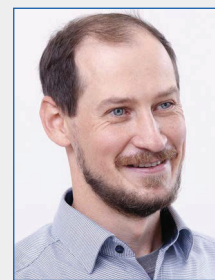
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Thorben Neumann



Thorben was interested in chemistry since he learned about the subject and was curious how materials of all kinds are made from a molecular point of view. Following that interest, he started to study chemistry at the University of Duisburg-Essen. In 2018 he finished his Bachelor degree with a Bachelor thesis on supramolecular materials based on dynamic covalent chemistry in the working group of Prof. Dr. Carsten Schmuck. To finish his Master's degree he joined the Giese group and worked on new functional luminescent liquid crystalline materials which can be manipulated by dynamic covalent chemistry for tailor-made properties. For his PhD studies he stayed in the Giese group with the focus on adaptive liquid crystalline materials based on dynamic covalent bonds.

Prof. Dr. Michael Giese



Michael Giese studied chemistry at RWTH Aachen University, where he received his doctorate in 2011 in the group of Prof. Markus Albrecht on the topic "Relevance and use of anion- π interactions". The research scholarship of the German Academic Exchange Service (DAAD) then took him to Vancouver, Canada. Here he discovered his passion for supramolecular materials in the group of Prof. Mark MacLachlan at the University of British Columbia. In 2014 he started his independent academic career as Juniorprofessor of the Professor-Werdelmann Foundation at the University of Duisburg-Essen. With his research group he is developing new supramolecular materials for sensing, optoelectronics and additive manufacturing. Since October 2021 he is Heisenberg-Professor for supramolecular materials and scientific director of the Co-Creation Lab for Product Innovations (CCL-P) at the University of Duisburg-Essen. When not playing with molecular building blocks in the lab, he and his two children share the passion for Lego bricks.