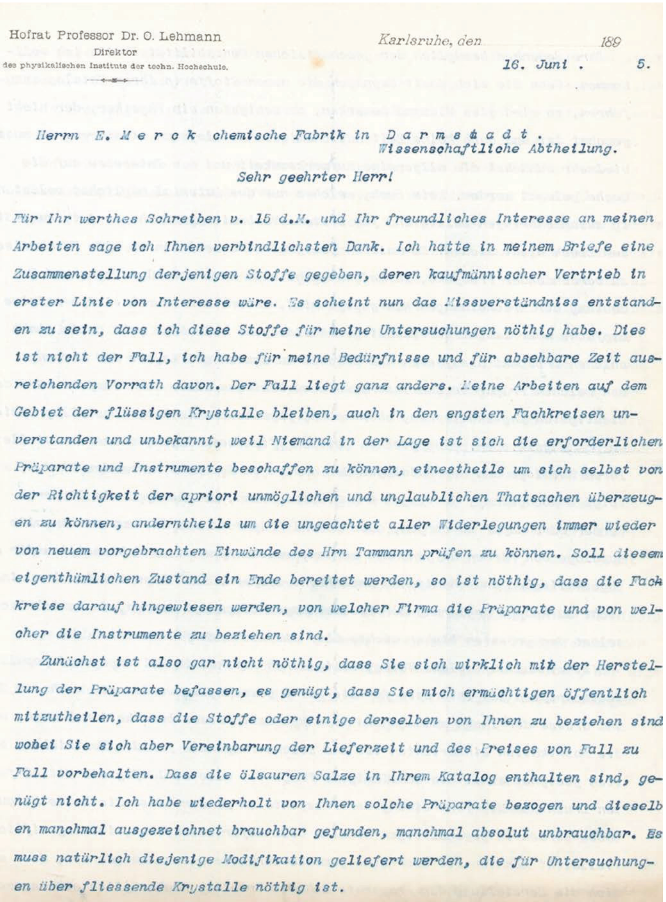
Rachel Tuffin, Melanie Klasen-Memmer, Sven Christian Laut, Sabine Bernschneider-Reif

Turning Curiosity into Business – Liquid Crystal Development for Displays at Merck

When Otto Lehmann wrote to E. Merck in 1905 asking for his help with research into liquid crystals (LC) (Fig. 1) and made the point "*no one is able to procure the necessary preparations, firstly in order to convince themselves of the a priori impossible and unbelievable facts, and secondly to repeatedly examine them within the scope of new objections that are raised.", he could never have imagined that the same sentiments would exist 120 years later. It was the request from Lehmann for Merck to provide high quality liquid crystals to the scientific community that led to the first liquid crystal sales at Merck. Merck was already known for the quality of its pharmaceutical products and so was well placed to supply the first commercial liquid crystals continuously until the 1930s*.



Hofrat Professor Dr. O. Lehmann
Direktor
des physikalischen Institute der techn. Hochschule.

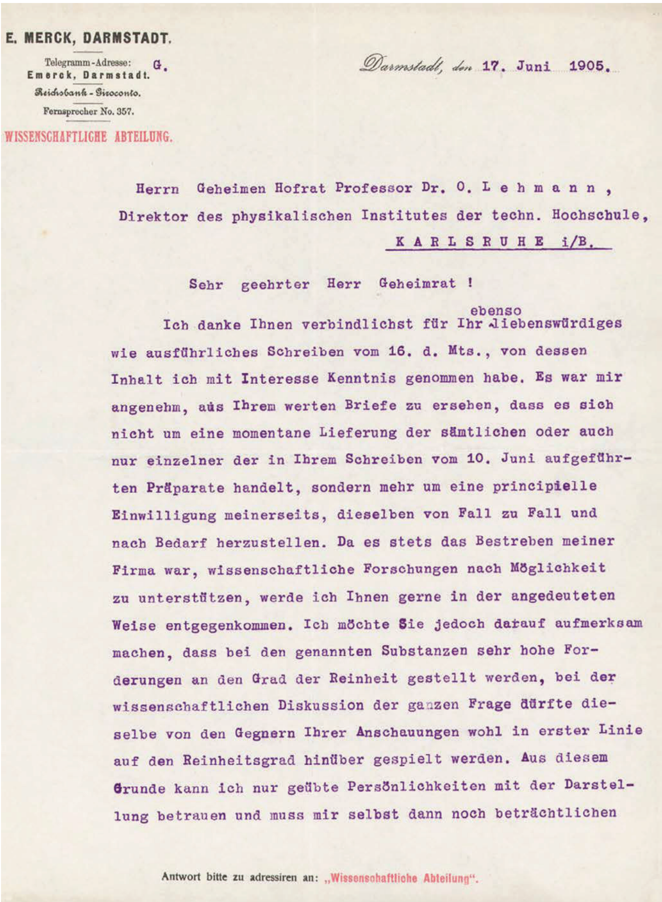
Karlsruhe, den 16. Juni . 189 5.

Herrn E. M e r c k chemische Fabrik in D a r m s t a d t .
Wissenschaftliche Abtheilung.

Sehr geehrter Herr!

Für Ihr werthes Schreiben v. 15 d.M. und Ihr freundliches Interesse an meinen Arbeiten sage ich Ihnen verbindlichsten Dank. Ich hatte in meinem Briefe eine Zusammenstellung derjenigen Stoffe gegeben, deren kaufmännischer Vertrieb in erster Linie von Interesse wäre. Es scheint nun das Missverständniss entstanden zu sein, dass ich diese Stoffe für meine Untersuchungen nöthig habe. Dies ist nicht der Fall, ich habe für meine Bedürfnisse und für absehbare Zeit ausreichenden Vorrath davon. Der Fall liegt ganz anders. Meine Arbeiten auf dem Gebiet der flüssigen Krystalle bleiben, auch in den engsten Fachkreisen unverstanden und unbekannt, weil Niemand in der Lage ist sich die erforderlichen Präparate und Instrumente beschaffen zu können, einestheils um sich selbst von der Richtigkeit der apriori unmöglichen und unglaublichen Thatsachen überzeugen zu können, anderntheils um die ungeachtet aller Widerlegungen immer wieder von neuem vorgebrachten Einwände des Hrn Tammann prüfen zu können. Soll diesem eigenthümlichen Zustand ein Ende bereitet werden, so ist nöthig, dass die Fachkreise darauf hingewiesen werden, von welcher Firma die Präparate und von welcher die Instrumente zu beziehen sind.

Zunächst ist also gar nicht nöthig, dass Sie sich wirklich mit der Herstellung der Präparate befassen, es genügt, dass Sie mich ermächtigen öffentlich mitzutheilen, dass die Stoffe oder einige derselben von Ihnen zu beziehen sind wobei Sie sich aber Vereinbarung der Lieferzeit und des Preises von Fall zu Fall vorbehalten. Dass die ölsauren Salze in Ihrem Katalog enthalten sind, genügt nicht. Ich habe wiederholt von Ihnen solche Präparate bezogen und dieselben manchmal ausgezeichnet brauchbar gefunden, manchmal absolut unbrauchbar. Es muss natürlich diejenige Modifikation geliefert werden, die für Untersuchungen über fliessende Krystalle nöthig ist.



E. MERCK, DARMSTADT.
Telegramm-Adresse: Emerck, Darmstadt.
Reichsbank-Giroconto.
Fernsprecher No. 357.
WISSENSCHAFTLICHE ABTEILUNG.

G.

Darmstadt, den 17. Juni 1905.

Herrn Geheimen Hofrat Professor Dr. O. L e h m a n n ,
Direktor des physikalischen Institutes der techn. Hochschule,
K A R L S R U H E i/B.

Sehr geehrter Herr Geheimrat !

Ich danke Ihnen verbindlichst für Ihr ebenso liebenswürdiges wie ausführliches Schreiben vom 16. d. Mts., von dessen Inhalt ich mit Interesse Kenntnis genommen habe. Es war mir angenehm, aus Ihrem werten Briefe zu ersehen, dass es sich nicht um eine momentane Lieferung der sämtlichen oder auch nur einzelner der in Ihrem Schreiben vom 10. Juni aufgeführten Präparate handelt, sondern mehr um eine principielle Einwilligung meinerseits, dieselben von Fall zu Fall und nach Bedarf herzustellen. Da es stets das Bestreben meiner Firma war, wissenschaftliche Forschungen nach Möglichkeit zu unterstützen, werde ich Ihnen gerne in der angedeuteten Weise entgegenkommen. Ich möchte Sie jedoch darauf aufmerksam machen, dass bei den genannten Substanzen sehr hohe Forderungen an den Grad der Reinheit gestellt werden, bei der wissenschaftlichen Diskussion der ganzen Frage dürfte dieselbe von den Gegnern Ihrer Anschauungen wohl in erster Linie auf den Reinheitsgrad hinüber gespielt werden. Aus diesem Grunde kann ich nur geübte Persönlichkeiten mit der Darstellung betrauen und muss mir selbst dann noch beträchtlichen

Antwort bitte zu adressiren an: „Wissenschaftliche Abteilung".

Fig. 1: Request from Prof. O Lehmann to Merck to supply liquid crystals and the reply from Merck [1].

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For the following 30 years, not much happened with LC, it remained a scientific curiosity. This began to change with the invention of the Heilmeier guest host cell [2] and in 1967 the publication of the scattering mode devices [3]. Research on LC in Merck really started in 1968 after the 2nd ILCC in Kent, Ohio and shortly afterwards the first "licristal™" appeared in the Merck catalogue [4]. Liquid crystals in the early 1970s were based on azoxy or Schiff's base structures [5], but they suffered from instability and high transition temperatures.

Therefore, the scientists started to make mixtures of two or more components to expand the nematic range. Mixture development became a key competence at Merck. The first mixtures which were used in, e.g., Casio calculators, needed a yellow filter to protect them from light. Room temperature and stable liquid crystals were urgently needed.

The access to cyanobi/terphenyls by acquiring British Drug Houses in 1973 and the synthesis of phenylcyclohexyls (PCH) in 1976 [6] by Merck, and two years later cyclohexylcyclohexanes (CCH) [7] allowed the TN mode display (Fig. 2) to operate in the first minimum [8], which led to a rise in demand of these devices (Fig. 3).

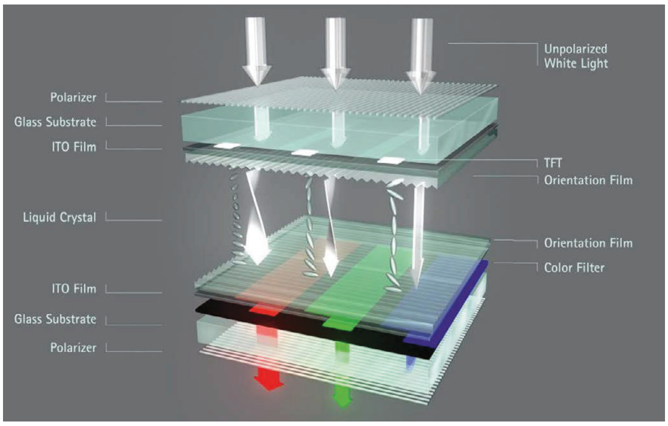

Fig. 2: Operating principle of a Twisted Nematic (TN) LCD.

To get the best out of Active Matrix LCD, improved voltage holding ratio was needed, which meant the mixture should have as few ions as possible, this was a massive problem with mixtures containing cyano groups. The concept of so-called "superfluorinated" LC (Fig. 3) was already in development in Merck, these showed better stability and performance and were well suited for use in active-matrix devices.

By 1989, Merck had over 1000 patents covering LC singles and mixtures. In 1995 Hitachi and Merck collaborated to develop and commercialise In-Plane-Switching (IPS) displays which had been patented five years previously by the Fraunhofer Institute in Freiburg, the patent was obtained by Merck in 1994 [9]. The increased viewing angle of 170 degrees allowed it to replace TN despite having slower response speeds.

In 1997 Merck worked with Fujitsu on the development of vertically aligned (VA) mode, where LC with negative dielectric anisotropywere needed (Fig. 3). In 2006 Merck co-developed polymer-stabilized vertical alignment (PSVA) again with Fujitsu [10], which gave increased transmission and reduced energy consumption. Both VA and IPS modes exhibit excellent viewing angles and contrast and dominated the market for large size panels for many years.

Between 1995 and 2010 a revolution in screen technology occurred – TV's, monitors and notebook screens worldwide were replaced with LCDs, most of the LC materials were supplied by Merck. TN and STN dominated small devices, but IPS and (PS)VA were the technologies of choice for TV. A variant of IPS, Fringe Field Switching (FFS), was developed by Hyundai [11], but was not widely used until adopted by Apple for the iPhone. This technology has the advantage of better transmission and switching speed.

The application of negative dielectric anisotropy LC in FFS geometry, marketed as ultra bright (UB) FFS reduced light-loss caused by tilting of the molecules at the electrode edges,

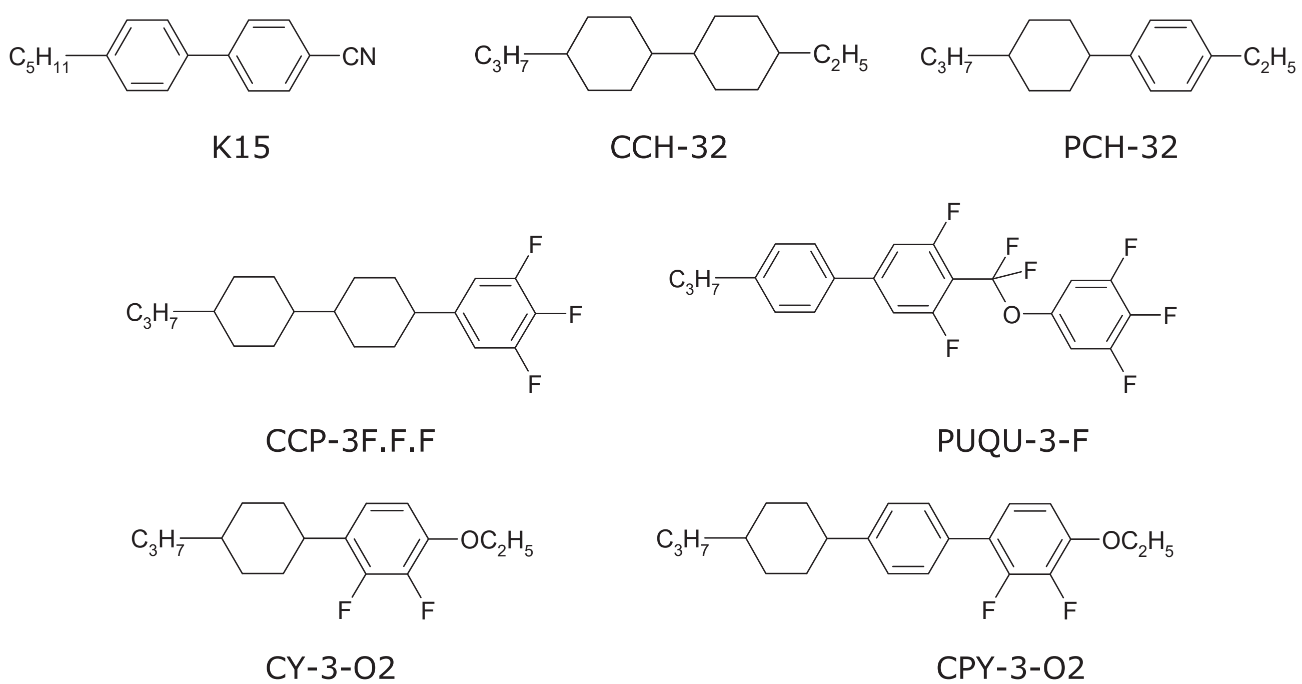

Fig. 3: Structures of LCs used for LCDs: Cyanobiphenyl K15, Cyclohexylcyclohexane CCH-32, Phenylcyclohexane PCH-32, Superfluorinated materials with positive dielectric anisotropy CCP-3F.F.F and PUQU-3-F and negative dielectric anisotropy CPY-3-O2 [13].

offering brighter visuals, longer battery life, lower power consumption for sustainability, and improved viewing angles. This technology was commercialized in 2014 by display manufacturers together with Merck [12].

By now Liquid Crystals had obviously become a serious business within Merck. The challenges from the customer for the LC varied over time but were, and still are, directed towards: Response speed, contrast ratio, operating voltage, operating temperature range, transmittance, and power consumption. These requirements were met by understanding how the key LC parameters varied with operating mode and the development and optimization of the respective formulations to get the right set of LC mixture parameters [13]. Equipment was purchased or made in house to accurately measure the mixture parameters. Co-location of the subsidiaries with the customer made it possible to do this with the required speed. Research related to chemical structure and how it affected the parameters was also of key interest, and Merck collaborated with universities globally to further LC research, particularly LC physics. Computer simulation tools were used from the beginning for the development of new LC materials, and to understand the physics of the different LC modes.

However, obviously not all liquid crystal technologies were successfully commercialized, among them was for example Blue Phase. The LC development for Blue Phase displays though has had a surprising upside – many of the highly polar singles used to reduce operating voltage in Blue Phase have turned out to show the newly discovered “ferroelectric nematic” (FNLC) phase or phases [14, 15]. Unlike existing nematics, these FNLC mixtures are polar and exhibit ferroelectricity, leading to exciting possible applications, e.g., in optics, entangled photon generation, energy harvesting etc. A liquid ferroelectric is about as believable as liquid crystals were in the beginning and so we come back to Lehmann’s request to Merck. We are proud to continue to support the academic community with the supply of liquid crystal mixtures to enable basic research into this phase. It is similar to the cyanobiphenyl development – without access to room temperature stable mixtures, physicists and engineers will struggle to find a commercial use for FNLC.

Besides the ongoing development of LCs for LCD to improve their performance and sustainability, new developments for future devices like Augmented and Virtual Reality (AR/VR) [16] are of high interest in the research field of liquid crystals. In addition, other non-display applications are under development, e.g. switchable LC Windows [17]. Hence, the success story of LC is far from over.

ZITATE

"Man hat mir wohl die Frage gestellt, ob sich die kristallin-flüssigen Substanzen technisch verwerten lassen? Ich sehe keine Möglichkeit dazu.”

Daniel Vorländer
Chemische Kristallographie der Flüssigkeiten, 1924

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Zurück zum Inhaltsverzeichnis

Dr. Rachel Tuffin

Rachel started early in a career in liquid crystals, following an undergraduate course on “crystals that flow”, she did her PhD on „Macrocyclic Liquid Crystals“ at the University of Hull, with supervisors Prof John Goodby and Prof Ken Toyne, in collaboration with BDH/Merck industrial supervisor Prof George Gray.
After a short stay working on swallow tailed LC at the Technical University Berlin, and a post doc at the University of Hull, she joined DRA/DERA working on ferroelectric smectic, as well as TN and STN LC, among other technologies. In 2010 with the closing of the research group in Malvern, Rachel joined Merck in Chilworth in the UK, primarily to work on novel LC modes and technologies. In 2017 she relocated to the Merck HQ in Darmstadt, Germany, initially working on UB-FFS before a brief foray into the bright world of OLED.
Rachel currently works on ferroelectric nematics and other new technologies in the “Future Displays” team.

Dr. Melanie Klasen-Memmer

Melanie studied Chemistry at the Technical University Kaiserslautern, Germany where she also obtained her PhD in the field of “Order parameters of Liquid Crystals (LCs) by means of ^{2}H-NMR-Spectroscopy” in 1996. In 1998, she joined Merck KGaA in Darmstadt, Germany and was involved in LC material development mainly for TV and monitor applications for VA, PSVA and IPS technologies. Currently, she is heading the R+D Future Display team within the Business Unit Display Solutions at Merck Electronics KGaA, Darmstadt, Germany.
She has published several research papers and reviews and holds numerous patents in the field of Liquid Crystal materials and their applications. She was awarded the “International Merck Innovation Award” in 2002 and 2009, and the "Performance Materials – Performance Award" of Merck in 2020 and recieved the “Deutscher Zukunftspreis”, the Federal President’s Award for Innovation and Technology in 2003.
Since 2022, she is Vice Chairman of the German Liquid Crystal Society.

Sven Christian Laut

Sven embarked on his research career in Liquid Crystals following the completion of his apprenticeship as a chemical laboratory technician in 2009. While engaged in R&D, he pursued and obtained his BSc degree in Chemical Engineering from the University of Applied Science Provadis – Frankfurt, supported by a scholarship from the Chamber of Industry and Commerce. During his tenure in the R&D laboratories at Merck KGaA, he focused on the discovery of new LC materials for all existing LC Display technologies, resulting in the acquisition of several related patents. In 2017, he assumed the position of Laboratory Manager within the Liquid Crystal R&D at Merck KGaA, specializing in in-plane switching technologies. Subsequently, from 2020 to 2022, he served as a Senior Project Manager in the LC R&D environment in Asia. He has since transitioned to his current role at Merck’s Headquarters in Darmstadt as the Head of the LC Innovation Pipeline, where he is tasked with identifying novel LC structures to enhance the performance and sustainability of future LCD displays.

Sabine Bernschneider-Reif

Sabine obtained a degree in pharmacy, before working as a pharmacist and a lecturer in pharmacology, she then completed a PhD with the topic: “Laboranten, Destillatores, Balsamträger. Das laienpharmazeutische Olitätenwesen im Thüringer Wald vom 17. bis zum 19. Jahrhundert”.
Sabine joined Merck in 1999 and became Head of the Merck Corporate History Research Department in 2000. Since 2004 she has been a Lecturer at the Association of German Company Archivists, Department of Education and Training and also currently holds a Lectureship at the University of Heidelberg, Germany, Institute for Pharmacy and Molecular Biotechnology with the topic: “History of Pharmacy and Natural Sciences”.
Sabine is a member of the board of the German Pharmaceutical Society and a Member of the scientific advisory council of the German Business History Society. In 2019 she won the Elsa-Ullmann-Medal from the German Pharmaceutical Society.