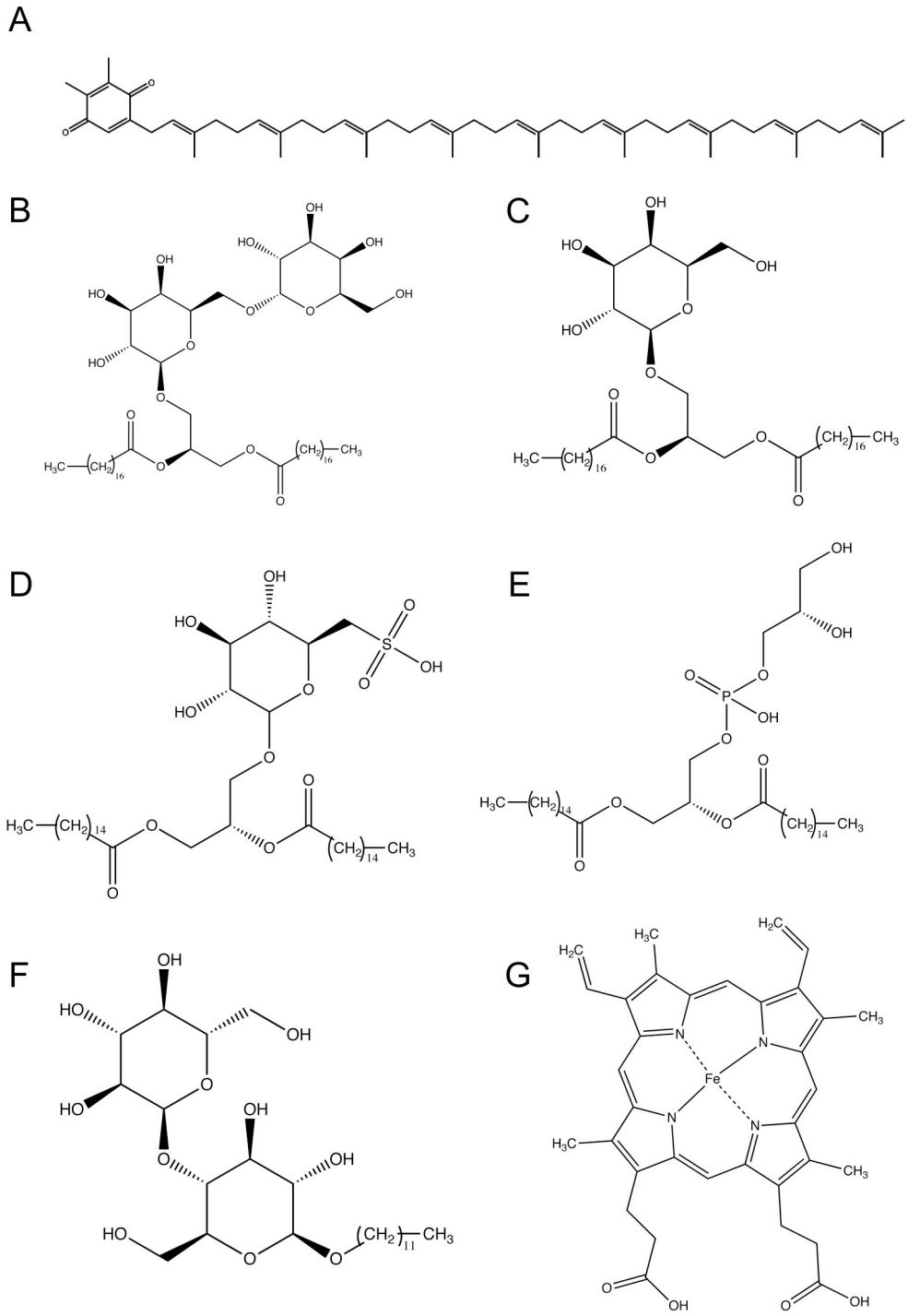

Figure 9. Chemical structures of main cofactors of PSII: A) plastoquinone (PQ9); B) digalactosyldiacylglycerol (DGDG); C) monogalactosyldiacylglycerol (MGDG); D) sulfoquinivosyldiacylglycerol (SQDG); E) phosphatidyldiacylglycerol (PG); F) dodecyl-beta-D-maltoside (β-DM); G) haem. See also Fig. 3 for structures of chlorophyll a and β-carotene.

There are three membrane extrinsic protein subunits: PsbO, PsbV and PsbU found at the lumenal side of the complex. They form a protective cap, shielding the Mn_4Ca cluster from the aqueous phase. It is believed that these subunits play a significant role in the

stabilization of the whole PSII complex and optimization of the efficiency of the oxygen evolution process [50-52].

The remaining eleven subunits are of low molecular weight and mainly single TMHs, except subunit PsbZ showing two helices, and of not yet known function(s). They are located either at the periphery of the complex (PsbH, PsbI, PsbJ, PsbK, PsbX, PsbY, PsbZ, ycf12) or at the monomer-monomer interface (PsbL, PsbM, PsbT).

1.3.2 Photosystem I

Cyanobacterial PSI is a large monomeric or trimeric [53] complex of twelve protein subunits with 128 cofactors (96 chlorophyll molecules, 22 carotenoids, four lipids, three Fe_4S_4 clusters, two phylloquinones and one putative Ca^{2+} ion) in each monomer [37] (Fig. 10). There is a high degree of identity between PSII and PSI core subunits, therefore general organization of protein subunits is similar to some extent, however ETCs are different. Subunits PsaA and PsaB (with their C-termini similar to D1 and D2, and their N-termini similar to CP43 and CP47 subunits in PSII) harbour almost all cofactors of the ETC and most of the antenna system. These subunits also provide the binding surface for the soluble electron donors plastocyanin and cytochrome *c6*.

Subunits PsaC, PsaD, PsaE are not folded into TMHs and form a hump at the stromal part of the complex. The main role of these subunits is to provide the docking site for the electron carrier ferredoxin.

The remaining seven small subunits (PsaF, PsaI, PsaJ, PsaK, PsaL, PsaM and PsaX), each contain from one to three TMHs, are located at the periphery of core subunits PsaA and PsB. Depending on location of each subunit, the following functions are assigned: promotion of trimerization (subunits PsaI and PsaL, located at trimerization interface), monomer-monomer interactions (subunit PsaM, located between two monomers), stabilization and linkage with external antenna systems (subunits PsaJ, PsaF, PsaK, PsaX).

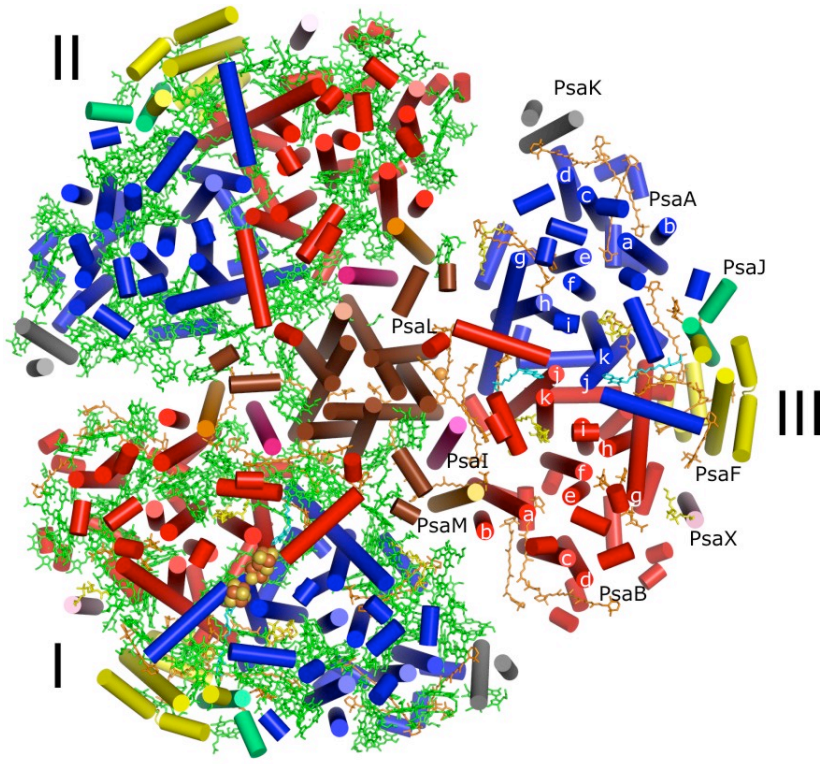

Figure 10. Trimeric PSI from *T. elongatus* (pdb code: 1jb0), view is from the cytoplasmic side onto the membrane, membrane extrinsic parts are omitted. In monomer I all cofactors are shown, in monomer II only Chl (green) are shown and in monomer III the subunits are assigned and the positions of Car (orange), lipids (yellow) and phylloquinones (light blue) are given and TMHs of PsaA and PsaB are labelled a-k.

1.3.3 Cytochrome b6f complex

The cytochrome b_6f (cyt b_6f) is a dimeric linker protein complex, connecting PSII to PSI. The main functions of cyt b_6f are the reoxidation of plastoquinols coming from PSII to plastoquinones and maintaining of trans-membrane proton electrochemical potential in Q-cycle manner (see [54] for application of the Q-cycle model to the cyt b_6f complex), as well as participation in the cyclic electron transfer around PSI [55] (Fig. 6), when electrons are cycled via PSI, ferredoxin or NADPH, plastoquinone and cyt b_6f in case of lack of electron supply from PSII. Cyt b_6f consists of eight subunits per monomer folded into 13 TMHs (Fig. 11). Four large core subunits (cytochrome *f*, cytochrome b_6, iron-sulfur protein (ISP, Rieske protein) and subunit IV) bind redox prosthetic groups (four haems and Fe_2S_2 cluster) and directly participate in electron and proton transfer. Subunit IV additionally binds Chl *a* and β-carotene molecules. Four small subunits (PetG, PetL, PetM, PetN) fence the core subunits at the periphery of each monomer and provide structural support.

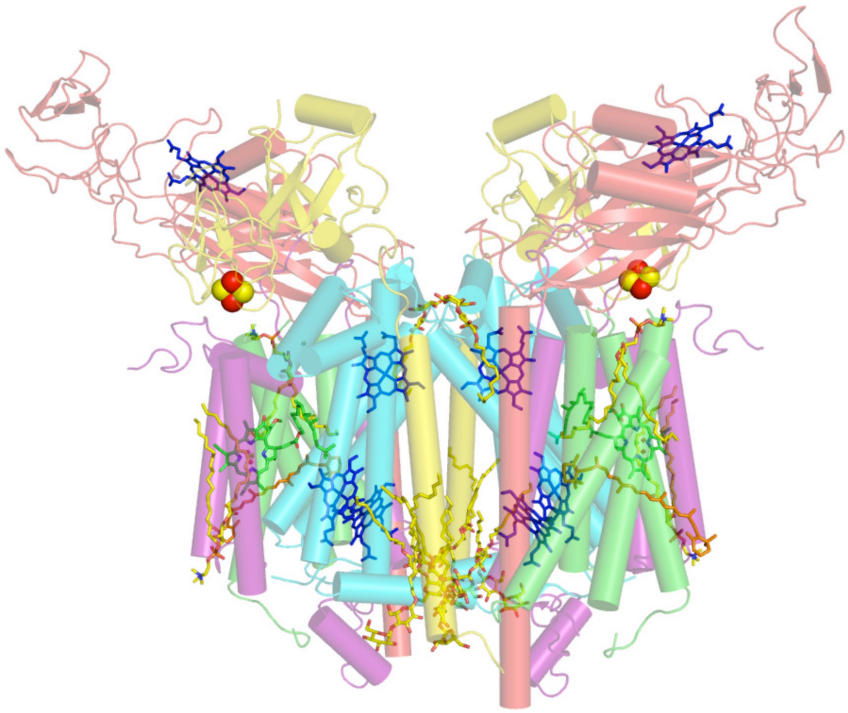

Figure 11. Protein and cofactor assignment in the cyt b_6f dimer from *Mastigocladus laminosus* (pdb code: 2e74). Cofactors are coloured in green for chlorophylls, blue for haems, orange for carotenoids, yellow for lipids, Fe_2S_2 clusters are shown as yellow (sulphur) and red (iron) spheres, subunits are given in yellow (ISP), cyan (cyt b_6), red (cyt *f*), green (PetN), magenta (subunit IV).

1.4 Aim of this work

At the beginning of this thesis the 3.0 Å resolution structure of PSII had already been elucidated [41]. But despite all novelties described in this structure, there was and still is a great demand for higher resolution structures of PSII because the given model has several limitations e.g. vast regions of unexplained electron density, uncertainty in rotamer selection of side chains, missing N- and C-termini that are disordered [56].

No structural information on the chloride ion was available, which is known to be associated with the unique Mn_4Ca cluster [57]. No concept of the transport pathways of products and educts in PSII existed, and no insights on plastoquinol exchange with the plastoquinone pool were made.

Beyond the ultimate goal to obtain a model with the highest possible resolution, several other experiments were planned in cooperation with the research group of Prof. Athina Zouni (Max-Volmer-Laboratorium, Technische Universität Berlin). Among them the

analysis of PSII crystals grown in bromide medium to determine the binding positions of halides in PSII and the treatment of crystals with noble gases to investigate internal channels and cavities were the target of this dissertation.