ABSTRACT

Climate change and the finiteness of fossil fuels call for the development of new energy sources. During the last 70 years, solar power has emerged as one of the most promising sources of renewable energy, and research has increased the power conversion efficiencies (PCE) of silicon solar cells from under 1% to over 25%. The high energetic and material costs for the required pure silicon have led to an increase in the search for viable alternative materials. The most promising material to date is the perovskite solar cell (PSC). Here the excitation takes place in the active layer (perovskite), and charge transport materials are in need to allow easy charge separation and prevent recombination. While the electron transport layers (ETLs) have been extensively studied and optimized, the hole transport layers (HTLs) emerged as the bottleneck for higher efficiencies. The synthesis and purification of the most-commonly used small molecule HTL spiro-OMeTAD are tedious and energy-intensive, and high PCEs can only be achieved by additional doping. In this thesis, various organic hole transport materials (HTMs) based on different core structures were synthesized as possible substitutes for spiro-OMeTAD. Apart from the core building block variation, different triarylamine-based donor moieties, and thiophene-based π-bridges (elongation of the conjugated system) were added to the cores to determine their influence on the optical and electrochemical properties. As a first building block, the [2.2]paracyclophane (PCP) was chosen, and eight different pseudo-*para*-substituted HTMs could be synthesized *via* CH activation. The highest occupied molecular orbital (HOMO) energy levels were determined optically, electrochemically, and theoretically, and for three of the materials, devices could be manufactured.

While all three materials displayed some extraction barriers and the implementation of dopants is still on the way, pristine Di-*p*-OMeTPAThio-PCP (**TM_31**) achieved a PCE of 8.4%. Secondly, the number of substituents was increased from two to four, and five different bis(pseudo-*meta*)-*para*-substituted [2.2]paracyclophanes could be successfully synthesized *via* NEGISHI cross-coupling. Tetra-*p*-OMeTPAThio-PCP (**TM_39**) provided the most promising results and reached 11.0% PCE as pristine HTM. Thirdly, *meso*-tetrakis-substituted porphyrins were introduced, and 17 different target materials could

be synthesized with variations in donor-π-moieties and coordinated metals. As the last building block, tetraphenylethene (TPE) was introduced and directly coupled to different methoxy-substituted donor groups to determine the influence of the substitution pattern on the overall properties. The comparison of the different properties led to several different trends, with triphenylamines, methoxy groups, and 3,4-ethylenedioxythiophene (EDOT) leading to shallower HOMO energy levels compared to carbazoles, no substituents, and thiophene, respectively. Methoxy groups, *tert*-butyl groups, and more substituents increased the solubility, and by variation of the coordinated metal inside the porphyrin, the band gap and the lowest unoccupied molecular orbital (LUMO) energy level could be tuned. All in all, 35 different potential HTMs were synthesized with a HOMO energy range from -4.98 eV to -5.57 eV, thus in the required range for application in perovskite solar cells.

INHALTLICHE ZUSAMMENFASSUNG

Durch den Klimawandel und die Endlichkeit fossiler Rohstoffe ist die Entwicklung neuer Energiequellen unabdingbar. In den letzten 70 Jahren hat sich die Solarenergie als eine der vielversprechendsten erneuerbaren Energien etabliert und durch extensive Forschung konnten die Wirkungsgrade von Siliziumsolarzellen von 1% auf über 25% erhöht werden. Die hohen Energie- und Materialkosten zur Herstellung von reinem Silizium haben jedoch für eine verstärkte Forschung nach Alternativen gesorgt. Der vielversprechendste Aufbau ist hier die Perowskit Solarzelle. Die Anregung findet hier in der Perowskit Schicht statt und Ladungstransportschichten werden für eine einfache Trennung der Ladungen und dem Verhindern von Rekombinationen benötigt. Während Elektronentransportschichten schon weit optimiert sind, bilden die Lochtransportschichten den aktuellen Flaschenhals für höhere Wirkungsgrade. Beim aktuellen Standard spiro-OMeTAD sind Herstellung und Aufarbeitung aufwendig und hohe Wirkungsgrade können nur durch zusätzliches Dotieren erreicht werden. Im Rahmen dieser Arbeit wurden verschiedene zentrale Bausteine, Substituenten und π-Brücken miteinander verglichen und eine Bibliothek an neuen Lochtransportmaterialen synthetisiert. Als erstes konnten acht verschiedene pseudo-*para*-substituierte [2.2]Paracyclophane synthetisiert werden. Durch optische, elektrochemische und theoretische Untersuchungen konnte die Lage der HOMO Energieniveaus bestimmt werden und drei der acht Materialien konnten in Solarzellen eingebaut werden. Während alle drei Materialien Extraktionsbarrieren offenbarten, konnte ein Wirkungsgrad von 8,4% für **TM_31** erreicht werden. Durch die Erhöhung der Substituenten wurden die Löslichkeit erhöht und die HOMO Energieniveaus leicht angehoben. Fünf verschiedene bis(pseudo-*meta*)-*para*-substituierte [2.2]Paracyclophane konnten erfolgreich hergestellt werden, für das Analogon zu **TM_31** (**TM_39**) konnte ein Wirkungsgrad von 11,0% gemessen werden. Experimente zur Dotierung sind aktuell in Arbeit. Als dritter Baustein wurden *meso*-tetrakis-substituierte Porphyrine verwendet, da diese neben der Variation an den Seitenketten auch bezüglich des koordinierten Metalls modifiziert werden können. Insgesamt 17 verschiedene Porphyrine wurde erfolgreich hergestellt. Als letzten Baustein wurde Tetraphenylethen verwendet und direkt mit verschieden substi-

tuierten Methoxy-Triphenylaminen gekuppelt. Hierbei sollte der Einfluss des Substitutionsmusters auf die Eigenschaften des Gesamtmoleküls untersucht werden. Zusammenfassend konnten verschiedene Trends bei der Variation der Seitengruppen und Metalle beobachtet werden. Die Verwendung von Triphenylaminen, Methoxysubstitution oder von EDOT sorgen für flachere HOMO Energieniveaus im Vergleich zu der Verwendung von Carbazolen, keinen Substituenten oder Thiophenen. Der Einbau von Methoxy- und *tert*-Butylgruppen erhöhte die Löslichkeit, während der Einfluss der Metalle in den Porphyrinen vor allem auf das LUMO Energieniveau und die Bandlücke zu beobachten war. Zusammenfassend konnten 35 verschiedene Lochtransportmaterialien mit HOMO Energieniveaus zwischen -4,98 eV und -5,57 eV hergestellt werden und damit im benötigten Bereich für die Anwendung in Perowskit Solarzellen.

1 INTRODUCTION

Energy has been vital for human development and survival since the domestication of fire. Starting with the use of wood and later coal as a primary resource for heating, the industrial revolution, with the invention of steam and combustion engines, opened up a new array of applications. Naturally, the need for more energy sources increased, and the era of coal, oil, and gas began. Since then, the production and consumption of these so-called fossil energies have grown yearly except for major events such as the financial crisis in 2008 and the Covid pandemic in 2020 (Figure 1).[1]

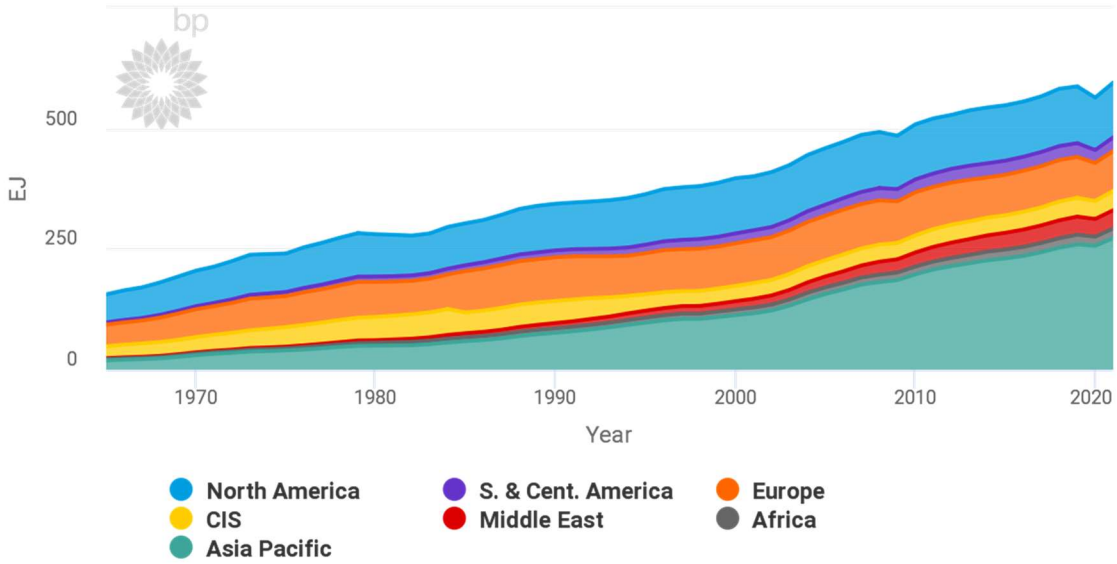

Figure 1: Energy consumption in exajoules (EJ) from 1965 to 2021. Reproduced from BP.[1]

With the increased consumption of carbon-based resources, the released amount of CO_2 and other greenhouse gases has increased to a level where climate change's effects are tangible. Having this in mind and regarding the finiteness of fossil fuels, finding alternative energy sources is of utmost importance. The shift from fossil power to renewable power sources such as hydro, wind and solar is one of the most promising and viable opportunities. Here, hydropower and wind power have faced many social pushbacks, showing that solar power, especially photovoltaics, is an attractive and decentralized option. In 2019, the world's energy demand added up to an astonishing 160 PWh, of which over 80% was

still generated from fossil resources.[2] With this number in mind, the global solar radiation, when only counting the landmasses, is significantly higher at 230 EWh. Harvesting only a part of the freely available energy would be sufficient to support a modern renewable energy-based industry and society. Since the late 1990s, there has been an increased effort to implement renewable energy sources into the resource grid (Figure 2), reaching up to 13% of the overall production of energy for 2021.[1]

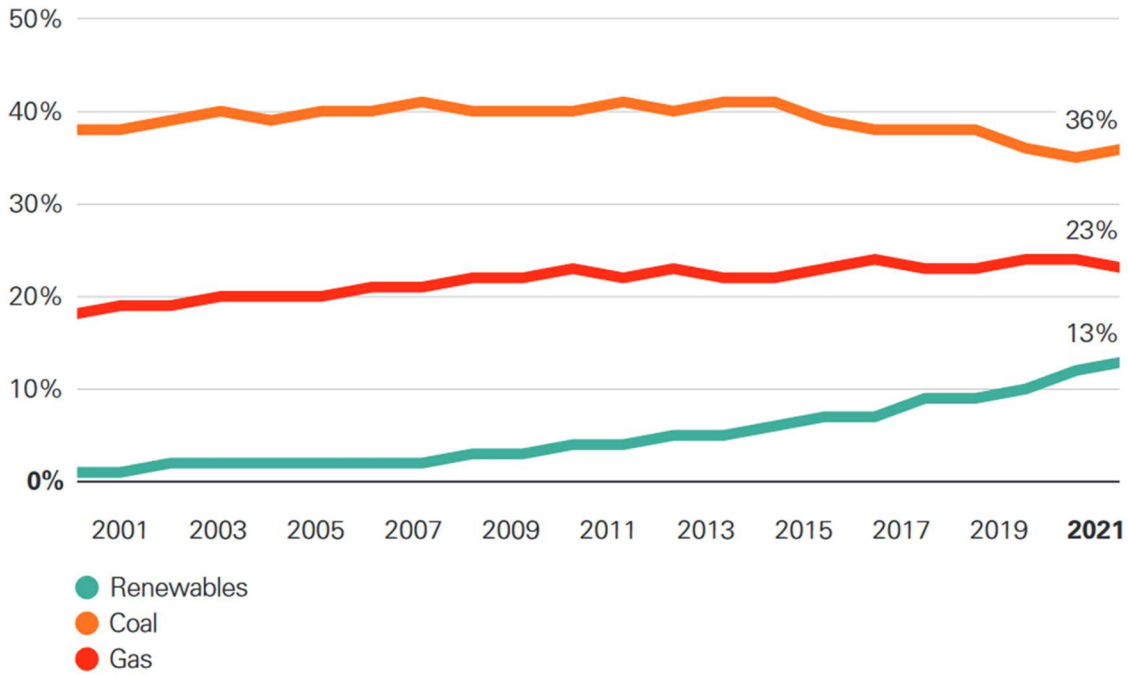

Figure 2: Global share of energy production. Reproduced from BP.[1]

Starting with the oil crisis of the 1970s, the adaption of solar energy from research purposes to commercial use began, and with the increased usage of renewable energy sources, the drive to develop more efficient and less costly devices and methods has amplified. The number of publications containing the words "solar energy" either in the title or abstract has increased yearly over the past 25 years, reaching over 26 000 publications in 2021 (Figure 3).[3]