# Synthesis and Characterization of Pyrazine and Phthalocyaninatonickel (II) Substituted PPV Analogous Oligomers

# Synthese und Charakterisierung von Pyrazin- und Phthalocyaninatonickel(II)-substituierten PPV-anologen Oligomeren

**Dissertation**

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My parents,
sisters and brother

# Abbreviations

| | |
|---|---|
| $Alq_3$ | tris(8-hydroxyquinolinato) aluminium |
| a.u. | arbitrary units |
| br | broad |
| °C | Centigrade |
| cald. | calculated |
| Cd | candela |
| CIE | Commission Internationale de L'Eclairage |
| cm | centimeter |
| d | doulet |
| $\delta$ | chemical shift |
| $\Delta E_e$ | energy barrier to injection of electrons |
| $\Delta E_h$ | energy barrier to injection of holes |
| DBU | 1,8-diazabicyclo[5.4.0]undec-7-ene |
| DC | direct current |
| dd | doublet of doublets |
| DIBAL-H | diisobutylaluminium hydride |
| DMF | dimethylformamide |
| DSB | distyrylbenzene |
| EA | electron affinity |
| $E_{gap}$ | energy gap |
| EI | electron impact |
| EL | electroluminescence |
| $E_p$ | average energy of the emitted photons |
| ETHB | electron transporting hole blocking |
| ETL | electron transport layer |
| EV | electron volt |
| $\Phi_A$ | work function of anode |
| FAB | fast atom bombardment |
| $\Phi_C$ | work function of cathode |

| | |
|---|---|
| FD | field desorption |
| $\Phi_W$ | work function |
| g | gram |
| $\gamma$ | the ratio of the number of exciton formation in the device to the number of electron in the external circuit |
| $h\nu$ | light quantum |
| HOMO | highest occupied molecular orbital |
| HPLC | high pressure liquid chromatography |
| HTL | hole transport layer |
| Hz | hertz |
| IC | internal conversion |
| $\eta_{ext}$ | external quantum efficiency |
| $\eta_{int}$ | internal quantum efficiency |
| $\eta_{lum}$ | luminous efficiency |
| IP | ionization potential |
| $\eta_{pow}$ | power efficiency |
| IR | infrared |
| ISC | intersystem crossing |
| ITO | indium tin oxide |
| J | coupling constant |
| $\lambda$ | wavelength |
| $\lambda_{abs}$ | absorption maximum |
| $\lambda_{PL}$ | photoluminescence emission maximum |
| LB | Langmir-Blodgett |
| LED | light-emitting diode |
| LUMO | lowest unoccupied molecular orbital |
| m | medium |
| m | multiplet |
| *m* | meta |
| M | molar |
| $[M^+]$ | molecule-ion |

| | |
|---|---|
| MALDI-TOF | matrix assisted laser desorption ionization-time of flight |
| mbar | millibar |
| mg | milligram |
| MHz | megahertz |
| mm | millimeter |
| mmol | millimole |
| μmol | micromole |
| m-MTDATA | 4,4′,4″-tris(3-ethylphenylphenylamino)triphenylamine |
| m.p. | melting point |
| MPLC | medium pressure liquid chromatography |
| MS | mass spectroscopy |
| m/z | mass/charge |
| n | refractive index |
| N | normal |
| ν | wavenumber |
| NBS | N-bromosuccinimide |
| NIR | near infrared |
| nm | nanometer |
| NMR | nuclear magnetic resonance |
| NPD | *N*,*N*´-bis(1-naphthyl)-*N*,*N*´-diphenyl)-1,1´-biphenyl-4,4´-diamine |
| *o* | ortho |
| OLED | organic light-emitting diode |
| p | page |
| p | positive |
| *p* | para |
| P′ | polarity index |
| PBD | 2-biphenyl-4-yl-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole |
| Pc | phthalocyanine |
| PcCu | copper phthalocyanine |
| PcM | metallophthalocyanine |

| | |
|---|---|
| PL | photoluminescence |
| POPOP | 1,4-bis(phenyloxazol-2-yl)benzene |
| ppm | parts per million |
| PPV | poly-*p*-(phenylenevinylene) |
| q | efficiency of radiative decay of singlet excitons |
| q | quartet |
| $r_{st}$ | fraction of excitons formed as singlets |
| s | second |
| s | singlet |
| s | strong |
| S | eye sensitivity curve |
| $S_0$ | singlet ground state |
| $S_1$ | first excited singlet state |
| $S_2$ | second excited singlet state |
| t | triplet |
| *tert* | tertiary |
| THF | tetrahydrofuran |
| TLC | thin layer chromatography |
| TPD | *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine |
| U | voltage |
| UV | ultraviolet |
| V | volt |
| Vis | visible |
| VR | vibrational relaxation |
| w | weak |
| W | watt |
| wt % | percent by weight |

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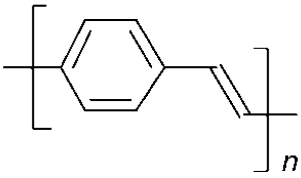
# I. General part

## 1.1 Introduction

World demand on display is nowadays growing enormously. The ongoing globalisation of information technology, especially the development of the internet infrastructures as well as handhold and wireless devices, will fuel this growth. The rapid development influences the demand for efficient materials used to make electronic components for such devices and other types of portable equipments. Many kinds of materials possess their interesting properties, such as electrical conductivity, photo- and electroluminescence, photoconductivity and non-linear optical properties. Due to their outstanding properties with tunabilty, conjugated polymers and low molecular weight organic materials have become integral part in the development of new electric devices. In the neutral state these materials are insulators or semiconductors, but upon doping metallic conductivity approaching that of copper can be achieved.[1]

Electroluminescence of organic materials was first observed for anthracene by POPE et al.,[2] HELFRICH and SCHNEIDER,[3] and MEHL and BUCHER[4] more than a quarter of a century ago. In 1987 TANG and VAN SLYKE,[5] as well as SAITO and TSUTSUI,[6] revived the research on electroluminescence of organic materials by developing an organic light-emitting diode (OLED) with luminescence over 1000 Cd $m^{-2}$, which is high enough for practical operation, at an applying voltage below 10 V. In 1990 FRIEND et al. [7] described a single-layer OLED based on a highly fluorescent poly-*p*-(phenylenevinylene) (PPV, **1**) which gave an yellow-green glow.



**1** (PPV)

This serendipitous discovery not only overcame the drawback of expensive and technologically inconvenient vapour deposition of fluorescent dyes and inorganic semiconductors, but also generated many research efforts since then.

## 1.2 Photoluminescence and Electroluminescence

Luminescence can be classified into many types depending on energy source used to generate excited state in the molecules of active materials. Luminescence stimulated by electric field or injected current is called electroluminescence (EL), whereas that based on photons in the Ultraviolet/Visible (UV/Vis) spectral range (150-1000 nm, 1-8 eV) is termed as photoluminescence (PL). JABLONSKI diagram of energy levels (Figure 1) illustrates the so-called photophysical primary processes in a two-atom molecule.

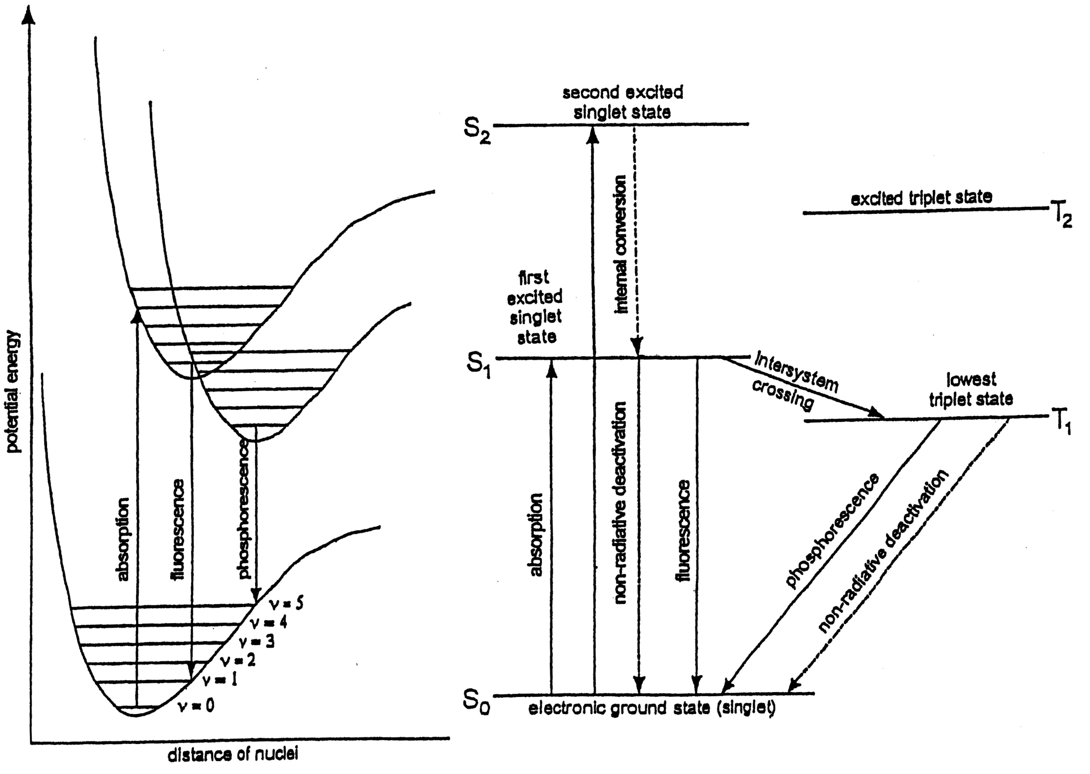


Figure 1 JABLONSKI diagram of energy level for two-atom molecule

If the molecule is supposed to be stimulated to the second excited state ($S_2$), there will be many possibilities in deexcitation mechanisms. If in solution, the molecule can transform its excess vibrational energy into thermal energy through vibrational relaxation process (VR) by colliding with other molecules. This $S_2 \rightarrow S_1$ energy transition is called internal conversion (IC). Both VR and IC are non-radiative process, which occur rapidly approximately within $10^{-2}$ s until the energy level of the molecule come down into the first excited state ($S_1$). Molecule in $S_1$ can decay itself in two ways. One is direct transition of electron from $S_1$ to ground state ($S_0$) called fluorescence which occurs very fast (in a range of $10^{-9}$-$10^{-7}$ s). If an electron in excited molecule reverses its spin through non-radiative intersystem crossing process (ISC), resulting in a change from singlet state to lower triplet state, the other transition called phosphorescence will occur. This relaxation process lasts longer time than fluorescence, $10^{-2}$ s up to hours, and mostly occurs at low temperatures.

## 1.3 Photoluminescence and electroluminescence in conjugated polymers

Conjugated polymers derive their semiconducting properties by having delocalized π-electron bonding along the polymer chain. The π- (bonding) and π*- (antibonding) orbitals form delocalized valence and conduction wave-function, which support mobile charge carriers.[8] To describe these properties, energy band model can be applied. There is a separation into an occupied valence band (π-band) and an unoccupied conductive band (π*-band) with an energy gap of 1-4 eV (1240-310 nm) which covers the whole infrared-visible-ultraviolet range. Figure 2 illustrates the band diagram of poly-*p*-vinylene under the assumption of complete delocalization of electrons compared with that under a consideration of partial delocalization in single and double bonds.

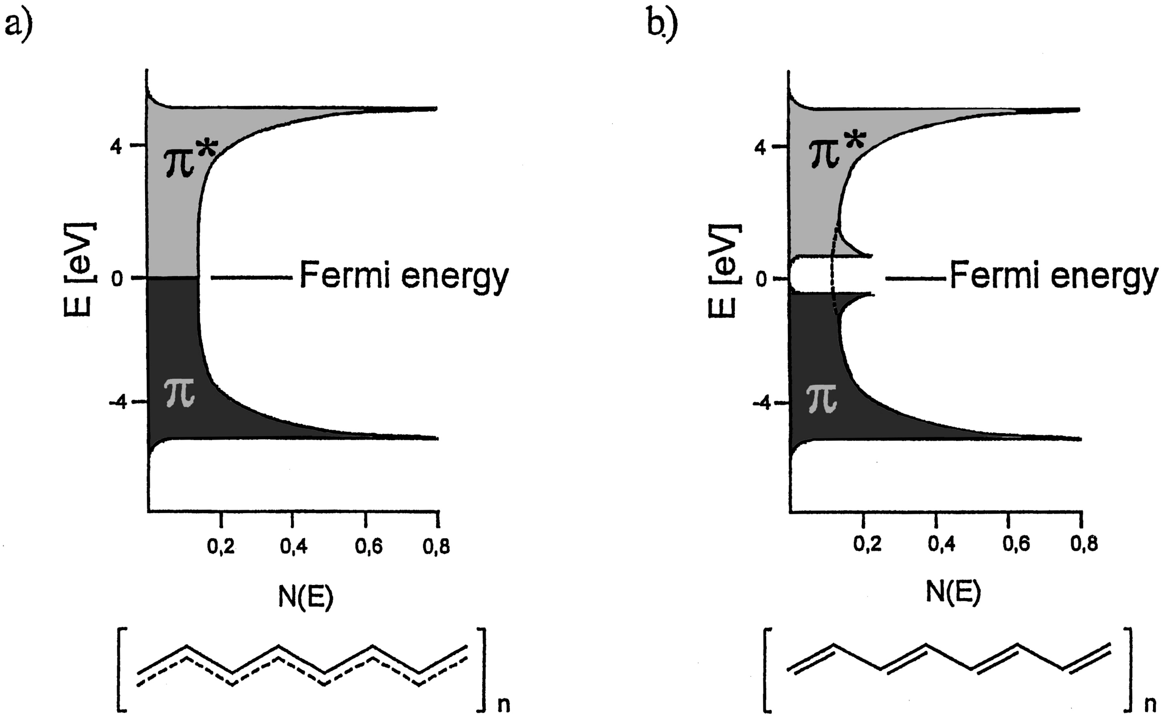


Figure 2 Band diagram of poly-*p*-vinylene a) under an assumption of complete delocalization of electrons and b) under a consideration of partial delocalization.

As mentioned above, in PL an excitation is based on an optical absorption of electrons from the highest occupied molecular orbital (HOMO) which shift into the lowest unoccupied molecular orbital (LUMO) and then form a singlet exciton. A photon is consequently given up as excess energy in the relaxation step (Figure 3). Due to Stokes shift, the wavelength of emissive light is always longer than that of absorbed.

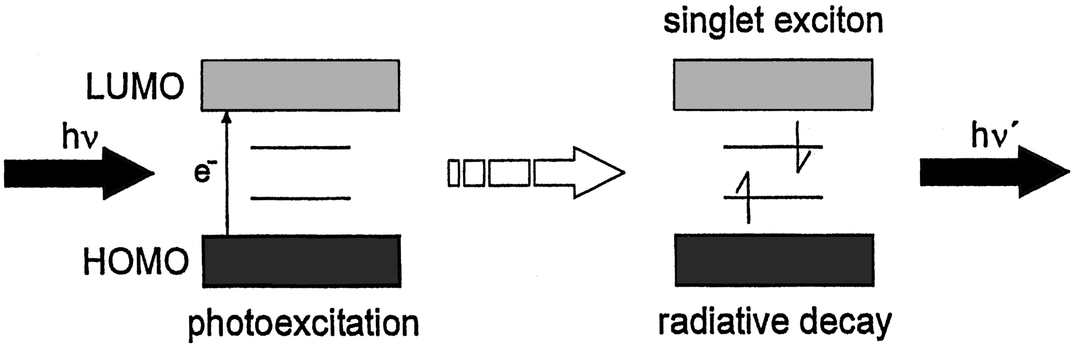


Figure 3 Schematic mechanism of Photoluminescence in organic polymers.

In EL, an electron is injected into LUMO from the cathode, giving rise to a negative elementary charge which is spatially distant and occupies a different energy level from the injected electron (radical), as shown in Figure 4 for PPV.

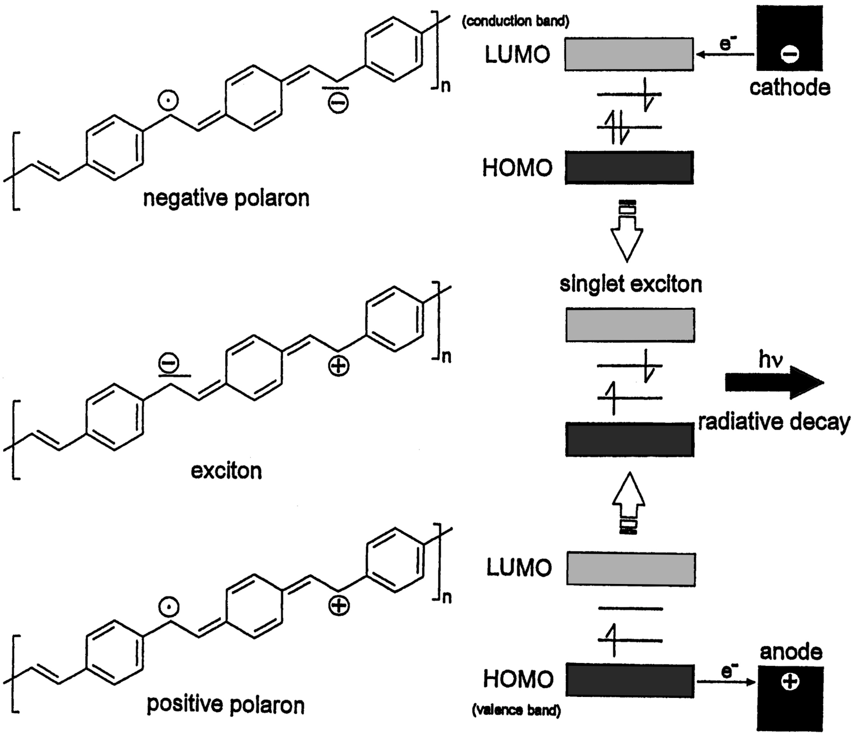


Figure 4 Schematic mechanism of electroluminescence (PPV).

The combination of this charge and radical is called negative polaron. Similarly, when a hole is introduced into HOMO from the anode, a positive polaron is generated. In the presence of an external circuit, both the polaron types move towards the other electrode and capture each other. Based on the spin ½ of electron and hole, an excited singlet (multiplicity = 0) and triplet (multiplicity = 1) states, the so-called exciton, is accordingly formed. However, spin-allowed radiative emission or fluorescence is possible from the singlet one only, and when the exchange energy is large, cross over from triplet to singlet state is unlikely, so that triplet excitons do not produce light other than by indirect process, such as triplet-triplet annihilation or by phosphorescence. Again, the emission of light in this case also exhibits a Stokes shift.

# 1.4 Organic light-emitting diodes

## 1.4.1 General remarks

The fundamental set-up of an OLED device shown in Figure 5 is composed by one or more organic thin layers, selected on the basis of their capacities to transport charge carriers and to act as fluorescent chromophores, sandwiched between conductive substrates as electrodes.

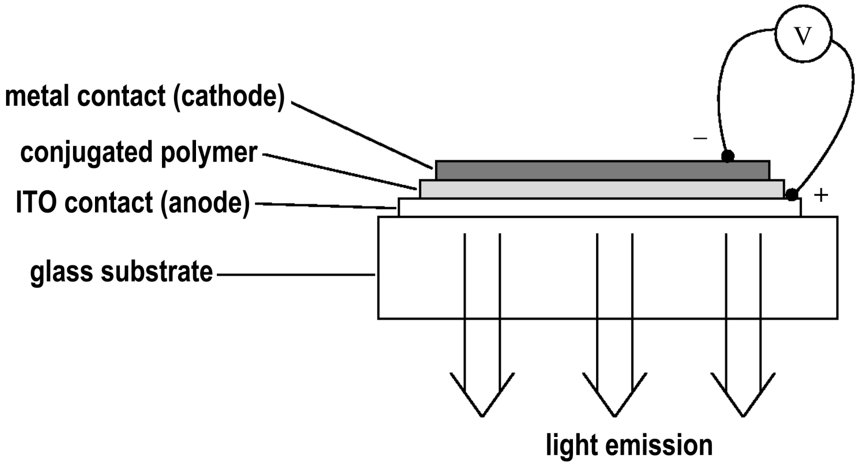


Figure 5 Fundamental set-up of organic light-emitting diode

Since one of these substrates has to be transparent in order to observe light emission from the emitting layer, indium tin oxide (ITO) coated on a glass substrate or on a transparent polymer is usually used as anode. Whereas electropositive metals with low work function ($\Phi_w$), such as Al, Ca, Mg and In which have $\Phi_w$ = 4.3, 2.9, 3.7 and 4.1 eV, respectively, are used as cathode in order to guarantee efficient electron injection.

Figure 6 illustrates the relative positions of energy level of ionization potential (IP) and electron affinity (EA) of emitting layer (PPV), and the work functions of anode (ITO, $\Phi_{ITO}$) and cathode (Al, $\Phi_{Al}$).

Generally, to obtain an efficient charge carrier injection the energy barrier to injection of electrons and holes, $\Delta E_e$ and $\Delta E_h$, has to be balanced. In the case of

PPV shown in Figure 6, there is a small barrier for hole injection and a considerably larger barrier for electron injection.

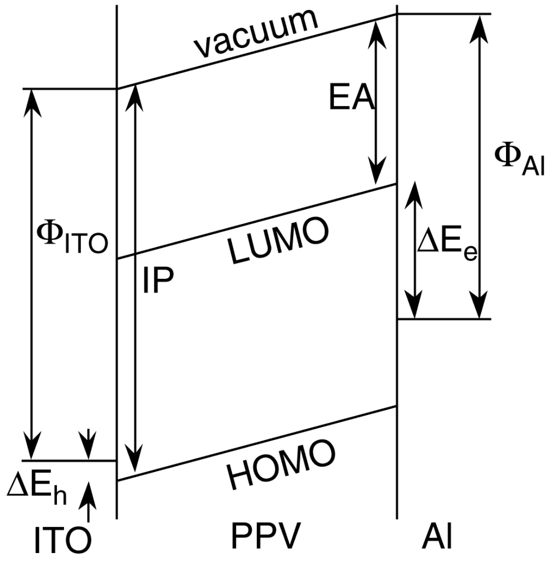


Figure 6 Schematic energy-level diagram of a single layer PPV electroluminescence diode.

The strategies to improve the charge injection and thus efficiency of the OLED are described below.

### 1.4.2 Quantum efficiency

Quantum efficiency or quantum yield of a LED is a quantity to determine the light emission efficiency of the device and is also used to compare the quality among optical devices.

The internal quantum efficiency ($\eta_{int}$) can be expressed as the ratio of the number of photons produced within the device to the number of electron flowing in the external circuit and is given by[8] :

$$\eta_{int} = \gamma \, r_{st} \, q$$

Where $\gamma$ is the ratio of the number of exciton formation events within the device to the number of electrons flowing in the external circuit, $r_{st}$ is the fraction of excitons formed as singlets which is, according to spin statistics, not more than 0.25, and q is the efficiency of radiative decay of these singlet excitons. Though the internal quantum efficiency can best represent the actual physical properties of the emitting layer, an external observer, due to refraction, cannot perceive all photons emitted. Therefore, external efficiency $\eta_{ext}$ is used to describe the usable yield of light whose value is diminished by the factor of $2n^2$ ($n$ = refractive index of the organic layer) with respect to $\eta_{int}$[9] :

$$\eta_{int} \quad = \quad 2n^2\, \eta_{ext}$$

Power efficiency $\eta_{pow}$, defined as the ratio of output light power to input electric power, can be calculated from the average energy of the emitted photons $E_p$ and the known value of the applied voltage U.

$$\eta_{pow} \quad = \quad \eta_{ext}\, E_p\, U^{-1}$$

Luminous efficiency ($\eta_{lum}$) is determined by using the above-calculated $\eta_{pow}$ and the eye sensitivity curve S as defined by the Commission Internationale de L'Eclairage (CIE) which represents the distinct sensitivities of the human eye with respect to different colours.

$$\eta_{lum} \quad = \quad \eta_{pow}\, S$$

In several cases the brightness, given in Cd $m^{-2}$, is also utilized to estimate the efficiency of the electroluminescent devices.

### 1.4.3 Multilayer light-emitting diode

According to Section 1.4.1, the single layer OLED can be applied efficiently only when energy barriers for charge injection are balanced and, moreover, the emitting materials have ambivalent charge transport abilities. Since most common organic semiconductors are intrinsic p-type conductors and therefore are better suited to transport holes[9], electrons and holes usually recombine in the immediate vicinity of the cathode where enhancement of non-radiative decay rate is expected. To solve this problem, low work function metals, such as Ca and Mg, are promising candidates for using as the cathode. However, due to their high susceptibility to atmospheric degradation which lead to a necessity for the device to be hermetically sealed, another solution was suggested in changing the device structure and introducing multilayer OLEDs in which electron and hole transport are performed in different materials and layers (Figure 7).

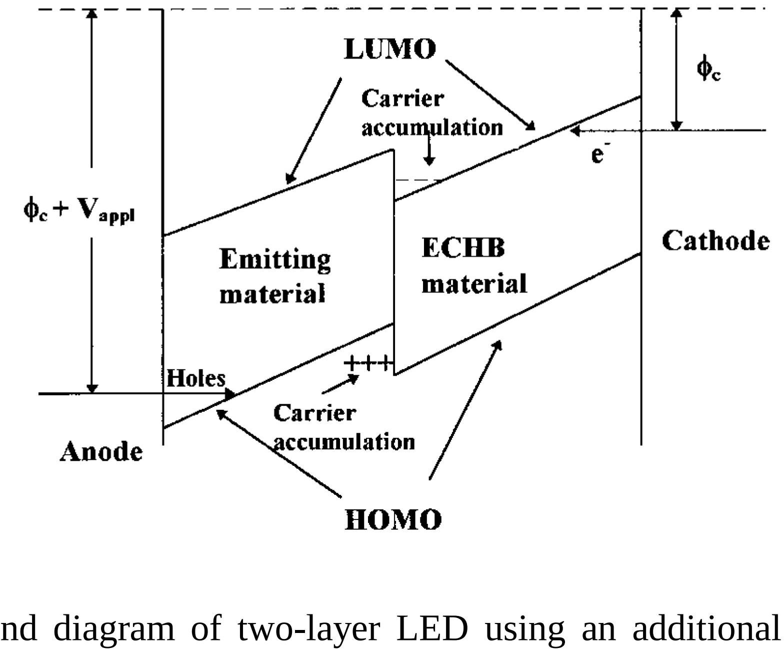


Figure 7 Band diagram of two-layer LED using an additional hole-blocking electron-conducting material.

Electron-conducting and hole-blocking (ECHB) material is added between the emissive layer and cathode, resulting in a substantial accumulation of space charge, thus balancing the charge transport. Other device configurations of multilayer OLED are also possible as shown in Figure 8.

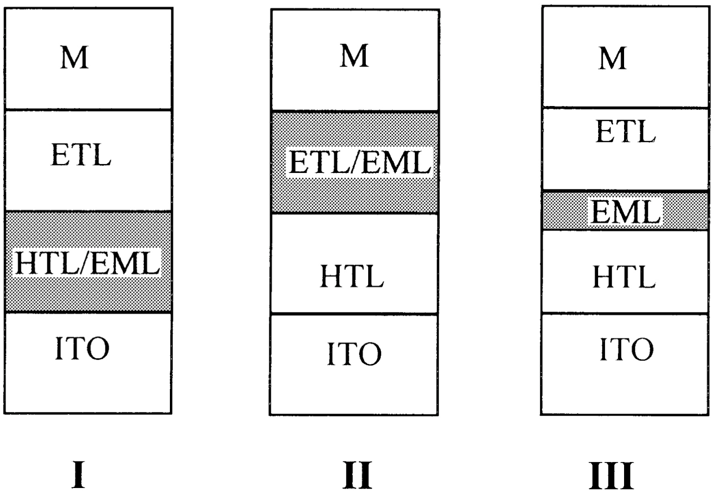
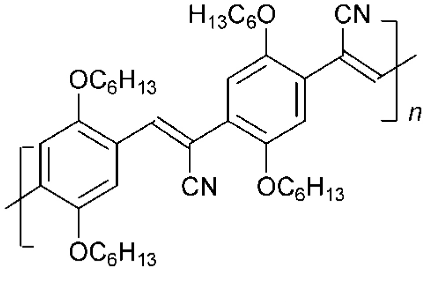


Figure 8 Schematic representation of different LED device configurations. ITO, indium tin oxide; HTL, Hole transport layer; ETL, Electron transport layer; EML, emitter layer and M, metal cathode.

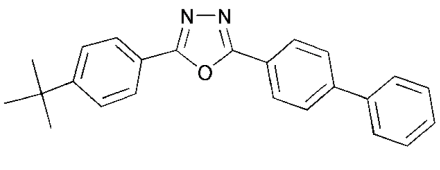
In 1993 FRIEND and HOLMES et al.[10] suggested another concept to provide balanced charge injection by introducing an electron-withdrawing group, namely the cyano group, to the vinylene bonds of a dihexyloxy-substituted PPV. High internal efficiency up to 4% of two-layer OLED comprising ITO/PPV/CN-PPV **2**/metal was reported, independent of the type of cathode material (Al or Ca).



**2** (CN-PPV)

### 1.4.4 Electron-conducting and hole-blocking materials

Several compounds have been suggested as ECHB materials for EL devices,[11-16] for example 2-biphenyl-4-yl-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole-(PBD, **3**),[17] the most important low molecular weight oxadiazole compound which has been widely used because of its extremely low hole affinity. Triazoles are another interesting class of electron deficient thermostable materials similar to oxadiazoles. The most representative derivative is 3-(1,1′-biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-4-phenyl-4*H*-1,2,4-triazole (**4**)[18] which exhibits even more significant hole blocking properties than PBD. Moreover, other interesting materials have been reported, such as low molecular weight materials containing electron deficient 1,3,5-triazine units **5**[19] and phenylquinoxalines compounds **6**.[20]



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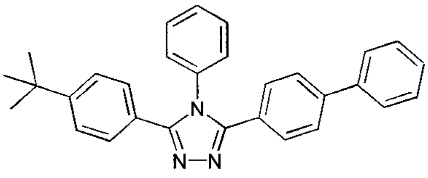

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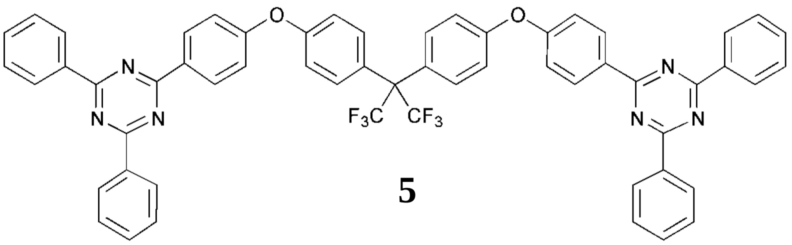
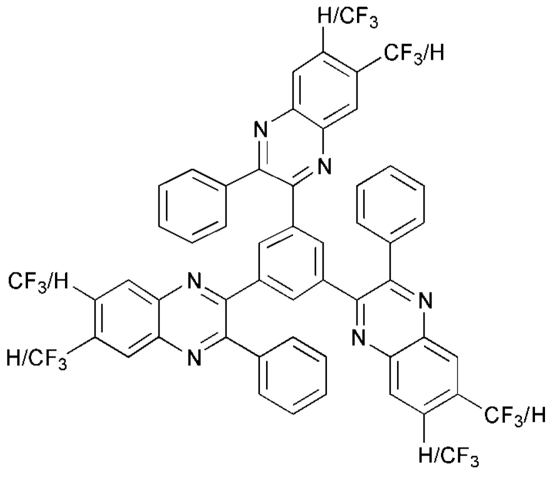


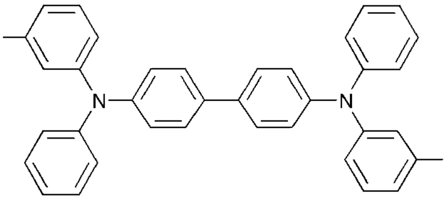
**5**



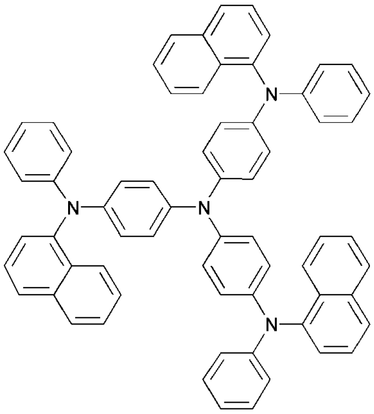
**6**

### 1.4.5 Hole transport materials

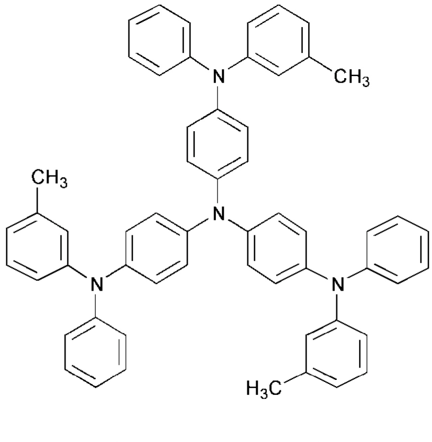
Initially conceived as hole transport compounds in xerography, triarylamine derivatives have gained importance due to their ability to be vacuum deposited and their high drift mobilities.[9] The most prevalent examples are *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD, **7**) and *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl)-1,1′-biphenyl-4,4′-diamine (NPD, **8**).[9] Recently, a thermostable amorphous film based on hole transport “starburst” shaped molecules of 4,4′,4′′-tris(3-methylphenylphenylamino)-triarylamine (*m*-MTDATA, **9**) was reported by SHIROTA et al.[19-22] and TANAKA et al.[23, 24] and became the most widely used material which has been incorporated in highly efficient multilayer devices with significant durability.[19, 21, 22a, 25, 26]



**7** (TPD)



**8** (NPD)

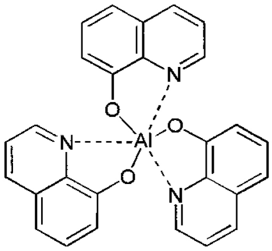


**9** (*m*-MTDATA)

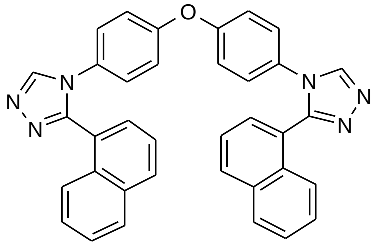
Moreover, phthalocyanine (Pc) and its derivatives are known as excellent hole transport materials because of their capability for being easily oxidized together with their high thermal and chemical stability. Copper phthalocyanine (PcCu) is the most widely used derivative as the hole-transporting layer in OLEDs. An improvement of stability and efficiency of the devices by inserting PcCu layer has been described by many authors.[15b, 27-31] Review on Pc behavior in LED was published recently by our group.[32]

## 1.4.6 Electron transport materials

When a hole transport layer is used as an emitter, an electron transport material is required to enhance the electron transportation from the cathode to the organic heterojunction. Metal chelates, especially tris(8-hydroxyquinolinato) aluminium ($Alq_3$, **10**)[9] are the most prevalent materials because of their abilities to form morphologically stable film and their high electron mobilities. Furthermore, PBD (**3**) and 1,2,4-triazole **11** are also widely used as electron transport material with the combination with dopants.[33]



**10 ($Alq_3$)**



**11**

## 1.4.7 Emissive materials

In recent years unabated interest in the design and synthesis of organic emitting materials was generated on account of their simplicity of manufacture and the possibility to fabricate flexible, large-area, extremely thin and color-tunable displays using low DC operating voltage.

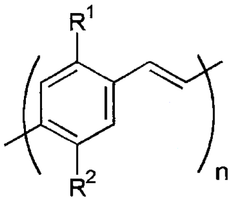
In principle, the basic requirements for the choice of EL material are:

1. good film-forming ability.
2. good thermomechanical stability.
3. non-crystalline behavior.
4. excellent heat, light and environmental stability.
5. strong PL and EL
6. low cost of synthesis and processability.

As previously stated, the discovery of PPV as emitter in OLED has generated many research efforts. In the field of chemistry, the synthetic research can be considered in two ways, one is an attempt to modify the electronic properties, for example band gap, electron affinity and ionization potential, and physical properties, such as solubility and glass transition temperature, of polymeric material through derivatization of PPV which results in a number of PPV analogous EL conjugated polymer. The other is design and synthesis of novel EL materials which are not only polymeric materials, but also low molecular weight compounds like fluorescent dyes and metal chelates.

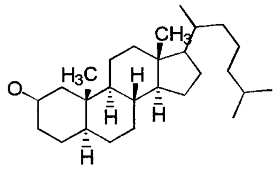
### 1.4.7.1 Conjugated polymeric materials

A variety of PPV derivatives containing long alkyl[34] and alkoxy[34a, 34b, 35] chains, cholestanyloxy[34a, 36] and oligoetheyloxy[37] substituents, for example compound **12** (MEH-PPV), **13** (BCHA-PPV) and **14** (DEO-PPV), have been reported.



**12** (MEH-PPV) : $R^1 = OCH_3$
$R^2 = OCH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$

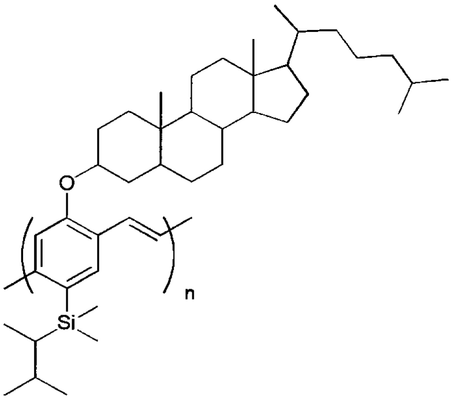
**13** (BCHA-PPV) : $R^1$, $R^2$ =



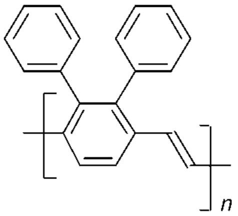
**14** (DEO-PPV) : $R^1$, $R^2$ $=OCH_2CH_2OCH_2CH_2OCH_2CH_3$

Not only the better solubility of these materials, but also the decrease in the formation of the non-emissive relaxation site in LED was observed, which give rise to higher fluorescence and EL efficiencies of the devices.

Moreover, the introduction of silyl substituents, as realized for PPV derivative **15**, gave an increase in the solubility and widening of band gap with respect to the PPV[38], while the introduction of phenyl groups at different positions of PPV skeleton had also proved to be effective in order to enhance the solubility, processability, photostability and PL efficiency. The most prevalent example is compound **16**.[39]



**15** (CS-PPV)

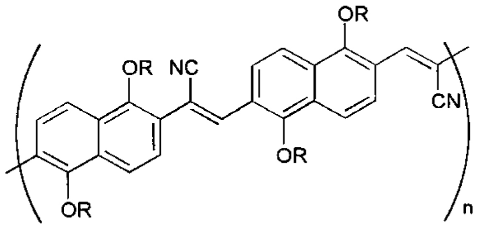


**16**

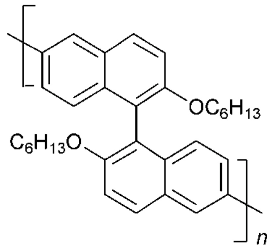
After electron-withdrawing group containing PPV **2** was presented as a high efficient fluorescent emitter in two-layer configuration with PPV, many synthetic research in order to produce EL materials containing other electron-withdrawing substituents, such as trifluoromethyl,[40] halide[41] and trifluoromethanesulfonyl[42] groups, have been reported. However, their PL and EL efficiencies were found to be uncompetitive with CN-PPV derivatives.

Besides the introduction of the substituents, partial or complete replacement of the phenylene rings in the PPV backbone by different moieties, for example anthracene, heterocycles and naphthalene, has been described.[43] According to the study by HANACK and coworkers,[44, 45] incorporation of the naphthalene moiety gives rise to a bathochromic shift in the emission if it is presented as a side unit, whereas the opposite effect is observed when it forms the central units. Modification of the band structure, optical properties and the color of the emission of polymer is possible because of its electron-rich property and steric hindrance caused by its bulky structure. Naphthalene units can be linked in the polymer in many different ways.[44] To date, only 1,4-[45] and 2,6-[46] naphthalene derivatives have been employed in the synthesis of electroluminescent conjugated polymers. Recently, HANACK et al. had success in preparing the first soluble poly(2,6-naphthalenevinylene) **17** containing alkoxy chains on the naphthalene units and cyano group on the vinylene linkage.[45] The effects of structure modification to the emission color of its derivatives had been reported.[44b]

On account of the twisted non-planar backbone, two-layer LED device based on **18**[47] gave excellent luminous efficiency and remarkable external quantum efficiency.

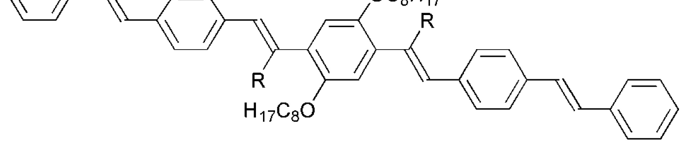


**17**

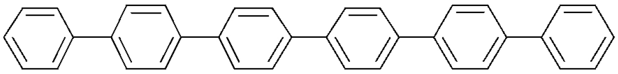


**18**

A number of conjugated oligomers have been synthesized not only as model compounds for preparing the corresponding polymeric materials, but also as emitter in LED devices because of its controllable and well-defined structure. OLED based on oligo(*p*-phenylenevinylene) analogue **19** revealed satisfactory quantum efficiency.[48] Sexi(*p*-phenylene) **20** is the most prevalent oligo(*p*-phenylene) used as a blue emitter in OLED.

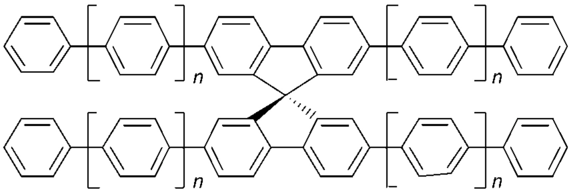


**19** n = 2 and 4



**20**

In order to overcome the drawback of recrystallization of the amorphous film during operation and storage, a new structural concept based on the introduction of spiro centers into defined molecular, oligomeric and polymeric structures was developed, leading to compounds with high quantum yield of the blue PL in the solid state and high glass transition temperature.[49] An example is the oligomeric material **21**.[49b, 50]

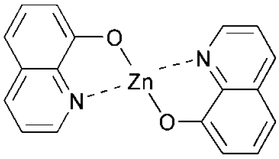


**21** n = 0-3

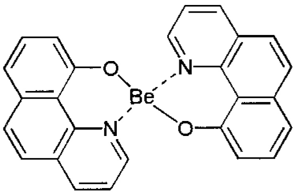
### 1.4.7.2 Low molecular weight materials

One of the most suitable molecular weight materials for EL applications terms to be Alq$_3$ (**10**)[5] which can act as an emitter and also an electron transporter. Taking advantages of the film stability, good charge transport mobilities and high solid-state luminescent yield, metal chelate **22** and **23**,[51-53] lanthanide[54-56] and boron[57] complexes have been utilized as an electron transport emitter.

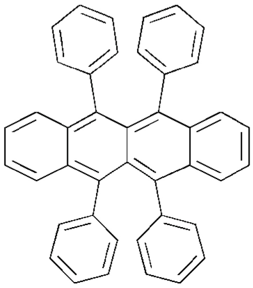
In order to minimize self-quenching which always occurs in highly efficient organic fluorescent dyes, dopant were presented as emitter. The molecules of dopant are dispersed in a host matrix and excited by energy transfer from the host molecules, giving rise to various emission colors. The use of condensed aromatics,[52b, 58] porphyrins,[59] benzoxazoles,[60] stilbene,[61] quinacridone,[62] coumarin[26, 30] and 4-dicyanomethylene-4H-pyran derivatives[52c, 61a, 63] has been reported. By far the most frequently used dopant is rubene (**24**).[52c, 61a, 64, 65]



**22**



**23**



**24**

# 1.5 Phthalocyanines[66]

## 1.5.1 General remarks

Since their accidental discovery more than seventy years ago and subsequent structural elucidation,[67] interest in phthalocyanines (Pcs) and their structurally related compounds, mostly as dyes and catalysts, has grown enormously. The attractive and challenging characteristics are their potential applicability in variety of fields, thermal and chemical stabilities, the relative ease with which they can be prepared and purified and the strong dependence of their properties on peripheral and axial substitution patterns.[68]. At present, they are one of the most widespread materials used in the applications on non-linear optics,[69] as liquid crystal,[70] in photodynamic cancer therapy,[71] in Langmuir-Blodgett (LB) films,[68, 72] in optical data storage,[73] as electrochromic and electro-luminescent substances,[74] as low dimensional metal,[72, 75, 76] in rectifying devices,[77] as gas sensor,[78] as photosensitizers[79] and as carrier generation materials in NIR.[80, 83]

## 1.5.2 Structures of phthalocyanines

Pc is a conjugated heterocyclic 18-$\pi$ electron containing compound and is structurally similar to porphyrin system. Unlike porphyrin, which can be found in the nature such as in hemoglobin, chlorophyll a and vitamin $B_{12}$, Pcs do not occur in nature. In Pc system, methine-bridges of porphyrin are replaced by aza-bridges and, therefore, Pcs can be regarded as tetrabenzotetra-azaporphyrins (Figure 9).

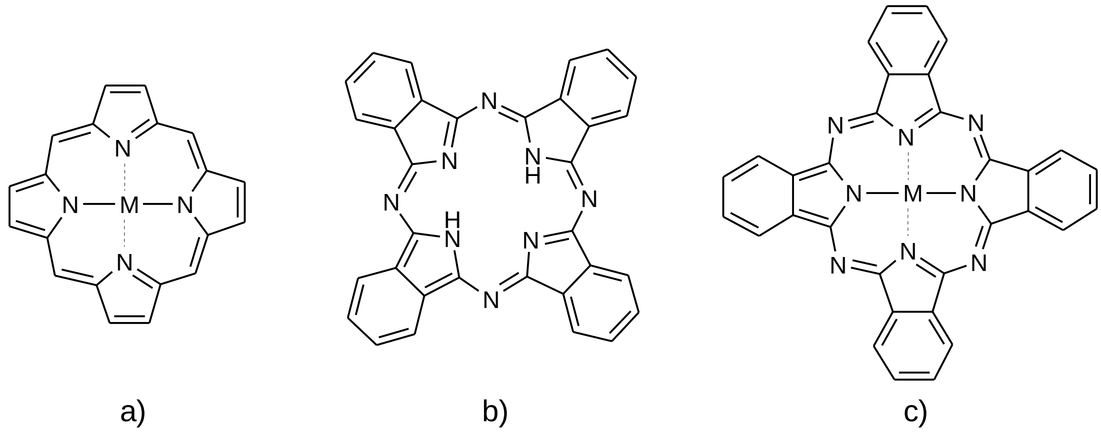


Figure 9 Structure of a) porphyrin, b) phthalocyanine and c) metallophthalocyanine.

Through the formal substitution of hydrogens in metal-free Pc ($PcH_2$) by metal atoms, metallophthalocyanine (PcM) is obtained. Pc complexes with small-sized metal element, such as $Cu^{2+}$, $Ni^{2+}$, $Pt^{2+}$, in its central cavity form quadratic-planar structures. Larger cations, such as $Pb^{2+}$, $Sn^{2+}$, form PcM complexes with a quadratic pyramidal configuration.[81] When large three- or four-fold charged cations, such as $Nd^{3+}$, $Gd^{3+}$, $Th^{4+}$, are introduced, bimolecular complexes in which they are sandwiched between both Pc rings are formed.[82]

## 1.5.3 Syntheses of phthalocyanine

Up to now over seventy different metallic and non-metallic cations have been incorporated in the central cavity of Pc moiety, thereby enabling the control of the oxidation potential and, consequently, the electrical properties of the complexes. The selection of the basic synthetic method of PcM compounds is shown in Figure 10

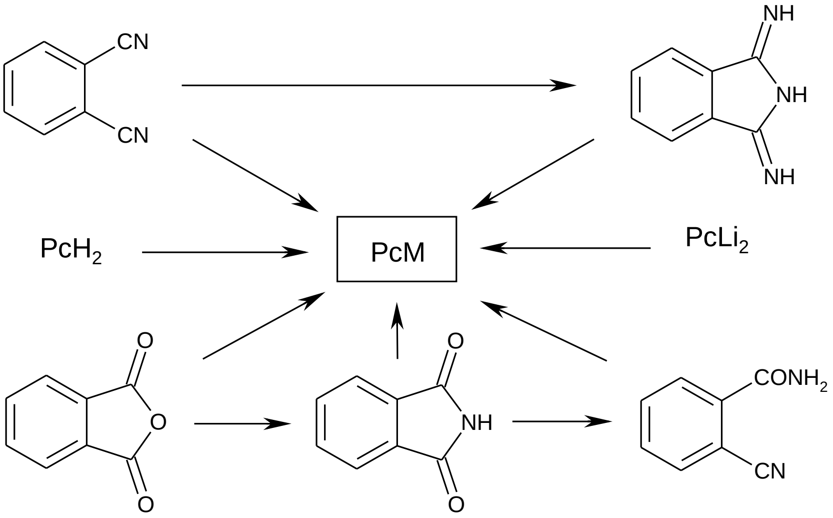


Figure 10 Synthetic methods of phthalocyanines.

The majority of PcM can be prepared by the high temperature cyclotetramerization of phthalodinitriles in the presence of corresponding metal or metal salt or by later insertion of the metal into $PcH_2$. On account of the insolubility of unsubstituted Pc in common organic solvent, soluble impurities can be removed by extracting with hot organic solvents or boiling in acids or bases. More soluble substituted Pc can be purified by common methods of other organic compounds, usually by chromatography, recrystallization and extraction.

### 1.5.4 Soluble phthalocyanines

Due to strong interactions between ring systems, unsubstituted PcMs are practically insoluble in common organic solvent, as mentioned above. The introduction of voluminous long-chain hydrophobic substituents into the periphery of the macrocycle enables an increased solubility. Another approach employed is the introduction of axial substituents at the central metal atom giving rise to the decrease of aggregation effect. By the introduction of selected substituents the physical and electrical properties of Pcs can be verified and tailored, resulting in the broadening of their applications.

The best investigated soluble substituted Pcs are the tetra- and octasubstituted ones.[83] The former generally has higher solubilities than the latter because of its lower degree of order compared with the symmetrical structure of the latter and its higher dipole moment caused by the unsymmetrical rearrangement.

### 1.5.4.1 Tetrasubstituted phthalocyanines

Synthesis of 1,8,15,22- and 2,9,16,23-tetrasubstituted Pcs can be achieved from 3- or 4-substituted phthalodinitriles, respectively, which results in a mixture of four possible constitutional isomers with different symmetries as shown in Figure 11 for 1,8,15,22-substituted Pcs.

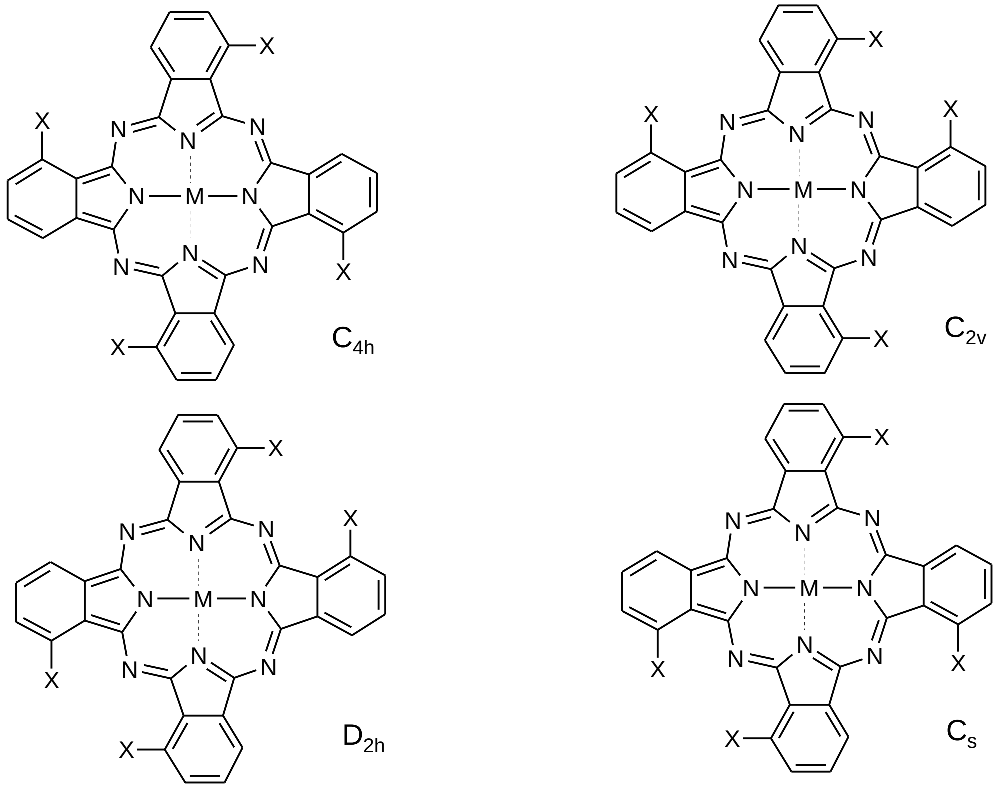


Figure 11 Possible constitutional isomers of 1,8,15,22-tetraubstituted phthalocyanines

The complete separation of the mixture can be carried out by MPLC and HPLC technique which was first achieved by us with the $C_{2v}$ and $C_s$ isomers of (2-Et-

$C_6H_{12}O)_4PcNi$.[84]. Recently, we reported the successful separation of the $D_{2h}$, $C_{2v}$, $C_s$ and $C_{4h}$ isomers of tetrasubstituted Pc and naphthalocyanines.[85]

### 1.5.4.2 Octasubstituted phthalocyanines

The synthetic pathway of octasubstituted Pcs is similar to that of tetrasubstituted one, only that 3,6- or 4,5-disubstituted phthalodinitriles are used instead of 3- or 4-substituted derivatives, respectively. Two different types of products are obtained. One having substituents in the 1,4,8,11,15,18,22,25- and the other in 2,3,9,10,16,17,23,24-positions, which are depicted as 1,4- and 2,3-octasubstituted Pcs, respectively. Their structures are represented in Figure 12.

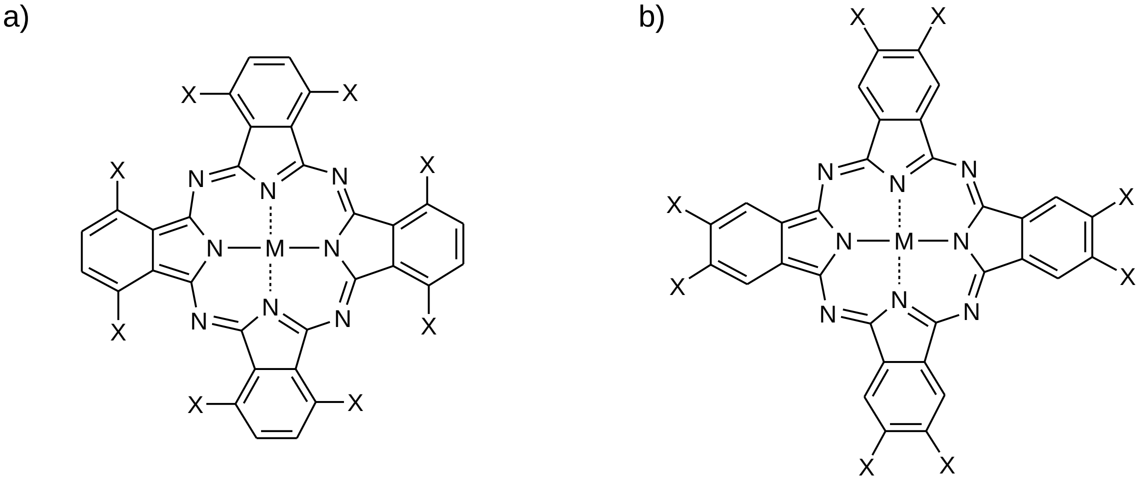


Figure 12 structure of a) 1,4,8,11,15,18,22,25- and b) 2,3,9,10,16,17,-23,24-octasubstituted phthalocyanines.

Compared to 2,3-macrocycles, the synthesis of 1,4-octasubstituted Pcs is more difficult and usually gives lower yields because of steric hindrance from the substituents. However, they are more soluble in common organic solvents than their isomers due to an out-of-plane arrangement of their substituents.

### 1.5.4.3 Unsymmetrically substituted phthalocyanines

This novel kind of Pcs has attracted interest in recent years not only because of their outstanding electronic and optical properties, but also due to their processability in various applications. For instance, the fabrication of versatile LB thin films,[86-87] the synthesis of ladder polymers[88] and the preparation of chemically modified electrodes.[89]

Up to now there are three methods employed for synthesizing unsymmetrically substituted Pcs comprising one different and three identical isoindol subunits ($A_3B$ form), namely subphthalocyanine approach, polymeric support method and statistical condensation.[90]

The first two pathways are regarded as selective methods with which, however, there are still many problems. In the case of the subphthalocyanine approach, fragmentation of the subphthalocyanine can occur in the reaction process, resulting in all possible Pcs containing all the combination of iminoisonidoline units presented in the starting material. The polymeric support method are unsuitable for large-scale preparation. Hence, the most usual method for the preparative work is the statistical condensation between two different phthalodinitriles A and B (Figure 13) in the appropriate stoichiometric ratio followed by chromatographic purification.[66b]

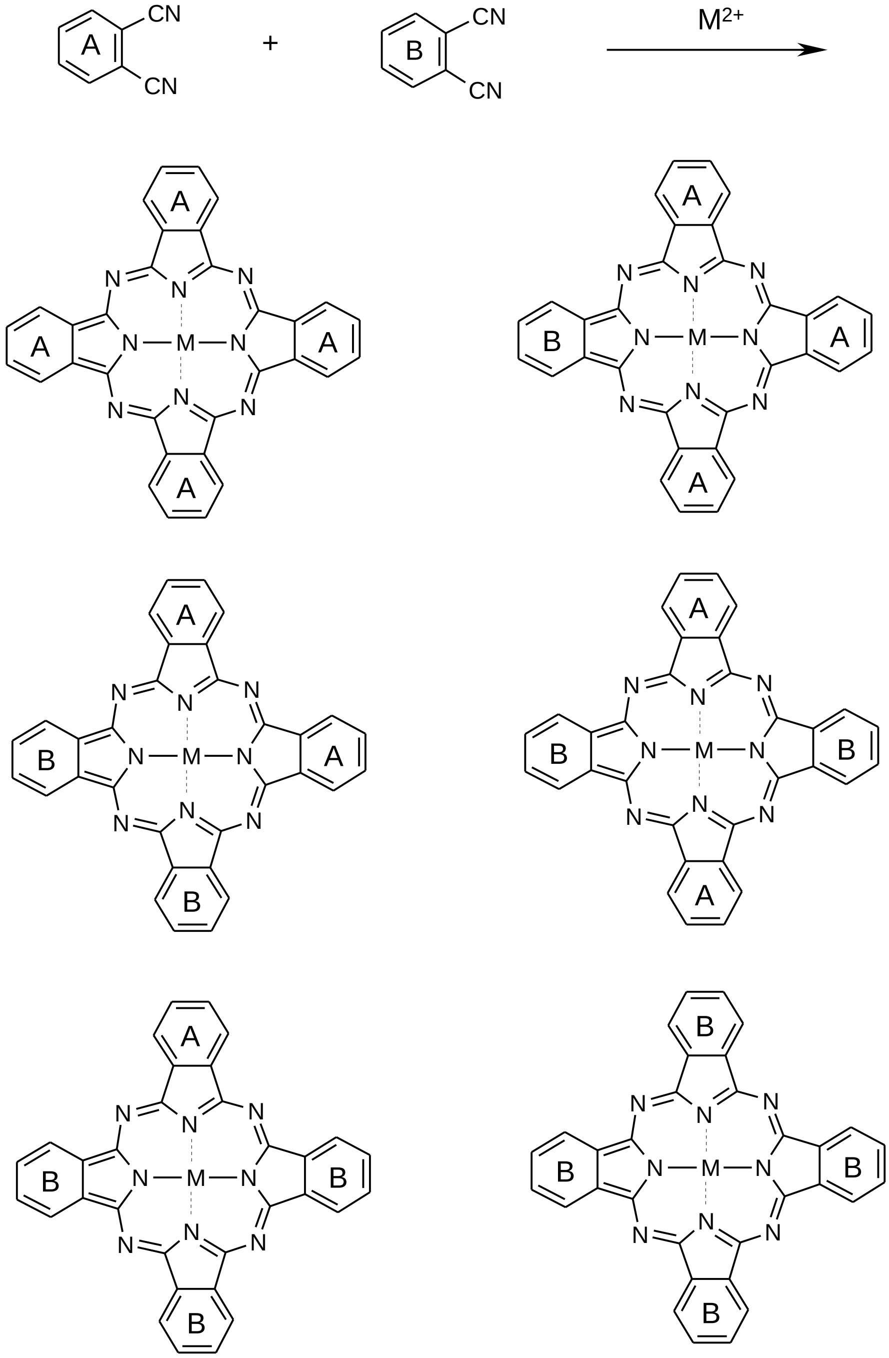
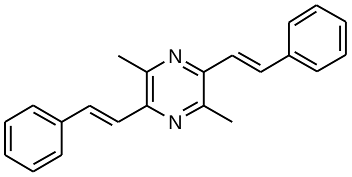


Figure 13 Statistical condensation and all possible phthalocyanine products.[66b]

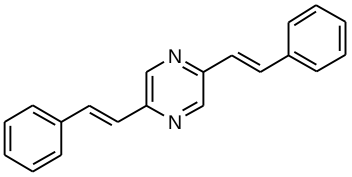
Many efforts have been made to synthesize a vast number of this kind of Pc derivatives bearing various functional groups. Recently, unsymmetrical substituted Pcs containing a formyl or aldehyde functional group for LED applications was successfully synthesized in our group.[91]

# II Aim of the work

The aim of this work is to synthesize PPV analogue compounds containing 2,5-substituted (**24**) and unsubstituted (**25**) pyrazine unit in the middle of the molecules.



**24**

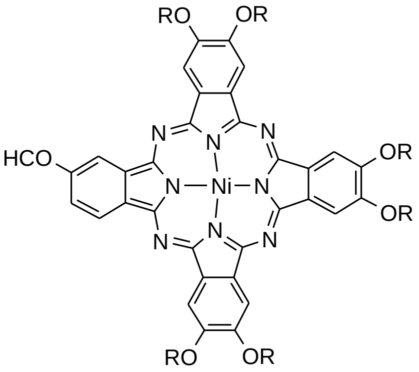


**25**

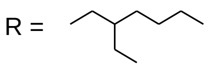
Due to the presence of two electronegative nitrogen atoms, the pyrazine unit exhibits an electron-deficient character. Thus, the modification of PPV skeleton by replacing the central phenylene moiety with pyrazine unit is expected to increase the electron mobility of the resulting LED device.

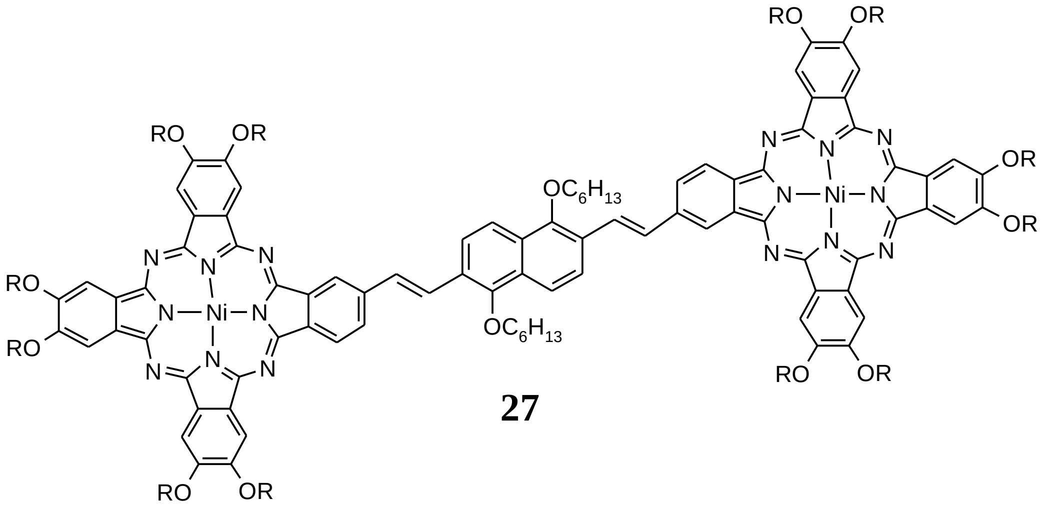
As previously stated, Pcs are not only thermally and chemically stable compounds, but they are also known as widely used hole transport materials. Therefore, the introduction of Pc units into the molecular framework should be able to improve the stability and the hole conductivity of the resulting materials. On account of this, it has been projected to synthesize PPV analogous compounds containing annulated benzene ring such as naphthalenes and Pc moieties at the end of the oligomeric chain whereby the Pc is attached to the naphthalene unit via vinylic linkages at 2 and 6 positions of the naphthalene system. Bulky groups can be introduced into Pc and/or naphthalene moieties in order to enhance the solubility of the system.

According to a recent study by HANACK et al.[91] in which the synthesis of bisvinylene-phenylene-bridged Pc dimers was described, the desired bisvinylene-naphthylene-bridged Pc dimers **27** and **28** should be synthesized by a similar route, namely by Wittig reaction of the mono-formyl substituted Pc **26** and the corresponding naphthalene phosphonium salt. The asymmetric Pc **26** can be prepared by statistic reaction between 3,4-dicyanobenzaldehyde ethylene acetal and 4,5-bis(2’-ethylhexyloxy)-benzene-1,2-dinitrile.[91a]

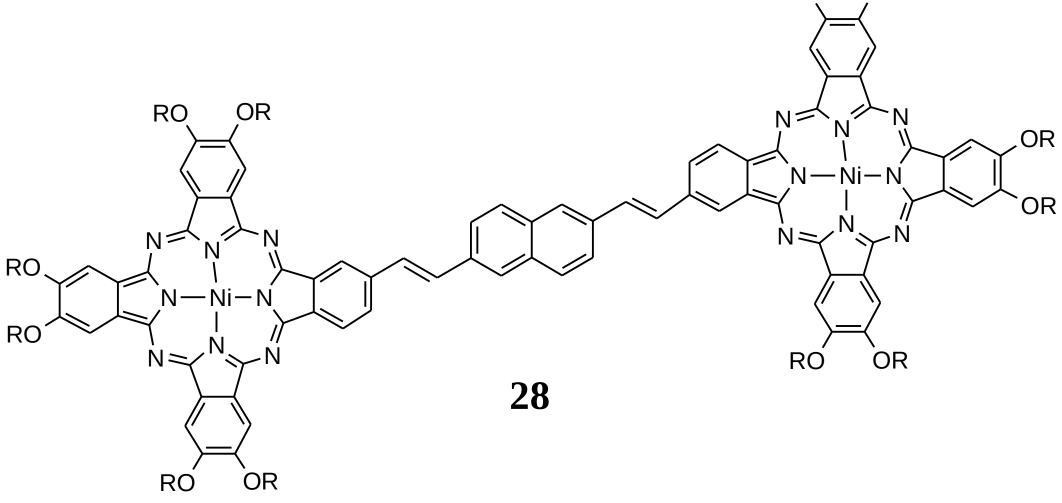


**26**





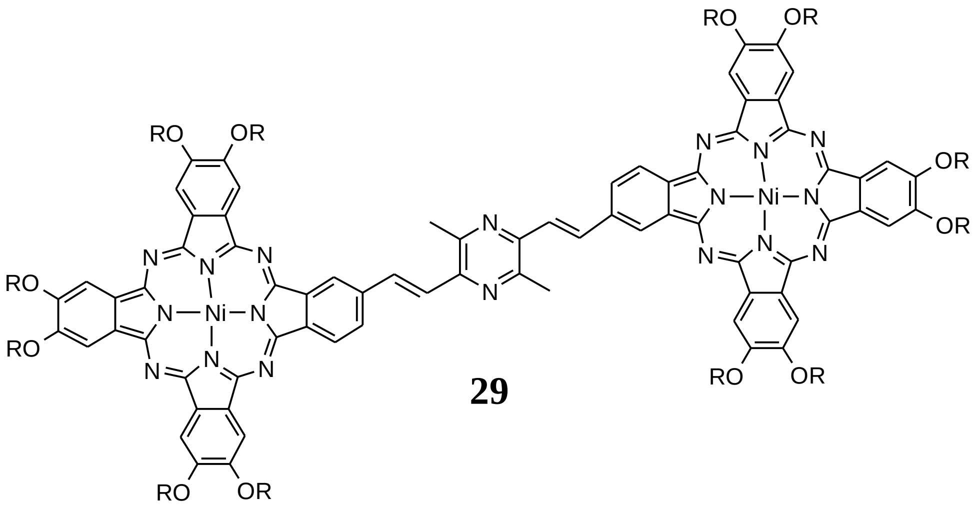
**27**



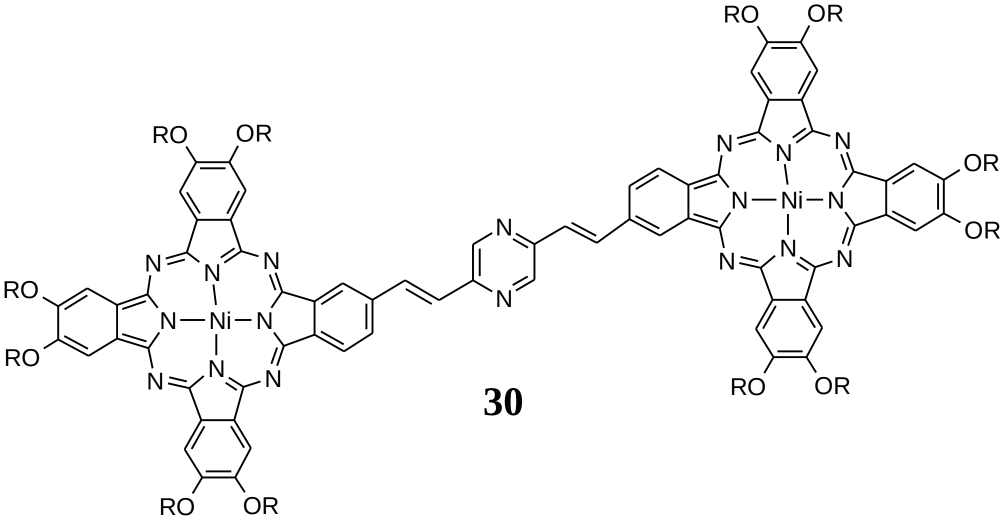
**28**

The resulting dimers **27** and **28** will be fully characterized and their organic light emitting properties investigated.

Moreover, the synthesis of the pyrazine dimer derivatives **29** and **30** are also aimed in order to study the effect of the combination between the electron-deficient property of pyrazine unit and the high stability as well as hole conductivity of Pc moieties to their optical properties. The synthesis pathway should be similar to that of naphthalene dimer derivatives.



**29**



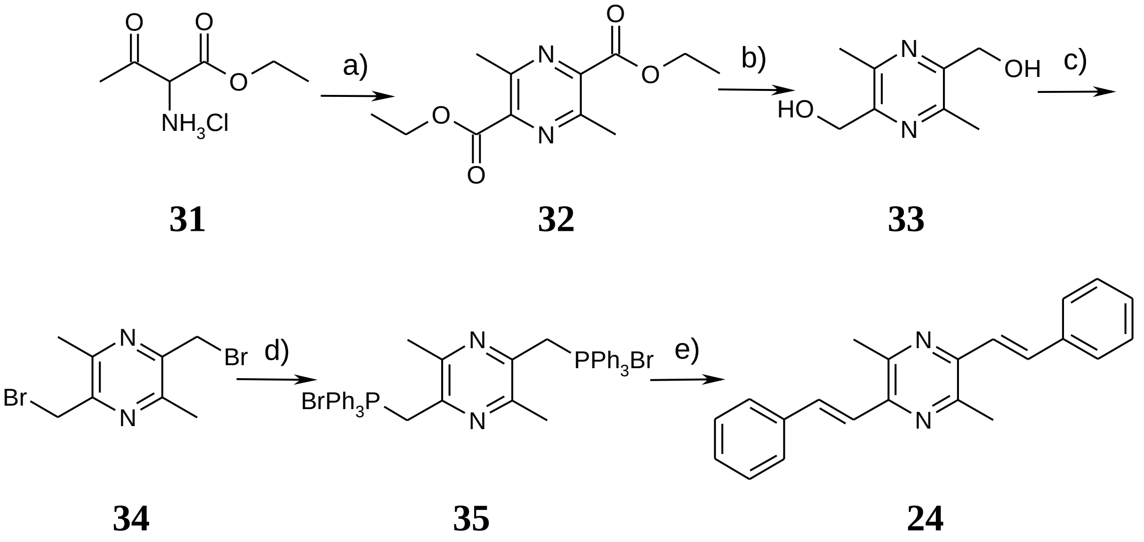
**30**

# III. Results and discussion

## 3.1 Synthesis and characterization of 3,6-dimethyl-2,5-distyrylpyrazine (24)

### 3.1.1 Synthesis

The synthesis starts from ethyl-2-aminoacetoacetate hydrochloride **31**, which was prepared according to previously reported procedure.[92] The synthesis pathway of **24** is summarized in Scheme 1.



Scheme 1 Synthesis of **24**: a) $Et_3N$, EtOH, b) $NaBH_4$, MeOH, c) $PBr_3$, toluene, d) $P(C_6H_5)_3$, toluene, 65 °C e) $C_6H_5CHO$, KOBu-t, EtOH.

#### 3.1.1.1 2,5-Bis(hydroxymethyl)-3,6-dimethylpyrazine (33)

Self-condensation of **31** with the help of triethylamine led to high yields (72.00 %) of diethyl ester **32** which was converted into the alcohol **33** by reduction with sodium borohydride in methanol. The more reactive lithium aluminium hydride, which is normally used in reduction of ester, was actually considered as the first candidate. However, after several efforts under different reaction conditions, **33** was not obtained. A possible explanation might be that a highly electron deficient pyrazine ring is normally susceptible towards nucleophilic attack. This effect is even more strengthened by the presence of the two strongly electron withdrawing ester groups, resulting in the formation of other by-products with reduced pyrazine ring or the decomposition of starting material **32**.[93] To achieve the reduction, a large excess of sodium borohydride is required which causes the formation of borate intermediate in huge amounts and, consequently, leads to great difficulty in the isolation of the desired product. Therefore, acetic acid was added to the reaction mixture, which decomposes this stable intermediate. However, one should be careful that acetic acid should be added only until the mixture become neutral or slightly acidic, otherwise an excess acid may protonate the pyrazine nitrogen atoms.

Similar to that of aliphatic amines, anilines and other nitrogen containing heterocyclic compounds, basic nitrogen atom of pyrazine derivative **33** exhibits an acid-base interaction with acidic silanol groups in the silica gel during the separation by column chromatography. This interaction slows down the elution of the product by hexane/$CH_2Cl_2$. By using more polar ethyl acetate and short column, the separation was readily carried out. However, this can be assumed to be a reason for the low yield of **33** (26.00 %).

### 3.1.1.2 2,5-Bis(bromomethyl)-3,6-dimethylpyrazine (34)

In a subsequent bromination with phosphorus (III) bromide, bis(hydroxy)methyl **33** was converted into the bis(bromomethyl) compound **34** in moderate yield (48.74 %). The reaction was performed in toluene with phosphorus(III) bromide/**33** in a ratio of 2:3. Two moles of pyridine were added stoichiometrically in order to impede a protonation of pyrazine during the reaction. Again, a short column and polar eluent were used in the purification step.

### 3.1.1.3 2,5-Bis(methyltriphenylphosphoniumbromide)-3,6-dimethyl-pyrazine (35)

The phosphonium salt **35** was prepared by the reaction of **34** with stoichiometric amounts of triphenylphosphine in dry toluene. Due to its high polarity, **35** was insoluble in toluene and the precipitate formed could be conveniently separated by filtration. However, the complete purification of **35** was unsuccessful. It could neither be carried out by Soxhlet extraction with several organic solvents nor by common chromatographic methods.

### 3.1.1.4 2,5-Dimethyl-3,6-distyrylpyrazine (24)

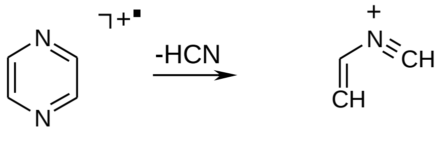
Synthesis of PPV analogue **36** was proceeded by the Wittig reaction of phosphonium salt **35** and two equivalents of benzaldehyde in the presence of potassium-*tert*-butoxide as a base in dry ethanol at room temperature. An occurrence of orange color was observed when the base was carefully added, which was ascribed to the intermediate ylide, and then the yellow product was formed. After workup and purification by chromatography as well as recrystallization, the all-*trans* product was obtained in 35.35 % yield. Due to lack of selectivity of Wittig reaction, a mixture of all three configurational isomers, namely *trans-trans*, *trans-cis* and *cis-cis*, was actually obtained. After recrystallization step to purify the product from other impurities the least soluble *trans-trans* isomer, due to its nearly planar conformation, could be readily separated from its isomers.

## 3.1.2 Characterization

### 3.1.2.1 2,5-Bis(hydroxymethyl)-3,6-dimethylpyrazine (33)

The $^1$H-NMR spectrum of **33** exhibits three singlets at 4.71, 4.14. 2.44 ppm with an integration of 2:1:3, which is consistent with the presence of three different kinds of protons in the molecule, namely -$CH_2$- protons adjacent to -OH group, O-H proton and -$CH_3$ protons, respectively. For $^{13}$C-NMR spectroscopy, signals at 149.0 and 146.0 ppm are ascribed to pyrazine carbons which are slightly more downfield than those of the parent pyrazine (145 ppm) due to the electron-donor methyl groups.

Electron impact mass spectrum of **33** shows the molecular peak ($M^+$) and those after losing its hydroxy group and both methyl substituents. A characteristic peak of pyrazine compound is observed at *m*/*z* 53.3 in the spectrum, which is assigned to the ring fragmentation with loss of HCN (scheme 2).



*m*/*z* 53

Scheme 2 Characteristic fragmentation of the pyrazine ring.

A strong O-H stretching band in the IR spectrum at 3246 cm$^{-1}$ confirmed the existence of -OH group in the structure of **33**. Moreover, a band at 1043 cm$^{-1}$ could be ascribed to the C-O stretching vibration.

### 3.1.2.2 2,5-Bis(bromomethyl)-3,6-dimethylpyrazine (34)

Similar to **33**, the $^1$H-NMR spectrum of **34** exhibits two singlet signals at 4.52 and 2.59 ppm with an integration of 2:3 which match the chemical shift of protons of -$CH_2$- group attached to bromines and $CH_3$ groups, respectively. Its

$^{13}$C-NMR spectrum is also nearly identical to that of **33**, only -CH$_2$- appears at more upfield due to the conversion from hydroxymethyl group in **33** to bromomethyl in **34**.

In the electron impact mass spectrum of **34**, there are three characteristic peaks, namely the molecular peak (M$^+$) and two fragment peaks after loss of one and both bromine atoms. Again, the peak at *m*/*z* 52.6, ascribed to the fragmentation type depicted in Scheme 2, also appears in the mass spectrum.

### 3.1.2.3 2,5-Bis(methyltriphenylphosphoniumbromide)-3,6-dimethyl-pyrazine (35)

Though compound **35** could not be completely purified as reported above, it could be assumed by considering its $^1$H-NMR spectrum that the compound **35** is pure enough to be characterized by spectroscopic methods.

$^1$H-NMR spectrum shows doublet of -CH$_2$-protons adjacent to phosphonium moieties at 5.57 ppm with coupling constant of $J$ = 13.5 Hz, resulting from the interaction with $^{13}$P atom. Singlet peak at 2.21 ppm belongs to CH$_3$ protons which match those of **33** and **34**.

In fast atom bombardment (FAB) mass spectrum, the fragment peak after loss of both bromine atoms appears as the highest *m*/*z* ratio peak. Moreover, the spectrum shows two other fragment peaks. One indicates the loss of a P(C$_6$H$_5$)$_3$Br group and the other is ascribed to the loss of the other bromine atom.

The IR spectrum confirms the presence of P(C$_6$H$_5$)$_3$Br moieties as shown by three strong characteristic C-H stretching bands of the terminal phenyl rings of the phosphorus atoms at 748, 719 and 690 cm$^{-1}$.

### 3.1.2.4 2,5-Dimethyl-3,6-distyrylpyrazine (24)

In $^1$H-NMR spectroscopy, the all-*trans* configuration of **24** is determined by an appearance of two doublet signals of vinylic protons (H$^a$ and H$^b$, for numbering see experimental part, Section 5.1.5) at 7.81 and 7.35 ppm with coupling constants of *J* = 14.9 and 15.4 Hz, respectively. It is obvious that the highly electron-deficient pyrazine ring effects significantly downfield shift of $H^a$ (Figure 14).

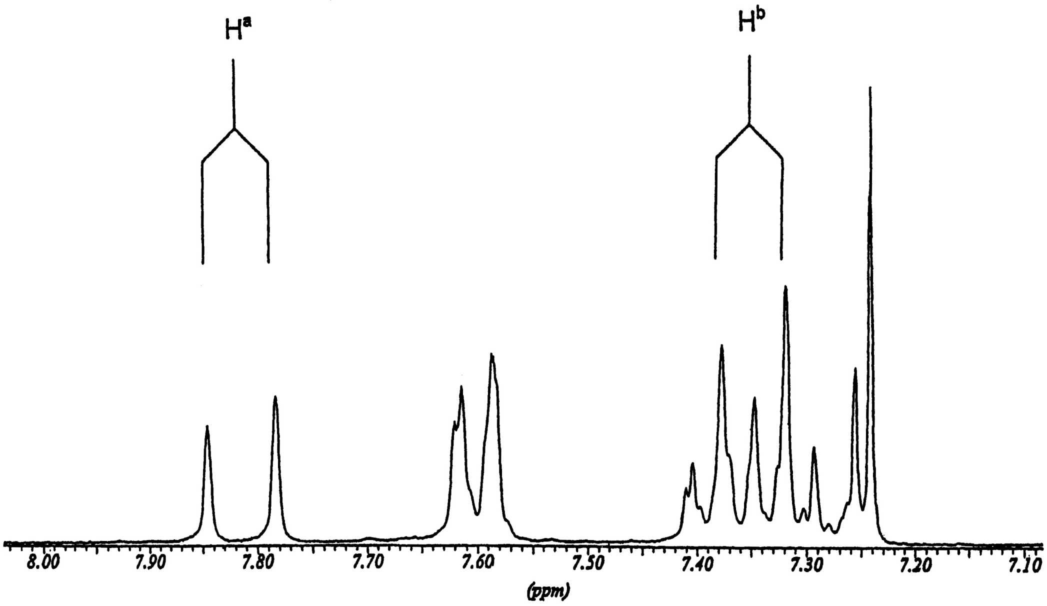


Figure 14 $^1$H-NMR spectrum of **24** in the aromatic region.

Additionally, the IR spectrum supports the *trans-trans* configuration by exhibiting the out-of-plane bending vibration of the *trans* -CH=CH- moieties at 964 cm$^{-1}$.

In the $^{13}$C-NMR spectrum, C-1 and C-2 appear at 148.1 and 146.1 ppm, respectively, which are downfield compared with the chemical shift of the parent benzene ring. This is caused by both of electronegative nitrogen atoms in the pyrazine ring.

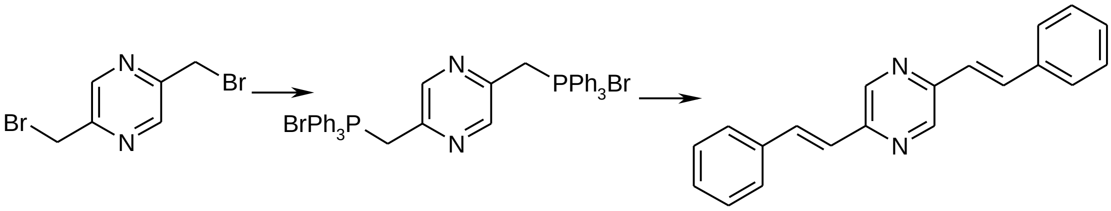
In the electron impact mass spectrum, molecular peak ($M^+$) is observed as a parent peak at *m*/*z* 312.3. Other peaks are ascribed to fragments with loss of methyl group and phenyl groups.

## 3.2 Synthesis and characterization of 2,5-distyryl-pyrazine (25)

### 3.2.1 Attempt to prepare 25 through Wittig reaction

Though 2,5-distyrylpyrazine is already known[94], it has been prepared in this work again in order to investigate its physical and optical properties to compare with those of its derivatives **24** and **30** (see p. 25 and 27, respectively). Moreover, the reaction condition in this preparation will be a good guide for the more complicate preparation of its Pc dimer **30**.

Through retro-synthesis approach, 2,5-bis(bromomethyl)pyrazine **37** is required as the starting material to prepare phosphonium salt **38** which reacts with benzaldehyde to furnish desired compound **25** (Scheme 3).



**37** **38** **25**

Scheme 3 Synthesis of 2,5-distyrylpyrazine (**25**).

Several reaction conditions were tried in order to prepare pyrazine **37**, namely bromination of 2,5-dimethylpyrazine, bromomethylation of pyrazine and conversion from hydroxymethyl group to bromomethyl group. No desired product was detected from the last two routes, whereas a mixture of **25** and other byproducts were obtained from the first one. However, the yield was low and pure **25** could not be successfully isolated. It might be that nucleophilic attack at 3- and/or 6-positions occurred competitively with the expected mechanism because of the electron deficiency of the pyrazine ring. Though the preparation of phosphonium salt **38** was performed with the mixture of products directly, no **38** was obtained.

On account of this failure, another alternative has to be tried. Several years ago it was previously reported that some styrylpyrazine derivatives could be produced in the condensation of methylpyrazines with aromatic compounds in the presence of zinc chloride.[94] Therefore this method was brought into the consideration in order to prepare **25** and Pc dimer **30** which are described below.

### 3.2.2 Synthesis of 25 through the condensation approach

According to the classical condensation method mentioned in the last section, 2,5-dimethylpyrazine reacted with 2 equivalents of benzaldehyde under the similar reaction condition but workup procedure was changed in order to simplify the process. Recrystallization of the brownish red crude product gave pure **25** as yellow crystals in moderate yield (34.99 %).

### 3.2.3 Characterization of 25

In the $^1$H-NMR spectrum, protons at the 3- and 6- positions exhibit a characteristic singlet at 8.58 ppm, whereas the signals of their carbons in the $^{13}$C-NMR spectrum, C-1 and C-2 (for numbering see experimental part, Section 5.1.6, p. 66), are observed at 149.1 and 143.3 ppm, respectively. Similar to **24**, the $^1$H-NMR spectrum of **25** shows two doublets at 7.72 ($H^b$) and 7.17 ($H^c$) ppm which are assigned to vinylic protons.

The stereochemistry of the *trans* double bonds is established by the coupling constant of the vinylic protons in the $^1$H-NMR ($J$ = 15.9 Hz) and by out-of-plane bending vibration in IR spectrum (at 974 cm$^{-1}$), typical for *trans*-substituted PPV analogue compounds.

## 3.3 Optical properties of 24 and 25

UV/Vis, PL- and EL- maxima were measured to monitor the effect of the pyrazine unit and of the methyl substituents on the HOMO-LUMO energy gap and the emitting light.

### 3.3.1 UV/Vis and PL spectroscopy

#### 3.3.1.1 PL instrument

To fulfill the understanding about PL-properties , an instrumental feature is described briefly in this section. Figure 15 illustrates a schematic set-up of the PL measurement apparatus.

Firstly the sample is sublimed in high vacuum as thin film onto a 25×25 mm glass slide. Light is generated from a 400 W high pressure xenon lamp c) and a suitable excitation wavelength is selected by a single graded monochromator d). The incident beam e) is then radiated towards the glass slide coated with sample a). The fluorescence light f) is monochromated in another double graded monochromator g) and detected by a photomultiplier h) which is driven by a 950 V light voltage source. Intensities of light can be adjusted by both slits i) which are normally set in a range of 0.2 to 1.0 mm. The excitation beam can be obstructed by two shutters k) to prevent the sample and photomultiplier from being damaged by the light. A personal computer j) is responsible for controlling parameters and analyzing the obtained signals. The measurement has to be conducted in a dark room.

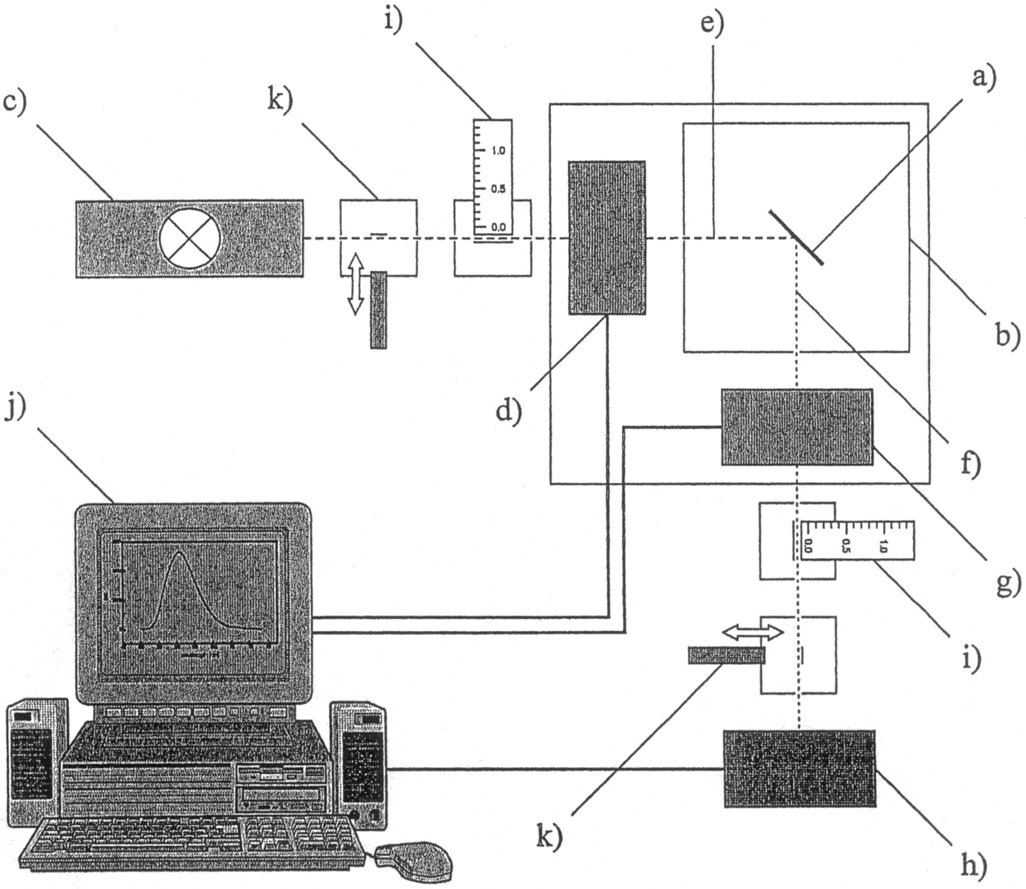


Figure 15 Schematic set-up of PL measurement apparatus.

### 3.3.1.2 Measurement

Since **24** and **25** are PPV analogue compounds in which the carbons at the 1- and 4- positions of the middle phenyl unit are replaced by nitrogen atoms, distyrylbenzene (DSB) is included for the comparison of their absorption and emission spectra which are summarized in Table 1.

Table 1 UV/Vis maxima in $CH_2Cl_2$ solution ($\lambda_{abs}$), PL-maxima in solid film ($\lambda_{PL}$) and calculated energy gap ($E_{gap}$) of **24**, **25** and reference molecule DSB.

| **Compound** | **$\lambda_{abs}$ (nm)** | **$\lambda_{PL}$ (solid, nm)** | **$E_{gap}$ [a] (eV)** |
|---|---|---|---|
| **DSB [b]** | 356 | 444, 467 [c], 500 [c, d] | 3.18 |
| **24** | 295 [c], 391 | 468 | 2.82 |
| **25** | 303 [c], 383 | 472, 494 [c, e]<br>482, 498 [c, f] | 2.89 |

[a] Determined from the onset of absorption.

[b] In $CHCl_3$ solution.[95]

[c] Shoulder.

[d] Nanocrystal, see [96] for more detail.

[e] γ-Form nanocrystal, which has molecular pair arrangement and was obtained from the vapour.[97a]

[f] α-Form nanocrystal, which has semi-infinite stacking arrangement and was obtained from the solution.[97a]

Absorption maxima of **24** and **25** (Figure 16) were measured in $CH_2Cl_2$ solution, whereas PL maximum measurement of **24** was carried out in the solid state as thin film. Both measurements are performed at room temperature.

Instead of $CH_2Cl_2$, the absorption data of DSB performed in $CHCl_3$ is used in this discussion. However, its absorption maximum is not strongly solvent dependent, in a range of 350-356 nm by an increase of solvent polarity index (P′) from cyclohexane (P′ = 0) to chloroform (P′ = 4.4) - P′ of $CH_2Cl_2$ is 3.4.[98]

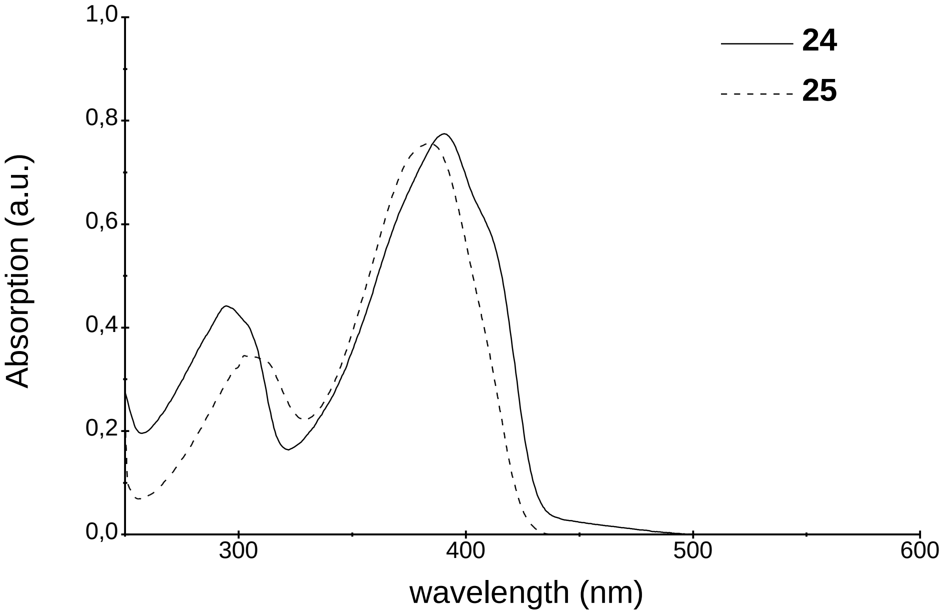


Figure 16 UV/Vis spectra of **24** and **25** measured in $CHCl_2$.

In the absorption spectra of both **24** and **25** shown in Figure 16, two broad bands are observed. An additional band, shoulder, located at shorter wavelength with regard to the main peak is due to excitation to the second excited state ($S_2$). In principle, the higher excited states relax the excess energy rapidly to the first excited state ($S_1$) and, hence, emission occurs predominantly from this state, resulting in an emission band in the spectrum. However, PL spectrum of **25** as thin film, preciously reported by HASEGAWA et al., exhibits two bands.[97a] The shoulder in the spectrum can be explained by the high tendency of recrystallization of **25**, leading to the formation of an excimer (excited-state dimer) whose emission wavelength is red-shifted with regard to that of a monomer. It is noteworthy that the introduction of methyl group into its carbon skeleton, as in **24**, can avoid the excimer formation which is demonstrated by its one-band PL spectrum (Figure 17).

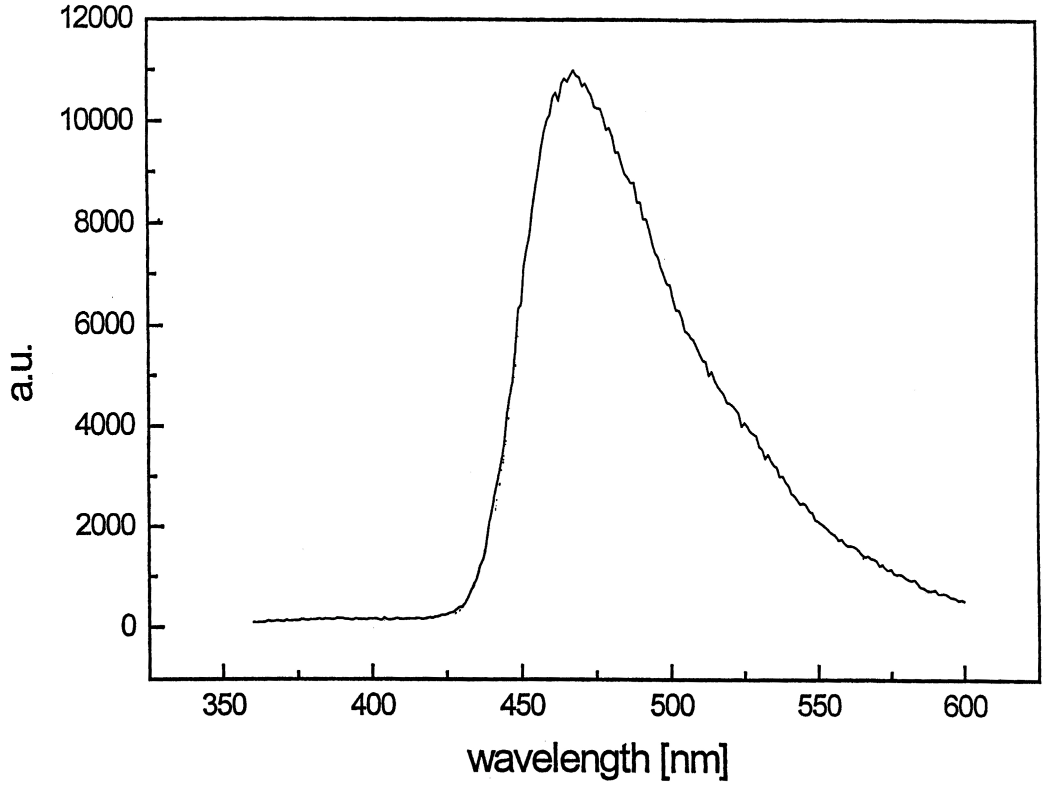


Figure 17 PL spectrum of **24** as thin film.

A comparison of the spectra of **24**, **25**, and that of DSB reveals that replacing the phenylene unit with its pyrazyl analogue leads to a bathochromic shift (red-shift) in both absorption (by 35 for **24** and 27 nm for **25**) and emission spectra (by 22 for **24** and 28 or 38 for **25**, depending on the form of the nanocrystal). The difference among energy gaps are indicative of a large separation of HOMO and LUMO in DSB, and are consistent with the greater aromatic stabilization energy of benzene compound compared to the pyrazine analogue.[99, 100]

Compared with **25**, the absorption maximum of **24** shows a small bathochromic shift by 8 nm. It is most likely that electron-donating character of methyl groups produces an asymmetric destabilization of the top of the valence band and the bottom of the conduction band, resulting in diminishing of the energy gap. However, its PL emission spectra is hypsochromic-shifted (blue-shifted) with regard to that of **25** by 4 ($\gamma$-form) or 14 nm ($\alpha$-form), respectively. This may be caused by a decrease of intermolecular interaction, which leads to the excimer or aggregate formation, due to both methyl substituents in **25**. These methyl groups may prevent planarization of the molecule, resulting in decrease of effective π-conjugation length in the excited state and, thus, red-shift emission spectrum is created.

## 3.3.2 EL spectroscopy

### 3.3.2.1 EL instrument

To study the use of compound **24** in LED device, a simple EL device based on **24** has to be fabricated. As previously stated in Section 1.4.1, the device is composed of one or more emitting layers sandwiched between a cathode and an anode. In the case of **24**, the electron-deficient pyrazylene unit is known to make the molecule a potential electron transport material. Therefore, an additional hole transport layer between anode, ITO, and emitting layer, **24**, was introduced in the device set-up in order to increase the recombination efficiency. Many kinds of compounds are promising candidate for this purpose, as mentioned in Section 1.4.5. However, on account of its chemical and thermal stability, copper phthalocyanine (PcCu) is chosen for this work. A set up of ITO/PcCu/**24**/Al device is shown in Figure 18.

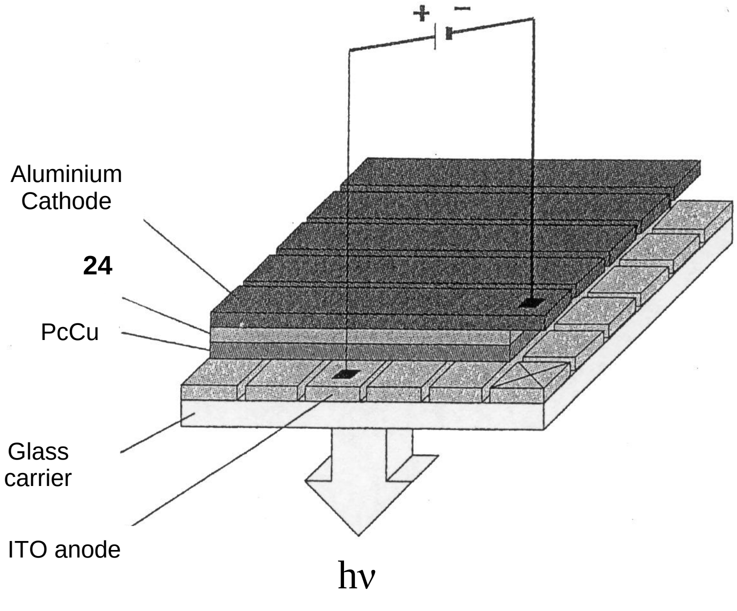


Figure 18 Schematic set-up of ITO/PcCu/**24**/Al device.

The purchasable ITO-glass substrate (from Merck Balzer Company) was cut in 50×50 mm piece. In order to produce several small EL devices within one carrier, ITO layer was divided in six columns by a method previously reported by us.[101] PcCu and then the emitter materials were coated on the ITO layer, respectively by vacuum deposition technique. Finally aluminium was deposited on the top in five lines and, thus, twenty five EL devices were obtained.

The LED plate is fixed in two card edge connectors b) and c) (Figure 19) mounted on a specimen fixture d) which enables an adjustment of the position of the LED segment in front of a waveguide f). Voltage is applied to the LED by power supply e) and then a waveguide leads the emitting light to a monochromator g). The EL signal is detected by a diode array h) and then analyzed with a personal computer i). Like PL, EL measurements have to be performed in a dark room.

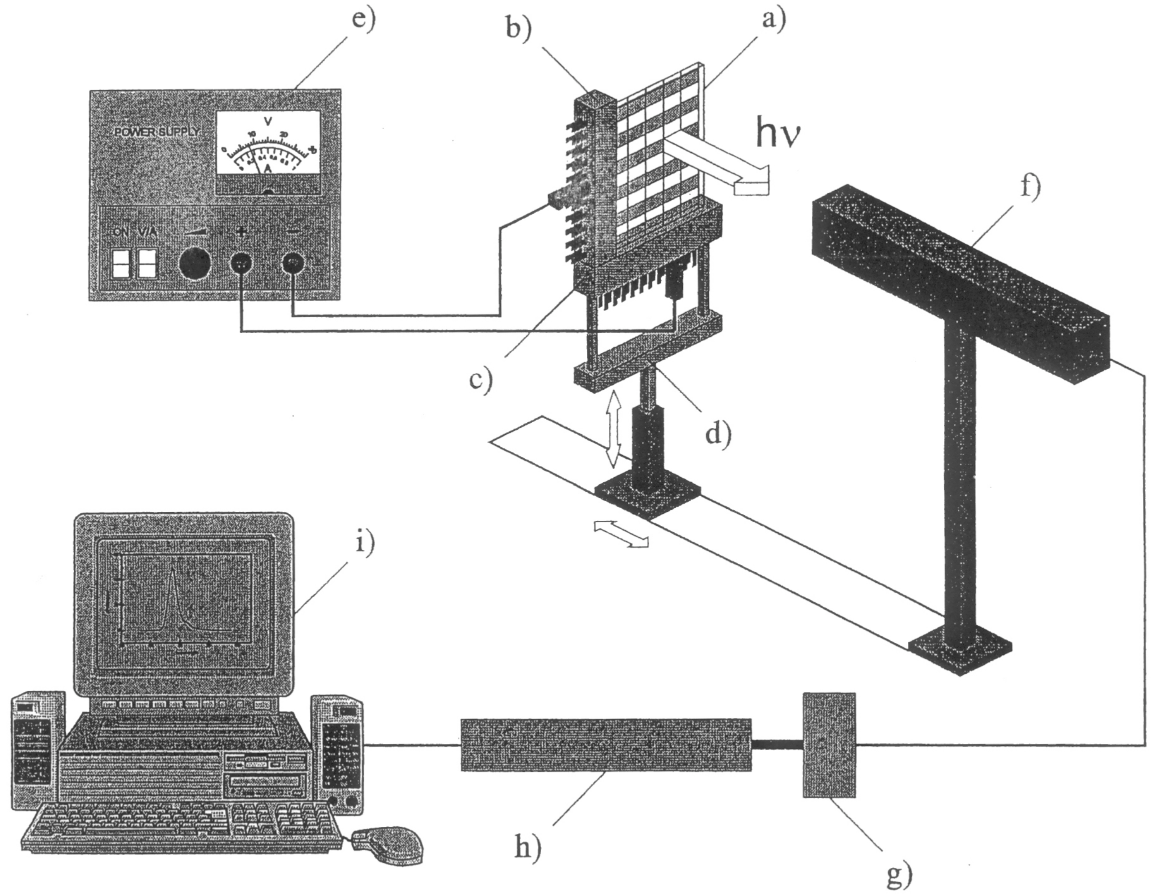


Figure 19 Schematic set-up of EL measurement apparatus.

### 3.3.2.2 Measurement

The ITO/PcCu/**24**/Al device emits brightly greenish blue light at λ 500 nm at an operating voltage of 7.5 V. The higher applied voltage causes breaking down of the device which can be determined by drastic decrease of the signal intensity in the spectra shown in Figure 20. This results from the high tendency of recrystallization of **24** in the film.

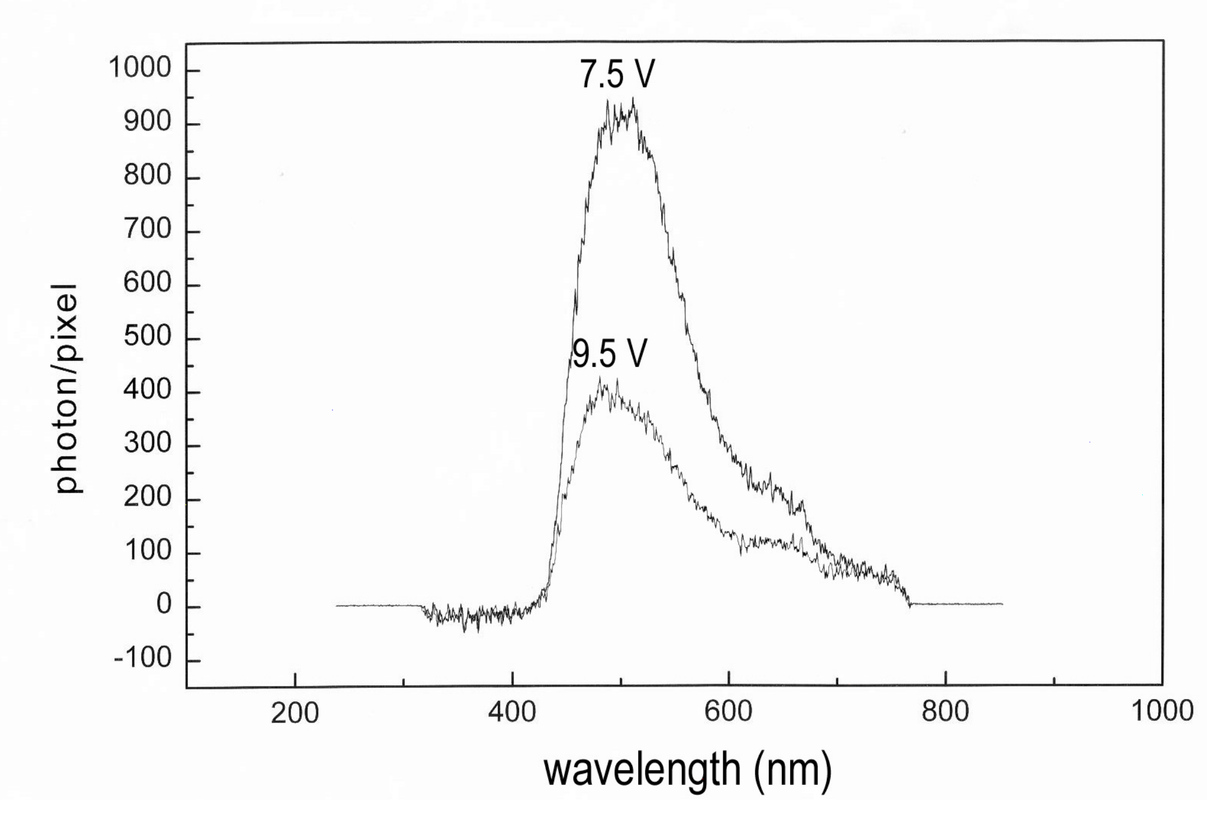


Figure 20 EL spectra of **24** at an apply voltage 7.5 and 9.5 V.

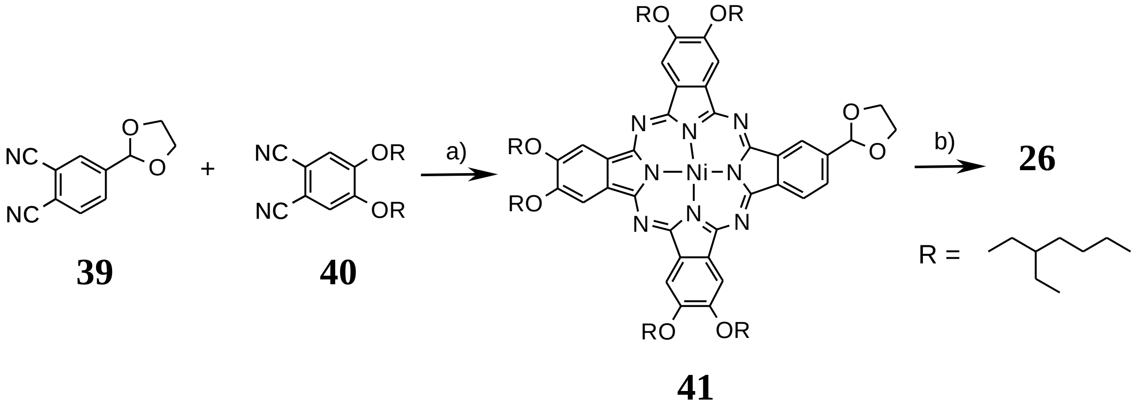
In general, the EL emission spectrum is expected to be almost identical to the corresponding PL spectrum. Due to the high tendency of recrystallization of **24**, the bathochromic shift by 32 nm of its EL spectrum compared with the PL spectrum can be explained on account of the fact that in electronic excitation, an interchain interaction in an excited state, involving the formation of excimer, is more accelerated compared with photoexcitation. The appearance of the fine structures at 650-780 nm of the EL spectrum of **24** is probably caused by the non-radiative decay in the form of heat, which is usually generated when LED device is damaged by the high-energy electronic excitation.

## 3.4 Synthesis and characterization of bisvinylene-naphthylene-bridged phthalocyaninatonickel(II) dimers

### 3.4.1 Preparation of formyl phthalocyaninatonickel(II) 26 and the naphthalene phosphonium salts 49 and 52

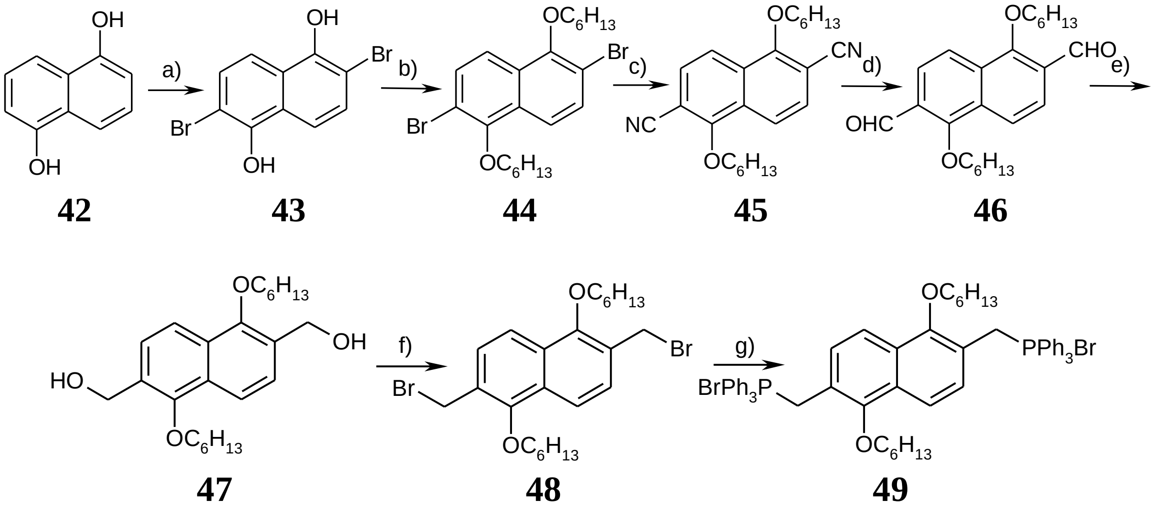
As stated in Section 2, two new derivatives **27** and **28** (see p. 26) are synthesized in this work and investigated in detail with regard to their optical properties. In order to form bridging naphthalene unit with two phthalocyanine moieties, the Wittig reaction is applied. Hence, formyl Pc **26** (see p. 26) and the naphthalene phosphonium salts **49** and **52** are required.

Recently, the statistical synthesis of Pc **26** was reported by our group[91a] (Scheme 4). The condensation of **39** and **40** in a 1:2 ratio afforded the α-functionalized Pc **41** whose acetal group was deprotected under acidic condition to give formyl Pc **26**.



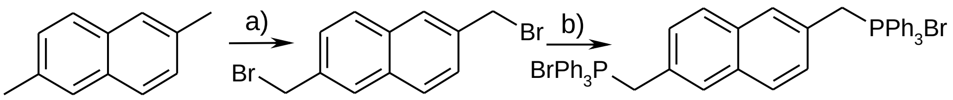
Scheme 4 Synthesis of formyl Pc **26** : a) Ni $(OAc)_2.4H_2O$, DBU, pentanol, 135 °C, b) 2N HCl. THF.

The substituted naphthalene phosphonium salt **49** was obtained by a multi-step procedure (Scheme 5).[102] First, bromination of the commercially available 1,5-dihydroxynaphthalene (**42**) was performed to give the dibromo product **43** which was hexylated to afford **44**. In a Rosenmund-von Braun reaction, both bromo groups of **44** were converted into cyano groups (compound **45**) which were then reduced with DIBAL-H to yield the diformyl derivative **46**. Further reduction with sodium borohydride and then hydroxy-to-bromo functional group conversion afforded the bromo compound **48** which finally reacted with triphenylphosphine to give phosphonium salt **49**. The overall yield amounts to 5.56 %.



Scheme 5 Multi-step synthesis of **49** : a) $Br_2$, AcOH, 80 °C, b) $C_6H_{13}Br$, NaOEt/EtOH, 78 °C, c) CuCN, NaI, DMF, 150°C, d) DIBAL-H, $Et_2O$, 34 °C, e) $NaBH_4$, $CH_2Cl_2$/MeOH, f) $Et_4NBr$, $BF_3.Et_2O$, $CH_2Cl_2$, g) $PPh_3$, DMF, 150 °C.

Phosphonium salt **52** can be conveniently prepared by classical pathway starting from commercially available 3,6-dimethylnaphthalene (**50**), by first brominating with NBS and then reacting with triphenylphosphine (Scheme 6).



**50** **51** **52**

Scheme 6 Synthesis of phosphonium salt **52** : a) NBS, $CCl_4$, $Bn_2O$, hν, b) $PPh_3$, DMF, 150 °C.

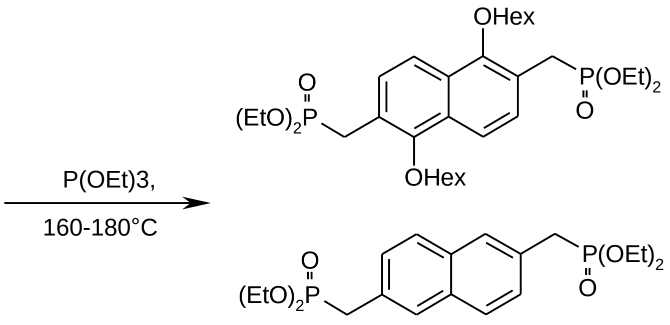
## 3.4.2 Synthesis of the bisvinylenenaphthylene-bridged phthalocyaninatonickel(II) dimers 27 and 28

After all precursors were successfully prepared, phosphonium salt **49** and **52**, respectively, were reacted with formyl Pc **26** in a Wittig reaction. Though many reaction conditions were tried (LiOEt, BuLi, PhLi and KOBu-*t* were utilized as base; $CH_2Cl_2$, $CHCl_3$, THF and mixed solvent $CHCl_3$/ethanol were used as solvent and reaction temperature, as well as reaction time were varied), neither **27** nor **28** were formed. By checking with thin layer chromatography (TLC) and mass spectroscopy, the majority of starting material **26** and other decomposed compounds were observed. This result indicates that the precursors did not react with each other effectively and thus their reactivity should be increased.

To overcome this problem, the more reactive phosphonates **53** and **54** were prepared (Scheme 7). The reactivity of the substrates is enhanced by the high stability of the resulting anions, formed after deprotonation of the methylene groups.

**48**

**51**



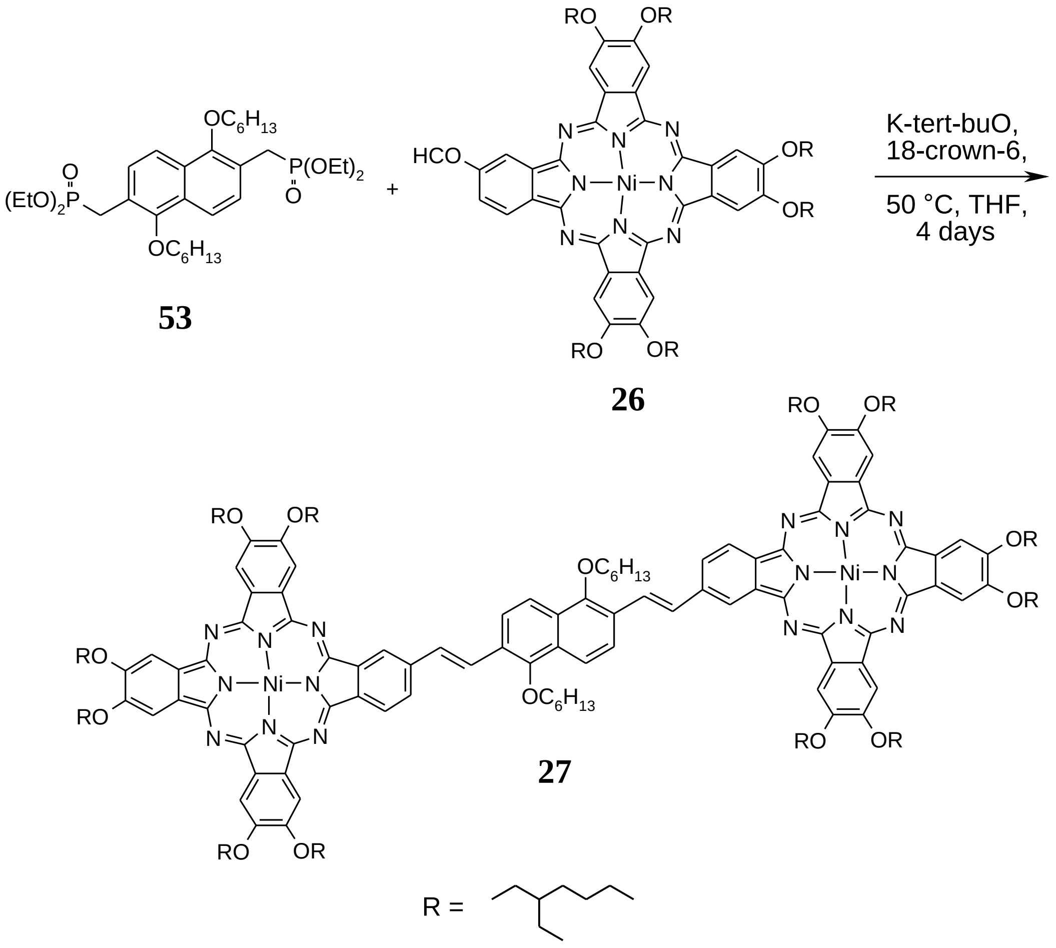
**53**

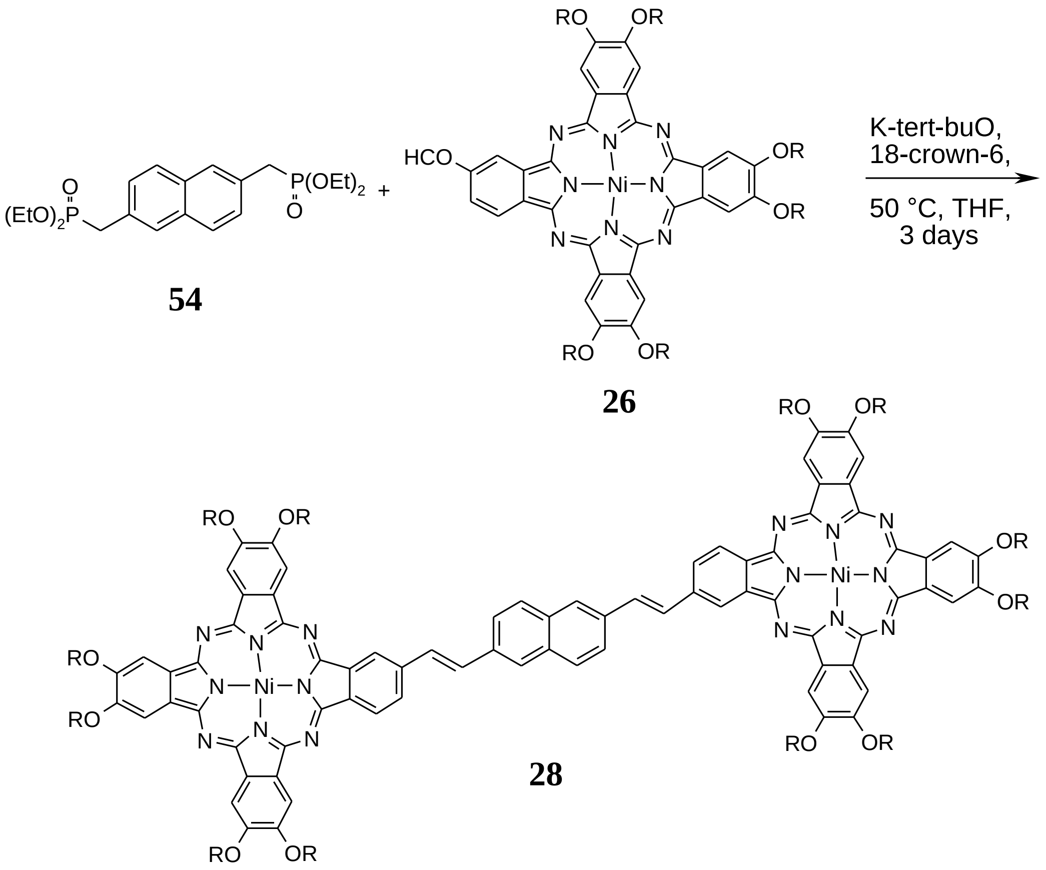
**54**

Scheme 7 Preparation of phosphates **53** and **54**.

The starting phosphonates are easily obtained by Michaelis-Arbuzov reaction. The halides **48** and **51** were heated with triethyl phosphite, acting both as reagent and as solvent, until the evolution of bromoethane gas was stopped. Phosphate **54** was obtained in moderate yield as a white solid and could be separated by filtration. On account of its higher solubility due to its bulky hexyloxy group, **53** was obtained in a good yield as colorless viscous liquid, which can be solidified by standing at ambient temperature for a few days, and was purified by chromatography.

The resulting phosphonates **53** and **54** were reacted with formyl Pc **26** in a Wittig-Horner reaction which was accomplished at 50 °C in the presence of 18-crown-6 by using potassium-*tert*-butoxide as base and THF as solvent (Scheme 8). To prevent the dimer products from being damaged by the light, the reaction was performed in the flasks covered with aluminium foil.





Scheme 8  Synthesis of **27** and **28** through Wittig-Horner reaction.

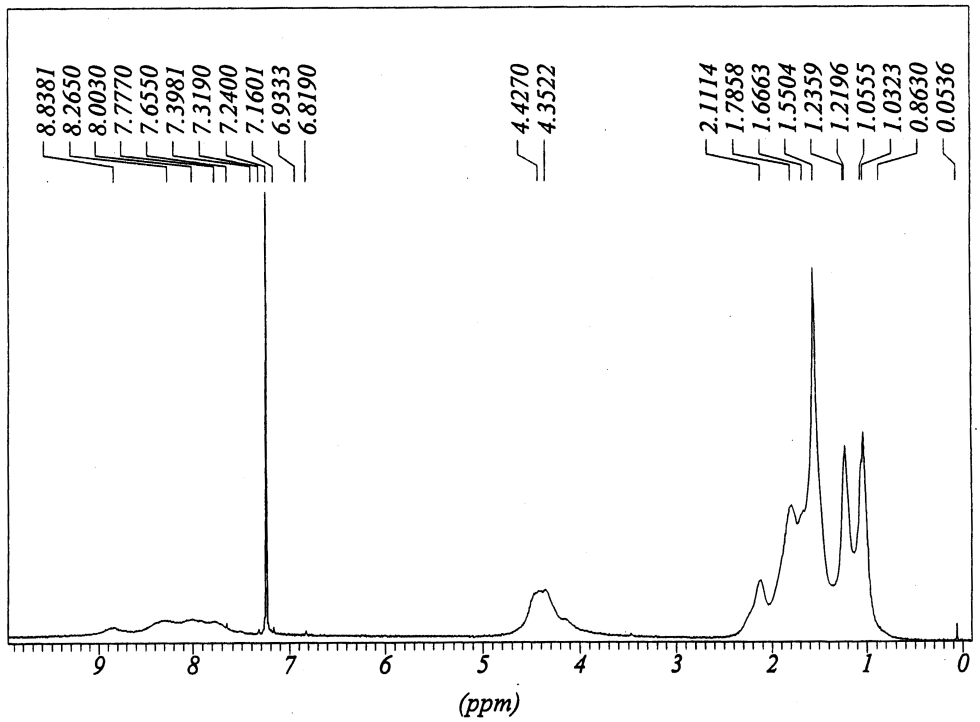
Though the reactive phosphonates and high temperature were used, the reaction still lasted long time (monitored by TLC; silica gel, $CH_2Cl_2$ / hexane 2:1), namely around a week, when the phosphonates are handled under normal condition. However, it was observed that the use of freshly prepared phosphonates kept under inert atmosphere could shorten the reaction period to 3-4 days. This demonstrates  that the phosphonates **53** and **54** are hygroscopic. The crude products were purified by flashed chromatography to remove the impurities and by preparative TLC to separate the pure products from the remaining formyl Pc **26** and other byproducts. Yields obtained were quite low, 10-12 %, which might be caused by the low reactivity of the bulky aldehyde **26**.

## 3.4.3 Characterization of bisvinylenenaphthylene-bridged phthalocyaninatonickel(II) dimers 27 and 28

### 3.4.3.1 2,6-Bis([9,10,17,18,25,26-hexakis(2¢-ethyl)hexyloxy-2-vinylphthalocyaninato]nickel(II))-1,5-dihexyloxynaphthalene (27)

The NMR-spectra of **27** (Figure 21) are difficult to interpret due to aggregation effects and the possible existence of the isomer mixtures, *trans-trans*, *cis-trans*, and *cis-cis*. However, all signals in both of $^{1}$H- and $^{13}$C-NMR spectra are consistent with the proposed structure (for interpretation see experimental part, p. 77).

a)



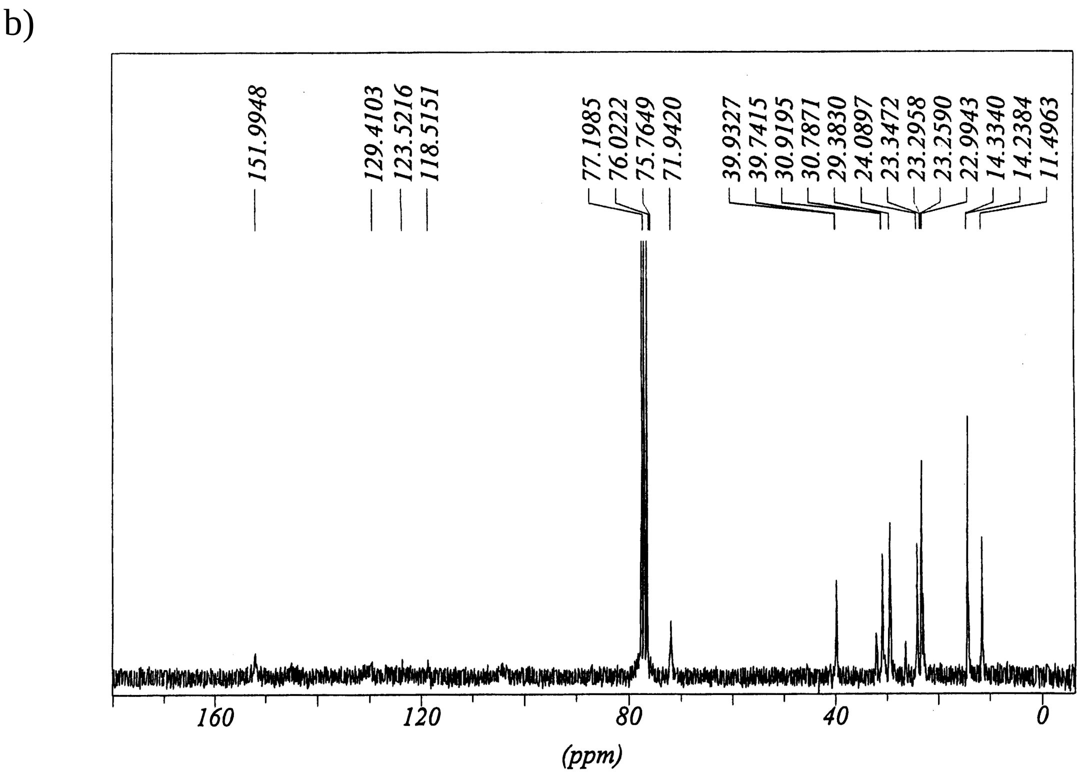


Figure 21 a) $^1$H-NMR and b) $^{13}$C-NMR spectra of **27**

Since dimer **27** exhibits a high tendency of fragmentation by showing only fragment peaks in FD and FAB spectra, other mass spectroscopy technique like MALDI-TOF has to be employed. The spectrum features molecular peak ($M^+$) at *m*/*z* 3056.8 and also isotope peaks.

In the IR spectrum, a weak band at 964 cm$^{-1}$ indicates the *trans* configuration of the vinylene linkages and the one at 1028 cm$^{-1}$ is caused by C-O vibration of hexyloxy groups.

### 3.4.3.2 2,6-Bis([9,10,17,18,25,26-hexakis(2¢-ethyl)hexyloxy-2-vinylphthalocyaninato]nickel(II))naphthalene (28)

Similar to **27**, $^1$H- and $^{13}$C-NMR of **28** show broad signals only in moderate quality because of the aggregation phenomenon and the presence of the isomeric mixture. Nevertheless, all signals are consistent with the proposed structure (Figure 22, for interpretation see experimental part, p. 79).

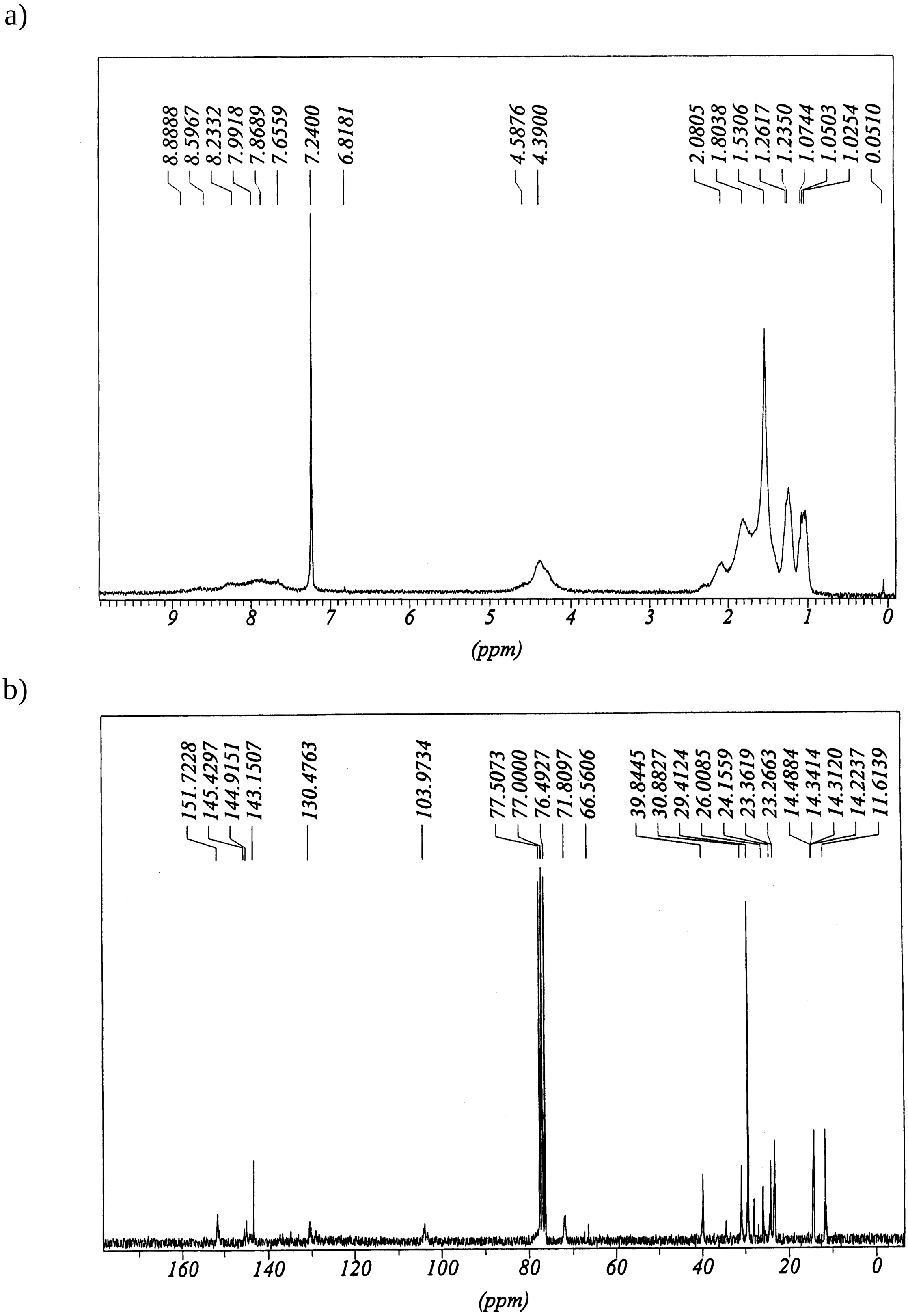


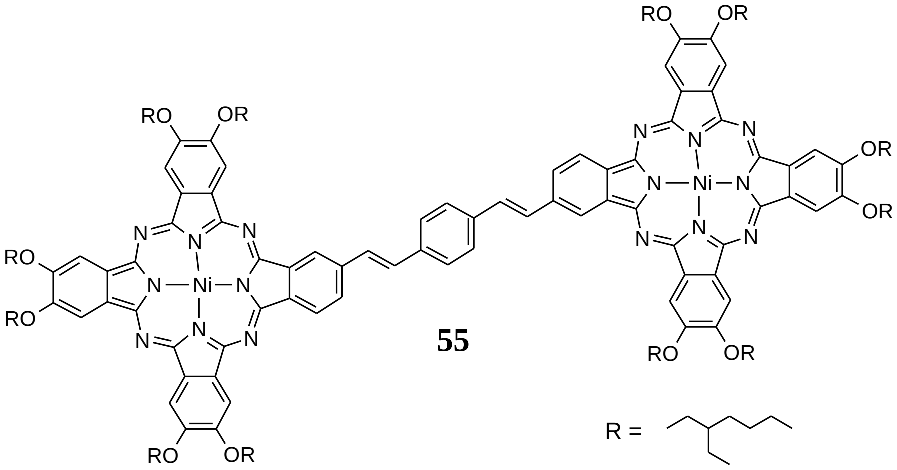
Figure 22 a) $^{1}$H-NMR and b) $^{13}$C-NMR spectra of **28**

Compound **28** could be analyzed by laser desorption mass spectroscopy with or without matrix (matrix used is 1,4-bis(phenyloxazol-2-yl)benzene, POPOP,[103, 104] or α-cyanocinnamic acid). Molecular peak ($M^+$) at *m*/*z* 2856.5 is observed and, similar to **27**, the isotope peaks are found as well.

In IR spectroscopy, band pattern of **28** looks similar to that of **27**. A weak band ascribed to the *trans* configuration of vinylic bridges is observed at 972 $cm^{-1}$.

### 3.4.3.3 UV/Vis spectroscopy

Absorption spectra of **27** and **28** recorded in THF solution are broadly shaped and lowly resolved, which is due to the intermolecular aggregation of the planar macromolecules. Q-band and B-band maxima of **27** are almost identical with that of **28** (Figure 23). Moreover, both of their absorption maxima are also similar to that of phenylene-Pc dimer (**55**) which was previously synthesized in our group.[91a] This result demonstrates that the introduction of hexyloxy substituents into the naphthalene moiety of **28** and the insertion of longer annulene segment between the peripheral Pc-subunits does not effect significantly on the band gaps. (Table 2 and Figure 23).



**55**

Table 2 UV/Vis absorption maxima in THF solution ($\lambda_{abs}$) of **27**, **28** and **55**.

| **Compound** | **$l_{abs}$ (nm)** |
|---|---|
| **27** | 405, 673, 685 |
| **28** | 406, 673 |
| **55** | 403, 672 |

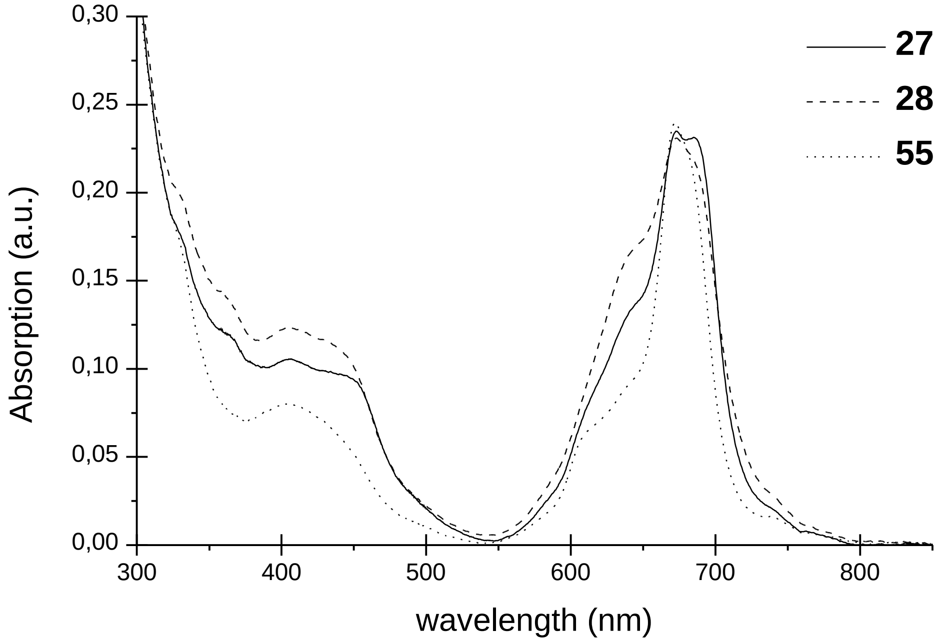


Figure 23 UV/Vis spectra of **27**, **28** and **55** measured in THF.

Splitting of Q-band in absorption spectrum of **27** is indicative of a splitting of the excited electronic levels (LUMO) in the unsymmetrically substituted compound.[105] The lowering in symmetry of Pc moieties with regard to the symmetric Pc, the change from $D_{4h}$- to $D_{2h}$-symmetry, removes the degeneracy of two LUMO ($e_g$), resulting in the splitting in two energy levels ($b_{2g}$ and $b_{3g}$).[106] Thus, two possible electronic transitions from HOMO can occur, resulting in $Q_x$ and $Q_y$ bands (Figure 24).

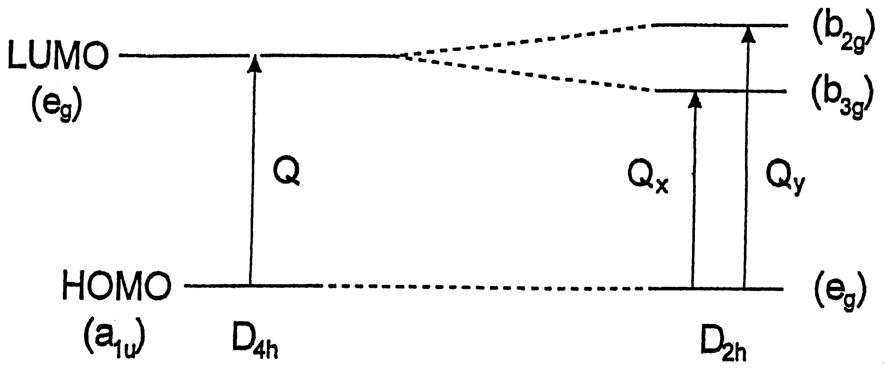


Figure 24 The splitting of Q-band due to the lowering of the molecular symmetry of Pc unit.

Moreover, this observation is more obvious for dimer **27** than **28,** which can be explained that aggregation effect in **27** is weaker than that in **28** due to the presence of bulky hexyloxy substituents. Nevertheless, it should be noted that the extent of the degeneracy of LUMO in Pcs does not only depend on the symmetry of the macrocycles, but also on the type of substituents and their capability of perturbing the electronic levels.[105]

### 3.4.3.4 PL spectroscopy

The photoluminescence of the new compounds **27** and **28** was investigated in THF solution with the instrument described in Section 3.3.1.1. Both **27** and **28** feature no PL emission band, which is explained in term of the presence of a stacked arrangement of the Pc subunits, leading to the quenching of emitted light. This explanation is consistent with the observation of the broad bands in the UV/Vis spectra. However, the bulkiness or steric hindrance introduced into the vinylene bridge might be able to distort the planarity of the molecule and thus impede the stacking arrangement of the macrocycles. By this strategy, luminescence may occur.

### 3.4.4 Attempt to synthesize bisvinylenepyrazylene-bridged phthalocyaninatonickel(II) dimers 29 and 30

As mentioned in Section 2, p. 27, dimers **29** and **30** are expected to give the interesting optical properties due to the combination of the remarkable charge conducting properties of pyrazine and Pc units. Similar to the synthesis of **25**, the condensation of 2,5-dimethylpyrazine (**36**) with mono-formyl Pc **26** in the presence of zinc chloride at high temperature was employed to synthesize **30**. However, no desired product was detected (no peak was observed in mass spectroscopy).

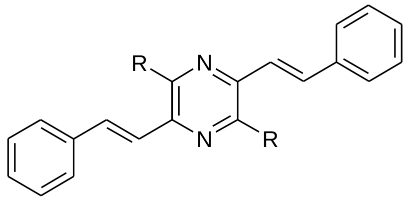
For the synthesis of dimer **29**, Wittig reaction of pyrazine phosphonium salt **35** (see p. 28) and Pc **26** was performed. By monitoring by TLC, a new green spot of compound was observed which was expected to be the Pc dimer **29**. MALDI-TOF mass spectrum exhibits the molecular peak ($M^+$) at *m*/*z* 2833.8 but other fragment peaks are observed as well. However, the remaining amounts of compounds after workup and purification step were too low for the complete purification and characterization by any other spectroscopic methods.

In the case of **30**, a possible explanation of the low yield is that the desired product is unstable under the drastic reaction condition and then fragments or decomposes during the reaction process. By reducing the reaction temperature, some of starting material Pc **26** was still remained, while the yield was not improved.

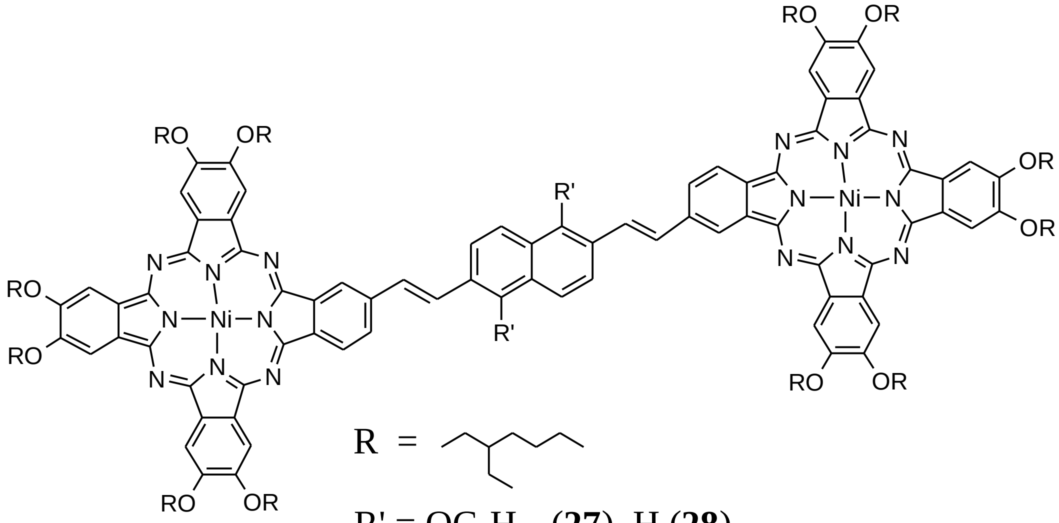
For dimer **29**, as described in Section 3.1.1.4, the low reactivity of ylide formed from phosphonium salt **35** may cause the low yield and even lower when it reacts with bulky and low-reactivity aldehyde like Pc **26**. The preparation of the corresponding phosphonate was also tried but no phosphonate was detected.

# IV. Summary

Two novel series of compounds are prepared, characterized and studied in detail with regard to their optical properties. One is the PPV analogue containing pyrazine moiety as a middle subunit (**24**) and the other are dimers based on the combination of naphthalene and Pc (**27** and **28**).



R = $CH_3$ (**24**), H (**25**)



R' = $OC_6H_{13}$ (**27**), H (**28**)

**24**, prepared by a Wittig reaction of the phosphonium salt **35** and two equivalents of benzaldehyde by using potassium-*tert*-butoxide as a base in dry ethanol at room temperature (see p. 34), exhibits bright luminescence under UV-irradiation and greenish blue emission in PL (solid state) and EL measurements. On account of electron-deficiency of pyrazine unit, an additional PcCu hole transport layer was introduced in OLED based on **24**, prepared by vacuum deposition coating technique, in order to increase the charge recombination efficiency. The device emits light at $\lambda$ 500 nm at an applied voltage of 7.5 V, whereas the thin film of **24** exhibits PL at $\lambda$ 468 nm (Section 3.3, p. 36).

The influences of pyrazine unit to the optical properties are investigated by the comparison of the absorption and emission spectra of **24** with those of the reference molecule DSB (Section 3.3.1.2, p. 37). The results demonstrate that the electron-deficient property of pyrazylene moiety causes the bathochromic shift and creates blue emission. A known compound **25** was also prepared in this work in order to study the effect of the introduction of methyl substituents into the pyrazine unit. As expected, the electron-donating effect of the methyl groups leads to a decrease of the band gap and of the intermolecular interaction or excimer formation, resulting in the bathochromic shift in absorption spectrum of **24** with regard to that of **25**, whereas its PL maximum is shifted hypsochromically.

The novel bisvinylenenaphthylene-bridged Pc dimers **27** and **28** were successfully synthesized, by Wittig-Horner reaction of the phosphonates **53** and **54**, respectively, with two equivalents of asymmetric formyl Pc **26** in the presence of 18-crown-6 as a catalyst and potassium-*tert*-butoxide as a base in dry THF at 50 °C (see p. 47), and fully characterized by IR, $^{1}$H-NMR, $^{13}$C-NMR and MS (MALDI-TOF) as well as by elemental analysis. The similarity of the absorption spectra of dimer **28** and its phenylene analogue **55**[91a] reveals the insignificant effect to the optical properties of the conjugated $\pi$-system extension of the middle segment between the peripheral Pc-subunit. The absence of PL of both **27** and **28**, measured in the THF solution, is possibly caused by the stacked arrangement of Pc subunits, leading to quenching effects. In the absorption spectrum of **27**, the splitting of Q-band, which is clearly observed, indicates that the introduction of the bulky hexyloxy groups into the naphthalene moiety not only enhances the solubility of the substrates, but also reduces the stacking effect of the macrocycles. However, this effect is still strong on the compound and thus the luminescence could not be induced.

# V. Experimental part

**Materials**

Commercially available chemicals were used as delivered by Fluka and Aldrich. All solvents were dried according to standard procedures[107]. The melting point are uncorrected.

All compounds were analysed using the following instruments :

**IR-spectroscopy**

Bruker IFS 48. All spectra were recorded as KBr pellets. Absorption bands are given as : s (strong), m (medium) and w (weak).

**UV/Vis-spectroscopy**

Shimadzu UV 2102 PC. All spectra were measured in $CH_2Cl_2$ solution, except for compounds **27** and **28** which were recorded in THF. All spectra displayed are normalized.

**$^1$H-NMR-spectroscopy**

Bruker AC 250 (250 MHz). Internal standard $CHCl_3$ ($\delta$ = 7.24 ppm). All data are given as : chemical shift $\delta$ [ppm] (multiplicity, coupling constant *J* (Hz), integration, correlated protons).

**$^{13}$C-NMR-spectroscopy**

Bruker AC 250 (62.9 MHz). Internal standard $CHCl_3$ ($\delta$ = 77.00 ppm). All data are given as : chemical shift $\delta$ [ppm] (correlated carbons).

**Mass spectroscopy**

| | |
|---|---|
| EI (electron impact) | : Finnigan TSQ 70 MAT, direct inlet, ion source temperature 200°C, electron energy 70 eV. |
| FD (field desorption) | : Finnigan MAT 711 A. |

FAB (fast atom bombardment) :Finnigan TSQ 70 MAT or Finnigan MAT 711 A.
MALDI-TOF (matrix assisted laser desorption ionization): Bruker, Biplex II or Bruker, Proflex II, matrix is α-cyano-cinnamic acid or 1,4-bis(phenyloxazol-2-yl)benzene (POPOP).

**Elemental Analysis**

C, H, N : Elementar Analysensysteme GmbH VarioEL V. All further elements by titration (Schöninger Decomposition). Owing to the usual difficulties of combustion analysis of Pcs, it was almost impossible to obtain satisfactory elemental analyses for the compounds **27** and **28**.[108]

**Photoluminescence spectroscopy**

SPEX fluorolog 112. Measurements were performed as thin films on glass carriers in 45°C configuration.

**Electroluminescence spectroscopy**

HP 6030A voltage source together with a Keithley 171 DMM. Spectra were taken from devices with ITO/PcCu/compound/Al configuration with a waveguide diode array set-up in air at room temperature.

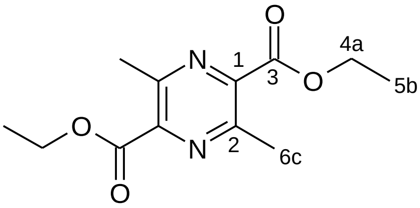
## 5.1 Pyrazine derivative

### 5.1.1 3,6-Dimethylpyrazine-2,5-dicarboxylic acid diethyl ester (32)

A solution of 2.00 g (19.80 mmol) of triethylamine in 25 ml of ethanol was added into a solution of 3.50 g (19.28 mmol) of ethyl-2-aminoacetoacetate hydrochloride (**31**) in 25 ml of ethanol and the mixture was then violently stirred at room temperature for 6 hours. After vacuum evaporation of solvent, the residue was dissolved in 200 ml of ethyl acetate and the insoluble ammonium salt was filtered off. The mixture was vacuum evaporated and recrystallized from ethanol to furnish the desired product.

Yield : 3.50 g (72.00 %), white crystals, m.p. 89.0-90.0 °C.

$C_{12}H_{16}N_2O_4$ (252.14)



**IR** (KBr), [$\nu$ cm$^{-1}$] : 3006 w, 2988 w ($CH_3$), 2976 w ($CH_3$),2935 w ($CH_2$), 1720 s (C=O), 1464 w, 1452 w, 1398 m, 1389 m, 1371 w, 1304 w, 1259 m, 1177 m, 1126 s (C-O), 1096 w, 1009 w, 866 w, 789 w, 758 w.

**$^1$H-NMR** (250 MHz), $CDCl_3$, $\delta$ [ppm] : 4.47 (q, *J* = 7.10 Hz, 4H, $H^a$), 2.78 (s, 6H, $H^c$), 1.42 (t, *J* = 7.10 Hz, 6H, $H^b$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, $\delta$ [ppm] : 165.1 (C-3), 150.7 (C-1), 144.1 (C-2), 62.4 (C-4), 22.3 (C-6), 14.2 (C-5).

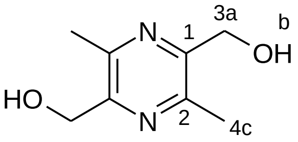
**MS** (EI, 70 eV), *m*/*z* [%] : 252.0 ($M^+$, 49), 222.9 ($M^+$-$C_2H_5$, 34), 207.6 ($M^+$-$OC_2H_5$, 27), 179.9 ($M^+$-$O_2C_3H_5$, 100), 150.8 ($M^+$-$O_2C_5H_{10}$, 9), 134.1 ($M^+$-$O_2C_6H_{13}$, 10), 105.8 ($M^+$-$O_4C_6H_{20}$, 17), 81.1 (10), 54.0 (5), 43.0 (7).

### 5.1.2 2,5-Bis(hydroxymethyl)-3,6-dimethylpyrazine (33)

A 1.50 g (39.65 mmol) of sodium borohydride was suspended in a mixture of 0.50 g (1.98 mmol) of **32** in 50 ml of methanol under 0 °C. After the mixture was stirred at room temperature for an hour, acetic acid was added dropwise until the mixture became neutral and the solvent was then evaporated. The residue was chromatographed (silica gel, ethyl acetate) to obtain pure **33**.

Yield : 86.67 mg (26.00 %), white crystals, m.p. 113.0-113.5 °C.

$C_8H_{12}N_2O_2$ (168.10) calcd. : 57.16, H 7.14, N 16.67
found : 57.10, H 7.22, N 16.61



**IR** (KBr), [ν $cm^{-1}$] : 3246 s (O-H), 2995 w ($CH_3$), 2925 m ($CH_2$), 2858 m ($CH_2$), 1429 s, 1383 w, 1367 w, 1312 m, 1252 w, 1215 w, 1171 m, 1043 s (C-OH), 1028 s, 976 m, 802m, 774 m, 698 m.

**$^1$H-NMR** (250 MHz), $CDCl_3$, δ [ppm] : 4.71 (s, 4H, $H^a$), 4.14 (s, 2H, $H^b$), 2.44 (s, 6H, $H^c$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, δ [ppm] : 149.0 (C-1), 146.0 (C-2), 60.9 (C-3), 19.2 (C-4).

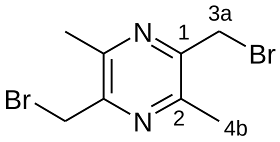
**MS** (EI, 70 eV), *m*/*z* [%] : 167.9 ($M^+$, 100), 150.1 ($M^+$-OH, 12), 138.8 ($M^+$-$C_2H_6$, 80), 121.2 ($M^+$-$OC_2H_6$, 28), 110.2 (11), 80.0 (6), 69.1 (10), 52.1 (10), 42.1 (14).

### 5.1.3 2,5-Bis(bromomethyl)-3,6-dimethylpyrazine (34)

A solution of 50 mg (0.63 mmol) of pyridine in 5 ml of dry toluene was added dropwise to a solution of 50 mg (0.30 mmol) of **33** in 5 ml of dry toluene. Then, a solution of 54 mg (0.19 mmol) of phosphorus(III) bromide in 5 ml of dry toluene was added carefully by means of a syringe. After stirring during a period of an hour at room temperature, the reaction mixture was washed with cold water and 5% aqueous sodium hydrogen carbonate solution and then dried over sodium sulphate for 12 hours. Removal of the solvent afforded a white solid which was purified by chromatography on silica gel ($CH_2Cl_2$/ethyl acetate 2:1).

Yield : 43 mg (48.74 %), white crystals, m.p. 146.0-147.0 °C.

$C_8H_{10}Br_2N_2$ (293.91) calcd. : 32.69, H 3.40, N 9.53, Br 54.37
found : 33.07, H 3.23, N 9.65, Br 52.30



**IR** (KBr), [ν $cm^{-1}$] : 2980 m ($CH_3$), 2924 s ($CH_2$), 2877 w ($CH_2$), 1740 m, 1587 w, 1526 w, 1454 m, 1421 s, 1393 m, 1234 m, 1215 s, 1088 m, 991 w, 797 s, 773 w, 681 w.

**$^1$H-NMR** (250 MHz), $CDCl_3$, δ [ppm] : 4.52 (s, 4H, $H^a$), 2.59 (s, 6H, $H^b$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, δ [ppm] : 149.3 (C-1), 148.7 (C-2), 30.5 (C-3), 20.3 (C-4).

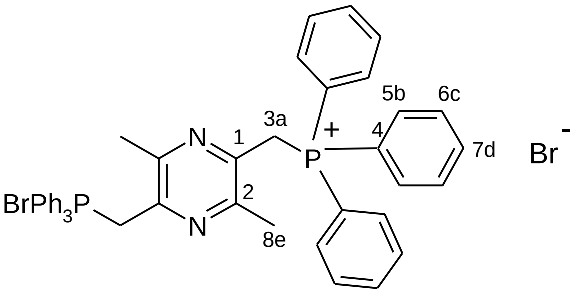
**MS** (EI, 70 eV), *m*/*z* [%] : 294.0 ($M^+$, 19), 215.0 ($M^+$-Br, 100), 200.0 ($M^+$-$CH_2$Br, 4), 173.9 (9), 151.0 (21), 133.2 ($M^+$-2Br, 37), 92.8 (14), 52.6 (20).

### 5.1.4 2,5-Bis(methyltriphenylphosphoniumbromide)-3,6-dimethylpyrazine (35)

A mixture of 100 mg (340 µmol) of **34**, 194 mg (749 µmol) of triphenylphosphine in 5 ml of dry toluene was heated to 65 °C with slow stirring for an hour. The white solid formed was filtered off and washed with toluene .

Yield : the product could not be purified completely.

$C_{44}H_{40}Br_2N_2P_2$ (818.25)



**IR** (KBr), [ν $cm^{-1}$] : 3055 w, 3009 w, 2990 m ($CH_3$), 2964 w ($CH_2$), 2812 m, 2754 w, 1587 m, 1485 m, 1439 s, (P-phenyl), 1402 w, 1111 s, 748 s, 719 s, 690 s.

**$^1$H-NMR** (250 MHz), $CDCl_3$, δ [ppm] : 7.72-7.57 (m, 30H, $H^b$, $H^c$, $H^d$), 5.57 (d, $J$ = 13.5 Hz, 4H, $H^a$), 2.21 (s, 6H, $H^e$).

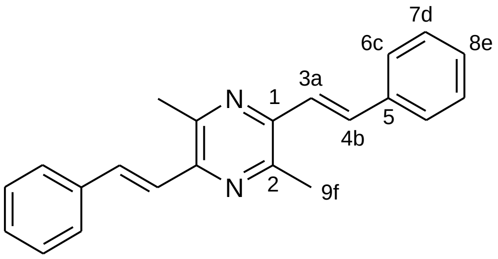
**MS** (FAB), *m/z* [%] : 657.4 ($M^+$-2Br, 3), 475.1 ($M^+$-$PPh_3Br$, 99), 397.3 ($M^+$-$PPh_3$-2Br, 100), 279.0 (11), 262.0 (65), 183.1 (70).

### 5.1.5 2,5-Dimethyl-3,6-distyrylpyrazine (24)

Benzaldehyde 60 mg (0.57 mmol) was added dropwise to a solution of 200 mg (0.25 mmol) of phosphonium salt **35** in dry ethanol at room temperature and then 65 mg (0.58 mmol) of potassium-*tert*-butoxide was added carefully. After stirring for 3 hours, 20 ml of water was poured into the reaction mixture and the yellow precipitate formed was filtered off. The precipitate was then flash chromatographed and, afterward, recrystallized for further purification.

Yield : 27 mg (35.35 %), yellow needles, m.p. 217.0-218.0 °C.

| | |
|---|---|
| $C_{22}H_{20}N_2$ (312.26) | calcd. : 84.62, H 6.41, N 8.97 |
| | found : 82.35, H 6.51, N 8.90 |



**IR** (KBr), [ν $cm^{-1}$] : 3080 w, 3053 m, 3020 m, 2963 m ($CH_3$), 2926 m ($CH_3$), 1627 s, 1597 m, 1572 m, 1489 s, 1419 m, 1391 s, 1362 m, 1317 m, 1275 m, 1216 m, 1211 s, 1136 s, 1103 s, 1074 s, 1024 s, 964 s (=C-H, trans), 758 s, 746 s, 692 s.

**$^1$H-NMR** (250 MHz), $CDCl_3$, δ [ppm] : 7.81 (d, *J* = 15.4 Hz, 4H, $H^a$), 7.61-7.58 (m, 4H, $H^c$), 7.41-7.24 (m, 6H, $H^d$, $H^e$), 7.35 (d, *J* =14.9 Hz, 2H, $H^b$), 2.68 (s, 6H, $H^f$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, δ [ppm] : 148.1 (C-1), 146.1 (C-2), 136.9 (C-5), 134.6 (C-7), 128.7 (C-3), 128.5 (C-4), 127.3 (C-6), 122.9 (C-8), 21.4 (C-9).

**MS** (EI, 70 eV), *m*/*z* [%] : 312.2 ($M^+$, 100), 297.2 ($M^+$-$CH_3$, 32), 270.1 (8), 235.2 ($M^+$-phenyl, 40), 197.1 (10), 155.9 ($M^+$-2phenyl, 23), 141.1 ($M^+$-2phenyl-$CH_3$, 68), 128.1 (10), 115 (40), 77.1 (phenyl, 5), 39.6 (8).

**UV/Vis** ($CH_2Cl_2$), λ [nm] : 294, 390.

**PL** ($CH_2Cl_2$), λ [nm] : 468.

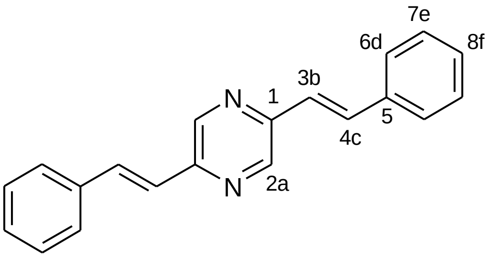
**EL** λ [nm] : 500.

### 5.1.6 2,5-Distyrylpyrazine (25)

A mixture of 1.00 g (9.25 mmol) of 2,5-dimethylpyrazine (**36**), 2.00 g (18.85 mmol) of benzaldehyde and a catalytic amount of zinc chloride was heated to 200 °C in an autoclave for 8 hours. After that, the reaction mixture was recrystallized from toluene to afford a yellow product.

Yield : 0.92 g (34.99 %), yellow plate-form crystals, m.p. 220.0 °C.

$C_{20}H_{16}N_2$ (284.23)



**IR** (KBr), [ν cm$^{-1}$] : 3055 w, 3039 w, 2999 w, 1630 s, 1574 m, 1495 s, 1483 s, 1360 s, 1305 w, 1202 m, 1151 s, 1074 w, 1030 s, 974 s (=C-H, trans), 926 m, 758 s, 696 s.

**$^1$H-NMR** (250 MHz), $CDCl_3$, δ [ppm] : 8.58 (s, 2H, H$^a$), 7.72 (d, *J* = 15.9 Hz, 2H, H$^b$), 7.60-7.58 (m, 4H, H$^d$), 7.42-7.28 (m, 6H, H$^e$, H$^f$), 7.17 (d, *J* =15.9 Hz, 2H, H$^c$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, δ [ppm] : 149.1 (C-1), 143.3 (C-2), 136.3 (C-5), 134.4 (C-7), 128.8 (C-3, C-4), 127.3 (C-6), 124.1 (C-8).

**MS** (EI, 70 eV), *m*/*z* [%] : 284.3 (M$^+$, 40), 267.0 (2), 195.2 (5), 154.1 (4), 141.0 (41), 126.9 (27), 102.1 (12), 77.2 (11), 50.8 (11).

**UV/Vis** ($CH_2Cl_2$), λ [nm] : 303, 383.

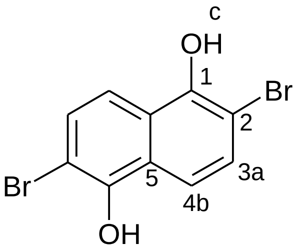
## 5.2 Naphthalene derivative

### 5.2.1 2,6-Dibromo-1,5-dihydroxynaphthalene (43)

A mixture of 10.00 g (62.46 mol) of the commercially available 1,5-dihydroxynaphthalene (**50**) and a catalytic amount of iodine crystal in 350 ml of glacial acid was stirred and heated to 80 °C. A solution of 6.5 ml (0.13 mol) of bromine in 25 ml of glacial acetic acid was added dropwise in 30 minutes. After cooling to room temperature, the pale olive green crystals formed were filtered off and washed with petroleum ether. Pure product was obtained from recrystallization from glacial acetic acid.

Yield : 15.00 g (75.54 %), colorless needles, decomposes before melting.

$C_{10}H_6Br_2O_2$ (317.92)



**IR** (KBr), [ν cm$^{-1}$] : 3398 s (O-H), 3080 w, 1699 w, 1583 s, 1497 w, 1414 m, 1360 s, 1246 s (=C-O), 1215 m, 1171 s, 955 m, 833 s, 789 s, 667 m.

**$^1$H-NMR** (250 MHz), $CDCl_3$, δ [ppm] : 7.68 (d, *J* = 9.0 Hz, 2H, H$^b$), 7.48 (d, *J* = 9.0 Hz, 2H, H$^a$), 5.95 (s, 2H, H$^c$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, δ [ppm] : 148.1 (C-1), 128.8 (C-5), 124.7 (C-3), 115.9 (C-4), 105.4 (C-2).

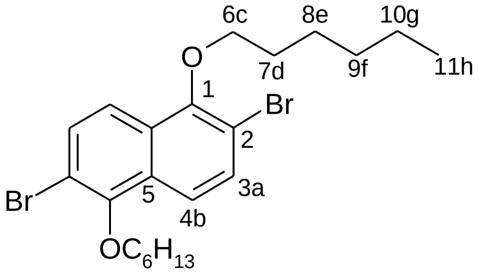
**MS** (EI, 70 eV), *m*/*z* [%] : 317.9 (M$^+$, 61), 238.2 (M$^+$-Br, 12), 208.9 (24), 158.1 (M$^+$-2Br, 11), 129.2 (119), 50.8 (100).

### 5.2.2 2,6-Dibromo-1,5-dihexyloxynaphthalene (44)

Sodium 4.32 g was dissolved in 250 ml of dry ethanol under argon and then 23.17 g (72.88 mmol) of **43** was added. To the refluxing mixture 26.4 ml (0.19 mol) of 1-bromohexane was added dropwise in 10 minutes. After additional 5 hours of refluxing, the reaction was allowed to reach room temperature and poured into 254 ml of a 1 N aqueous solution of sodium hydroxide. The black solid was filtered off and dissolved in 1 L of $CH_2Cl_2$. After the removal of insoluble particles, solvent was vacuum evaporated and residue was chromatographed on silica gel (hexane/$CH_2Cl_2$ 9:1)

Yield : 14.50 g (40.93 %), yellow solid, m.p. 62.0-63.0 °C.

$C_{22}H_{30}Br_2O_2$ (486.05)



**IR** (KBr), [ν $cm^{-1}$] : 2951 s ($CH_3$), 2926 s ($CH_2$), 2870 m ($CH_3$), 2856 m ($CH_2$), 1572 m, 1414 m, 1373 s, 1229 m, 1180 m, 1132 m, 1018 s, 837 m, 810 s.

**$^1$H-NMR** (250 MHz), $CDCl_3$, δ [ppm] : 7.76 (d, *J* = 8.8 Hz, 2H, $H^b$), 7.58 (d, *J* = 8.8 Hz, 2H, $H^a$), 4.05 (t, *J* = 6.7 Hz, 4H, $H^c$), 1.98-1.87 (m, 4H, $H^d$), 1.59-1.35 (m, 12H, $H^e$, $H^f$, $H^g$), 0.94-0.89 (m, 6H, $H^h$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, δ [ppm] : 152.8 (C-1), 131.0 (C-5), 130.1 (C-3), 119.4 (C-4), 113.8 (C-2), 74.7 (C-6), 31.7 (C-9), 30.2 (C-7), 25.7 (C-8), 22.7 (C-10), 14.1 (C-11).

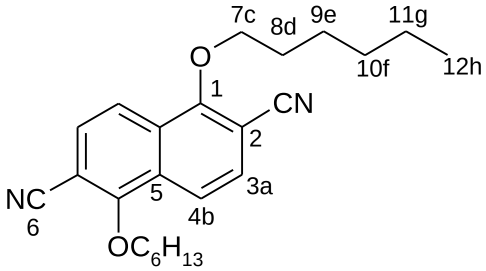
**MS** (EI, 70 eV), *m*/*z* [%] : 486.0 ($M^+$, 10), 408.0 ($M^+$-Br, 4), 328.2 ($M^+$-2Br, 3), 317.7 (100), 315.8 ($M^+$-$C_{12}H_{26}$, 51), 288.8 (5), 237.7 ($M^+$-$C_{12}H_{26}$Br, 28), 208.8 (6), 159.7 (12), 85.0 (5), 43.1 (57).

### 5.2.3 2,6-Dicyano-1,5-bis(hexyloxy)naphthalene (45)

A mixture of 5.00 g (10.29 mmol) of dibromo compound **43**, 2.76 g (30.82 mmol) of copper cyanide and 10 mg of sodium iodide suspended in dry DMF was refluxed for 2 days. After cooling to room temperature, the reaction mixture was poured into 170 ml of 15 wt % of aqueous ammonia solution. The solid formed was filtered off and washed with 150 ml of aqueous ammonia solution and then water. Afterward the solid was dried in desiccator over phosphorus pentoxide for a day at 0.13 mbar and then extracted with hot acetone in a Soxhlet apparatus for 5 hours. After vacuum evaporation of solvent, the residue was dissolved in 70 ml of chloroform and filtered through silica gel. Chloroform was then evaporated to obtain pure compound **44**.

Yield : 2.15 g (55.25%), yellow solid, m.p. 88.0-89.0 °C.

$C_{24}H_{30}N_2O_2$ (378.28)



**IR** (KBr), [ν cm$^{-1}$] : 2951 s ($CH_3$), 2928 s ($CH_2$), 2885 m ($CH_3$), 2870 m ($CH_2$), 2226 (CN), 1589 m, 1472 m, 1421 s, 1327 m, 1129 m (C=O), 1200 m, 1182 m, 1067 m, 1042 m (-C-O), 829 m.

$^1$**H-NMR** (250 MHz), $CDCl_3$, $\delta$ [ppm] : 7.94 (d, *J* = 8.6 Hz, 2H, $H^b$), 7.54 (d, *J* = 8.6 Hz, 2H, $H^a$), 4.46 (t, *J* = 6.6 Hz, 4H, $H^c$), 1.96-1.87 (m, 4H, $H^d$), 1.55-1.34 (m, 12H, $H^e$, $H^f$, $H^g$), 0.93-0.87 (m, 6H, $H^h$).

$^{13}$**C-NMR** (62.9 MHz), $CDCl_3$, $\delta$ [ppm] : 160.0 (C-1), 130.6 (C-5), 128.7 (C-3), 118.1 (C-4), 117.1 (C-6), 101.5 (C-2), 76.0 (C-7), 31.5 (C-10), 30.1 (C-8), 25.5 (C-9), 22.5 (C-11), 14.0 (C-12).

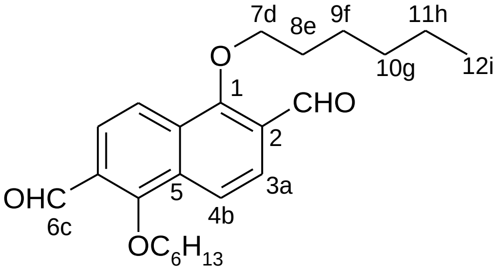
**MS** (EI, 70 eV), *m/z* [%] : 378.2 ($M^+$, 29), 353.2 ($M^+$-CN, 22), 328.2 ($M^+$-2CN, 10), 269.1 ($M^+$-$C_7H_{13}N$, 5), 210.0 ($M^+$-$C_{12}H_{26}$, 100), 185.0 ($M^+$-$C_{13}H_{26}N$, 23), 159.9 ($M^+$-$C_{14}H_{26}N_2$ , 4), 85.0 (5), 43.1 (24).

### 5.2.4 2,6-Diformyl-1,5-bis(hexyloxy)naphthalene (46)

A 1.5 M solution of DIBAL-H in dry toluene (12 ml) was added dropwise to a solution of 3.00 g (7.93 mmol) of **45** in 200 ml of dry diethyl ether and then the mixture was refluxed for a day. After cooling down to room temperature, methanol and then water was carefully added. The white precipitate formed was treated portionwise with small amounts of concentrated hydrochloric acid during a period of one hour until all the precipitate was dissolved and two layers could be observed. These two layers were separated and the aqueous layers were washed with diethyl ether, whereas the combined organic layers were washed with water, with saturated solution of sodium hydrogen carbonate and then again with water. After drying the solution over magnesium sulphate and vacuum evaporation of solvent, the yellow oily residue was purified by chromatography on silica gel (hexane/$CH_2Cl_2$ 7:3)

Yield : 2.59 g, (84.99 %), yellow solid, m.p. 69.0-70.0 °C.

$C_{24}H_{32}O_4$ (384.26)



**IR** (KBr), [ν $cm^{-1}$] : 2947 s ($CH_3$), 2928 s ($CH_2$), 2854 s ($CH_3$), 1686 s (HC=O), 1499 m, 1414 m, 1377 m, 1227 m (=C-O), 1117 m, 1042 m (-C-O), 824 m, 762 m.

**$^1$H-NMR** (250 MHz), $CDCl_3$, δ [ppm] : 10.58 (s, 2H, $H^c$), 8.02 (d, *J* = 8.8 Hz, 2H, $H^b$), 7.92 (d, *J* = 8.8 Hz, 2H, $H^a$), 4.16 (t, *J* = 6.7 Hz, 4H, $H^d$), 1.99-1.93 (m, 4H, $H^e$), 1.59-1.35 (m, 12H, $H^f$, $H^g$, $H^h$), 0.94-0.89 (m, 6H, $H^i$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, δ [ppm] : 189.6 (C-6), 161.6 (C-1), 133.2 (C-5), 127.5 (C-3), 123.7 (C-4), 119.5 (C-2), 79.5 (C-7), 31.6 (C-10), 30.2 (C-8), 25.6 (C-9), 22.6 (C-11), 14.0 (C-12).

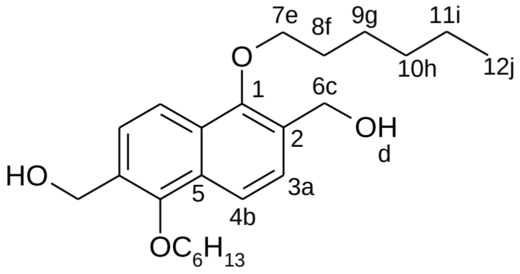
**MS** (EI, 70 eV), *m*/*z* [%] : 384.2 ($M^+$, 27), 300.0 ($M^+$-$C_6H_{13}$, 5), 215.9 ($M^+$-$C_{12}H_{26}$, 100), 196.9 ($M^+$-$OC_{14}H_{26}$, 10), 97 (6), 83.0 (12), 70.9 (28), 57.0 (27).

### 5.2.5 1,5- Dihexyloxy-2,6-bis(hydroxymethyl)naphthalene (47)

Sodium borohydride 214 mg (5.67 mmol) was suspended in a mixture of 30 ml of methanol and 30 ml of $CH_2Cl_2$. The solution was then stirred for additional 5 minutes at room temperature. To the yellow solution obtained was added 1 g (2.58 mmol) of **46** and the mixture was stirred for an hour and then diluted with $CH_2Cl_2$. Afterward, the reaction mixture was washed with saturated solution of sodium hydrogen carbonate and then water. After drying over sodium sulphate, the solvent was evaporated to obtain a residue which was then recrystallized from hexane.

Yield : 623 mg (61.66 %), white solid, m.p. 64.0 °C.

$C_{24}H_{36}O_4$ (388.26)



**IR** (KBr), [ν $cm^{-1}$] : 3283 s (O-H), 2963 s ($CH_3$), 2953 s ($CH_3$), 2923 s ($CH_2$), 2869 s ($CH_3$), 2856 s ($CH_2$), 1499 m, 1470 m, 1377 s, 1377 s, 1354 s, 1232 m (=C-O), 1082 s, 1066 s, 1051 s (-C-OH), 1042 s (-C-O), 814 s.

**$^1$H-NMR** (250 MHz), $CDCl_3$, δ [ppm] : 7.84 (d, *J* = 8.6 Hz, 2H, $H^b$), 7.49 (d, *J* = 8.6 Hz, 2H, $H^a$), 4.87 (s, 2H, $H^c$), 3.99 (t, *J* = 6.7 Hz, 4H, $H^e$), 2.13 (s, 2H, $H^d$), 1.97-1.85 (m, 4H, $H^f$), 1.58-1.35 (m, 12H, $H^g$, $H^h$, $H^i$), 0.94-0.89 (m, 6H, $H^j$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, δ [ppm] : 153.3 (C-1), 129.6 (C-5), 129.4 (C-3), 126.7 (C-4), 118.5 (C-2), 75.8 (C-7), 61.1 (C-6), 31.7 (C-10), 30.4 (C-8), 25.8 (C-9), 22.6 (C-11), 14.1 (C-12).

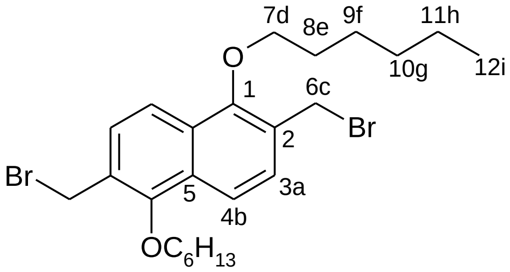
**MS** (EI, 70 eV), *m*/*z* [%] : 388.2 ($M^+$, 48), 286.1 ($M^+$-$OC_6H_{13}$, 12), 201.9 ($M^+$-$OC_{12}H_{26}$, 15), 184.0 ($M^+$-$O_2C_{12}H_{26}$, 100), 173.0 ($M^+$-$O_2C_{13}H_{26}$, 10), 156.0 ($M^+$-$O_2C_{14}H_{32}$, 4), 127.0 (6), 85.0 (3), 55.0 (10), 43.1 (46).

### 5.2.6 2,6-Bis(bromomethyl)-1,5-dihexyloxynaphthalene (48)

A mixture of 1.20 g (3.09 mmol) of **47**, 1.95 g (9.27 mmol) of tetraethylammonium bromide and 1 ml of fresh distilled boron trifluoride-diethyl ether in 10 ml of $CH_2Cl_2$ was refluxed for 3 hours and then allowed to reach room temperature. Afterward, 6 ml of a saturated solution of sodium hydrogen carbonate was added to obtain two layers which were separated to combine organic layers. The remaining aqueous layers were washed with 10 % aqueous solution of sodium hydrogen sulphate and then brine solution. After drying the solution over sodium sulphate, solvent was vacuum evaporated to obtain crude product which was then chromatographed on silica gel (hexane/$CH_2Cl_2$ 8:2)

Yield : 1.23 g (77.41 %), white solid, m.p. 61.0-62.0 °C.

$C_{24}H_{34}Br_2O_2$ (514.07)



**IR** (KBr), [ν $cm^{-1}$] : 2951 s ($CH_3$), 2934 s ($CH_2$), 2870 s ($CH_3$), 2854 s ($CH_2$), 1601 s, 1502 w, 1464 w, 1377 s, 1337 m, 1227 m (=C-O), 1207 s, 1059 s, 1043 s (-C-O), 825 s, 735 s, 635 m.

**$^1$H-NMR** (250 MHz), $CDCl_3$, δ [ppm] : 7.83 (d, *J* = 8.4 Hz, 2H, $H^b$), 7.47 (d, *J* = 8.6 Hz, 2H, $H^a$), 4.72 (s, 4H, $H^c$), 4.09 (t, *J* = 6.7 Hz, 4H, $H^d$), 1.98-1.92 (m, 4H, $H^e$), 1.60-1.37 (m, 12H, $H^f$, $H^g$, $H^h$), 0.95-0.90 (m, 6H, $H^i$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, δ [ppm] : 154.0 (C-1), 130.0 (C-5), 128.4 (C-3), 127.4 (C-4), 119.2 (C-2), 75.5 (C-7), 31.7 (C-10), 30.4 (C-8), 28.3 (C-6), 25.7 (C-9), 22.6 (C-11), 14.1 (C-12).

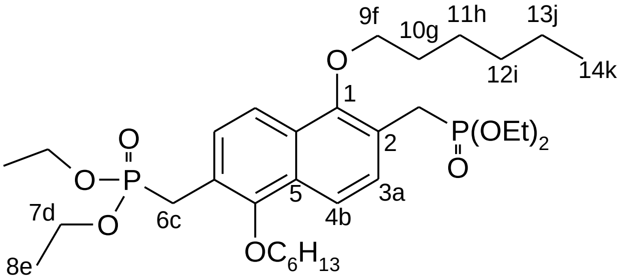
**MS** (EI, 70 eV), *m*/*z* [%] : 513.9 ($M^+$, 18), 434.9 ($M^+$-Br, 42), 350.8 ($M^+$-2Br, 100), 304.8 (10), 269.0 ($M^+$-$C_6H_{13}Br_2$, 36), 220.8 ($M^+$-$O_2C_{13}H_{28}Br$, 9), 198.9 (15), 184.7 ($M^+$-$C_{12}H_{26}Br_2$, 70), 148.9 (5), 127.0 (10), 110.9 (15), 96.9 (24), 82.9 (32), 70.7 (37), 43.0 (76).

### 5.2.7 [6-(Diethoxy-phosphoryl)-2,7-(dihexyloxy)-naphthalene-2-ylmethyl]-phosphonic acid diethyl ester (53)

A mixture of 100 mg (0.19 mmol) of **48** in 161 mg (0.97 mmol) of triethyl phosphite was heated to 160 °C until the generation of bromoethane gas was stopped and further heated to 180 °C for an hour. The excess of triethyl phosphite was then removed by vacuum distillation. After cooling down to room temperature, the crude product was purified by column chromatography (silica gel, ethyl acetate)

Yield : 98 mg (80.22 %), colorless solid, m.p. 55.0 °C.

$C_{32}H_{54}O_8\,P_2$ (628.29) calcd. : 61.17, H 8.59
found : 60.61, H 8.43



**IR** (KBr), [$\nu$ cm$^{-1}$] : 2957 m ($CH_3$), 2932 m ($CH_2$), 2862 s ($CH_2$), 1603 w, 1468 w, 1412 w, 1393 w, 1373 m (P=O), 1244 m, 1163 w (P-O), 1097 w, 1055 s (-C-O), 1028 s, 924 m, 843 w, 789 w.

$^1$**H-NMR** (250 MHz), $CDCl_3$, $\delta$ [ppm] : 7.76 (d, *J* = 8.6 Hz, 2H, $H^b$), 7.53 (d, *J* = 8.6 Hz, 2H, $H^a$), 4.10-3.96 (m, 12H, $H^d$, $H^f$), 3.37 (d, *J* = 21.7 Hz, 4H, $H^c$), 1.96-1.85 (m, 4H, $H^g$), 1.59-1.35 (m, 12H, $H^h$, $H^i$, $H^j$), 1.24 (t, *J* = 7.1 Hz, 12H, $H^e$), 0.94-0.89 (m, 6H, $H^k$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, δ [ppm] : 153.7, 153.5 (C-1), 129.1 (C-5), 128.3 (C-3), 120.8, 120.6 (C-4), 118.2 (C-2), 75.1 (C-9), 62.1, 62.0 (C-7), 31.8 (C-12), 30.4 (C-10), 28.2 (C-6), 25.9 (C-11), 25.8 (C-13), 16.4, 16.3 (C-8), 14.0 (C-14).

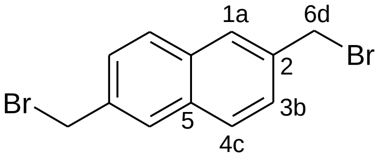
**MS** (FD), *m*/*z* [%] : 628.2 ($M^+$, 100).

### 5.2.8 2,6-Bis(bromomethyl)naphthalene (51)

A mixture of 1.00 g (6.40 mmol) of commercially available 2,6-dimethylnaphthalene (**50**), 2.51 g (14.10 mmol) of *N*-bromosuccinimide and a catalytic amount of dibenzoyl peroxide in 130 ml of dry $CCl_4$ was irradiated by means of a sunlamp at room temperature for 6 hours. Succinimide formed was removed by filtration and then the solvent was evaporated. Pure product was obtained by recrystallization from hexane.

Yield : 1.75 g, (87.09 %), white needles, m.p. 181.0-182.0 °C.

$C_{12}H_{10}Br_2$ (313.94)



**IR** (KBr), [ν $cm^{-1}$] : 1703 s, 1693 s, 1502 m, 1435 m, 1346 m, 1227 m, 1207 m, 1151 m, 1128 m, 897 s, 824 s, 702 s, 689 s.

**$^1$H-NMR** (250 MHz), $CDCl_3$, δ [ppm] : 7.80 (br, 2H, $H^c$), 7.77 (s, 2H, $H^a$), 7.50 (dd, $J$ = 8.3 Hz, $J$ = 1.6 Hz, 2H, $H^b$), 4.64 (s, 4H, $H^d$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, δ [ppm] : 135.9 (C-5), 132.8 (C-2), 128.1 (C-1), 127.7 (C-4), 127.4 (C-3), 37.7 (C-6).

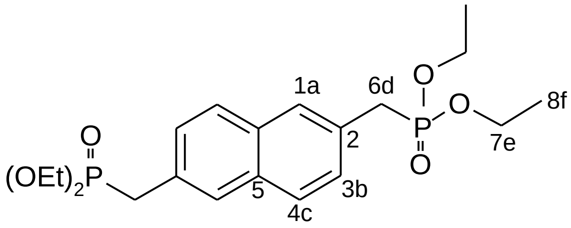
**MS** (EI, 70 eV), *m/z* [%] : 314.0 ($M^+$, 10), 235.0 ($M^+$-Br, 54), 154.1 ($M^+$-2Br, 100), 116.2 ($M^+$-$C_2H_4Br_2$, 5), 76.1 (40).

### 5.2.9 [6-(Diethoxyphosphoryl)naphthalene-2-ylmethyl]phosphonic acid diethyl ester (54)

A mixture of 1.00 g (3.19 mmol) of dibromo compound **51** and 2.12 g (12.74 mmol) of triethyl phosphite was heated to 160 °C until the evolution of bromoethane gas was stopped, about 30 minutes, and then heated to 180 °C for additional 30 minutes. Afterward, the reaction mixture was distilled under vacuum to remove an excess of triethyl phosphite and then allowed to reach room temperature. White solids formed were filtered off and then washed with small amounts of cold ethyl acetate.

Yield : 0.75 g (55.21 %), white solid, m.p. 144.0 °C.

$C_{20}H_{30}O_6P_2$ (428.16)



**IR** (KBr), [ν $cm^{-1}$] : 2982 m ($CH_3$), 2943 m ($CH_3$), 2908 s ($CH_2$), 1267 s (P=O), 1229 s, 1167 m (P-O), 1099 m, 1059 s , 1024 s, 966 s, 903 m, 837 m, 654 m.

**$^1$H-NMR** (250 MHz), $CDCl_3$, δ [ppm] : 7.72 (d, *J* = 8.6 Hz, 2H, $H^c$), 7.71 (s, 2H, $H^a$) 7.40 (d, *J* = 8.8 Hz, 2H, $H^b$), 4.05-3.93 (m, 8H, $H^e$), 3.28 (d, *J* = 21.3 Hz, 4H, $H^d$), 1.21 (t, *J* = 7.1 Hz, 12H, $H^f$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, $\delta$ [ppm] : 132.3 (C-5), 129.1, 129.0 (C-2), 128.3-182.2(C-3, C-4), 127.8 (C-1), 62.2, 62.1 (C-7), 35.0, 32.8 (C-6), 16.4, 16.3 (C-8).

**MS** (EI, 70 eV), *m*/*z* [%] : 428.2 ($M^+$, 100), 400.2 ($M^+$-$C_2H_5$, 4), 350.2 (9), 305.2 (14), 291.2 ($M^+$-$C_4H_{10}O_3P$, 97), 263.1 ($M^+$-$C_6H_{15}O_3P$, 21), 235.1 ($M^+$-$C_8H_{20}O_3P$, 15), 217.1 ($M^+$-$C_8H_{20}O_4P$, 31), 185.1 (5), 169.2 (15), 154.2 ($M^+$-$C_8H_{20}O_6P_2$, 93), 109.0 (14), 81.0 (15), 65.1 (5).

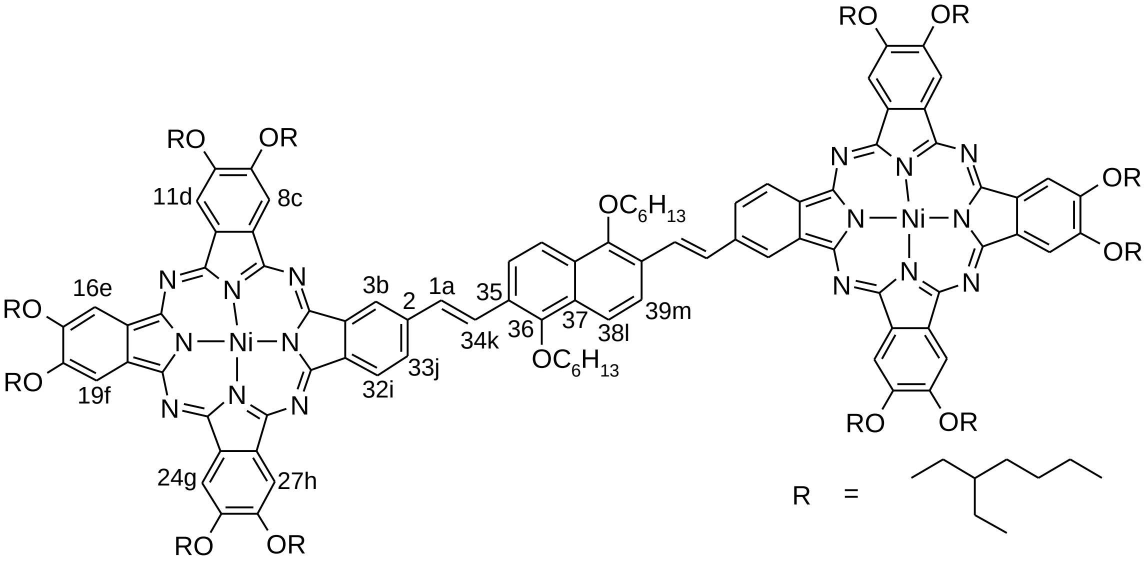
## 5.3 Bisvinylenenaphthylene-bridged phthalocyanine dimers 27 and 28

### 5.3.1 2,6-Bis([9,10,17,18,25,26-hexakis(2¢-ethylhexyloxy-2-vinylphthalocyaninato]nickel(II))-1,5-dihexyloxynaphthalene (27)

The formyl Pc **26** 219 mg (160 mmol) and 50 mg (80 µmol) of phosphonate **53** were dissolved in 10 ml of dry THF and then a solution of 20 mg of potassium-*tert*-butoxide in 3 ml of dry THF along with 20 mg of 18-crown-6 were carefully added. The mixture was slowly heated to 50 °C and stirred for further 4 days. After evaporation of the solvent, the crude product was chromatographed on silica gel ($CH_2Cl_2$/hexane 2:1) and then extracted with hot methanol to furnish pure **27**.

Yield : 29 mg (12.01 %), dark green solid.

| | |
|---|---|
| $C_{186}H_{256}N_{16}Ni_2O_{14}$ (3055.53) | calcd. : 73.11, H 8.38, N 7.33 |
| | found : 67.45, H 8.08, N 6.04 |



**IR** (KBr), [ν cm$^{-1}$] : 2959 s (CH$_3$), 2926 s (CH$_2$), 2858 m (CH$_2$), 1607 w, 1531 w, 1460 s, 1431 m, 1391 m, 1360 m, 1275 s, 1263 s, 1101 s, 1065 s, 1028 m, 964 w, 949 w, 930 w, 897 w, 802 m, 750 w.

**$^1$H-NMR** (250 MHz), CDCl$_3$, δ [ppm] : 8.83-7.32 (br, 26 H, H$^a$, H$^b$, H$^c$, H$^d$, H$^e$, H$^f$, H$^g$, H$^h$, H$^i$, H$^j$, H$^k$, H$^l$, H$^m$), 4.43, 4.45 (br, 28H, OC$\underline{H}_2$), 2.11 (br, 12H, C$\underline{H}$), 1.79, 1.67, 1.55 (br, 112H, C$\underline{H}_2$), 1.24, 1.22, 1.06, 1.03 (br, 78H, C$\underline{H}_3$).

**$^{13}$C-NMR** (62.9 MHz), CDCl$_3$, δ [ppm] : 152.8, 152.2, 152.0 (C-9, C-10, C-17, C-18, C-25, C-26, C-36), 145.1, 143.9 (C-5, C-6, C-13, C-14, C-21, C-22, C-29, C-30), 138.8, 138.4 (C-2, C-35), 135.5 (C-37), 132.7, 131.2 (C-4, C-31), 130.9, 129.5, 129.4 (C-3, C-7, C-12, C-15, C-20, C-23, C-28, C-32, C-33, C-39), 126.9 (C-1, C-34), 123.5 (C-1, C-34), 118.5 (C-38), 107.0, 104.2, 104.0, 103.5 (C-8, C-11, C-16, C-19, C-24, C-27), 71.9 (O$\underline{C}$H$_2$), 39.9, 39.7 ($\underline{C}$H), 32.1, 31.8, 30.9, 30.8, 29.7, 29.4, 26.4, 24.1, 23.3, 23.0 ($\underline{C}$H$_2$), 14.2, 11.9, 11.5 ($\underline{C}$H$_3$).

**MS** (MALDI-TOF), *m*/*z* [%] : 3056.8 (M$^+$, 100).

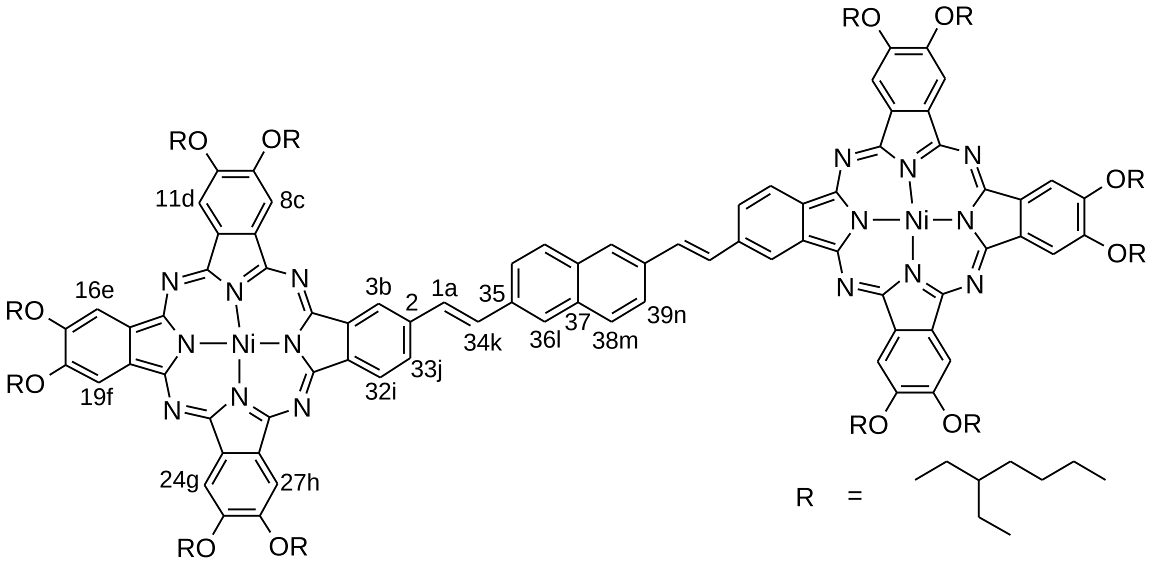
**UV/Vis** (THF), λ [nm] : 405, 673, 685.

### 5.3.2 2,6-Bis([9,10,17,18,25,26-hexakis(2¢-ethylhexyloxy-2-vinylphthalocyaninato]nickel(II))naphthalene (28)

The formyl Pc **26** 256 mg (187 mmol) and 40 mg (93 µmol) of phosphonate **54** were dissolved in 10 ml of dry THF. Then, a solution of 22 mg of potassium-*tert*-butoxide in 3 ml of dry THF along with 20 mg of 18-crown-6 were carefully added. The mixture was slowly heated to 50 °C and stirred for further 3 days. After evaporation of the solvent, the crude product was purified by chromatography (silica gel, $CH_2Cl_2$/hexane 2:1) and then extracted with hot methanol to furnish pure **27**.

Yield : 27 mg (10.00 %), dark green solid.

$C_{174}H_{232}N_{16}Ni_2O_{12}$ (2855.40) calcd. : 73.19, H 8.12, N 7.85
found : 65.27, H 7.45, N 6.66



**IR** (KBr), [ν $cm^{-1}$] : 2961 s ($CH_3$), 2924 s ($CH_2$), 2874 m ($CH_2$), 1607 w, 1529 w, 1501 w, 1462 m, 1433 m, 1379 m, 1279 m, 1105 m, 1065 s, 972 w, 901 w, 854 w, 750 w.

**$^1$H-NMR** (250 MHz), $CDCl_3$, δ [ppm] : 8.60-7.32 (br, 28H, $H^a$, $H^b$, $H^c$, $H^d$, $H^e$, $H^f$, $H^g$, $H^h$, $H^i$, $H^j$, $H^k$, $H^l$, $H^m$, $H^n$), 4.34 (br, 24H, $OC\underline{H}_2$), 2.06 (br, 12H, $C\underline{H}$), 1.79, 1.57 (br, 96H, $C\underline{H}_2$), 1.27, 1.23, 1.22, 1.09, 1.06, 1.02 (br, 72H, $C\underline{H}_3$).

**$^{13}$C-NMR** (62.9 MHz), $CDCl_3$, δ [ppm] : 151.7, 151.3 (C-9, C-10, C-17, C-18, C-25, C-26), 145.4, 144.9, 144.2, 143.2 (C-5, C-6, C-13, C-14, C-21, C-22, C-29, C-30), 137.3 (C-2, C-35), 136.6 (C-37), 134.8, 133.1 (C-4, C-31), 130.5, 130.2, 129.8, 129.1, 128.3 (C-3, C-7, C-12, C-15, C-20, C-23, C-28, C-32, C-33), 126.7 (C-36), 125.8, 125.3 (C-38, C-39), 123.2, 121.1 (C-1, C-34), 104.0, 103.4, 103.2 (C-8, C-11, C-16, C-19, C-24, C-27), 72.0, 71.8, 67.4, 66.6 ($O\underline{C}H_2$), 40.1, 39.8 ($\underline{C}H$), 34.5, 31.1, 30.9, 29.7, 29.4, 29.2, 28.0, 27.0, 26.0, 25.5, 24.4, 24.1, 23.5, 23.4, 23.3 ($\underline{C}H_2$), 14.5, 14.3, 14.2, 11.8, 11.6 ($\underline{C}H_3$).

**MS** (MALDI-TOF), *m*/*z* [%] : 2856.5. ($M^+$, 100).

**UV/Vis** (THF), λ [nm] : 406, 673.

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| 1982 - 1989 | Sacred Heart Convent Grundschule in Bangkok |
| 1989 - 1994 | The Demonstration School of Ramkhamhaeng University (Mittelschule und Gymnasium) |

## Universitätsausbildung

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| 05.1994 - 03.1998 | Studium der Chemie an der Naturwissenschaft Fakultät der Chulalongkorn Universität, Bangkok |
| 04.1997 - 03.1998 | Wissenschaftliche Forschung unter Anleitung von Prof. A. Petsom, Thema : “The determination of Additives in Diesel Lubricating Oil” |
| 04.1997 - 05.1997 | Training bei Petroleum Thailand |
| 19.03.1999 | Bachelor Degree of Science (first-class honour) |
| 04.1999 - 09.1999 | Deutscher Sprachkurs im Goethe-Institut in Bremen |
| 10.1999 - 01.2002 | Anfertigung der vorliegenden Arbeit auf Grund eines DAAD (Deutscher Akademischer Austauschdienst)-Stipendiums am Institut für Organische Chemie der Eberhard-Karls-Universität unter Anleitung von Prof. Dr. Dr. h.c. M. Hanack |

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