David Beichel, BSc

Dye-functionalized copolymers for upconversion layers based on triplet triplet annihilation

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Abstract

Triplet triplet annihilation upconversion (TTA-UC) is a multi-chromophore process that transforms the excitation wavelength *via* a sequence of energy transfer steps into luminescence emission with a shorter wavelength. In the first step a sensitizer molecule is excited into its singlet state. The triplet state is populated by intersystem crossing and in presence of a suitable emitter molecule triplet-triplet energy transfer from the sensitizer to the emitter takes place, followed by triplet triplet annihilation of two adjacent emitter triplets and radiative emission of a photon. TTA-UC in polymeric systems is a rather new field of research. In the last ten years appropriated combinations of chromophores were the first time embedded into a polymer matrix. There is a growing interest in low power photon upconversion in polymeric systems because a wide range of potential applications are discussed i.e. high-resolution optical microscopy, drug delivery, oxygen sensing and layers for light conversion. The efficiency of TTA-UC is in polymeric systems by orders of magnitudes smaller than in solutions. The mobility of the chromophores in polymers is hindered and the concentration is limited due to the solubility of molecularly dissolved chromophores. Additionally molecularly dissolved chromophores are prone to aggregation and phase separation. To get around with these problems the chromophores can be covalently bound to a matrix monomer and the TTA-UC efficiency can be increased with defined polymer architecture. The main aim of this master thesis was to synthesis an appropriate combination of polymerizable sensitizer and emitter chromophores with norbornene ester side groups and to statistically copolymerize sensitizer and emitter with various monomers *via* ring-opening metathesis polymerization (ROMP) to give defined polymers, which show low power photon TTA-UC in solution and in thin films as well. Three different perylene diimide derivatives and norbornene-functionalized Pt-tetraphenyltetrabenzo-*tert*-butly-porphyrin were synthesized and applied as emitter and sensitizer. The most promising perylene diimide derivative was statistically copolymerised with a matrix monomer. The concentration of the chromophore and respectively the inter-chomophore distance was varied over a wide range. The same approach was done for the sensitizer. In order to systematically evaluate the optimal concentrations for sensitizer and emitter a concentration series was made. The emitter was covalently bound and the sensitizer was molecularly dissolved. Beside the norbornene-functionalized sensitizer also acrylate-functionalized sensitizer was prepared. With this reagents it was possible to endgroup-functionalize the polymer strand by terminating the ring-opening metathesis polymerization.

Kurzfassung

Triplett-Triplett-Annihilierung Upconversion (TTA-UC) ist ein Prozess bei dem die Anregungswellenlänge über mehrere Energy-Transfer Schritte in Lumineszenz mit kürzerer Wellenlänge überführt wird. Im ersten Schritt wird ein Sensitizermolekül in den Singulettzustand angeregt und durch Intersystem Crossing in dessen Triplett-Zustand überführt. Ist ein passender Farbstoff (Emitter) vorhanden, kommt es zu einem Triplett-Triplett Energietransfer und in weiter Folge zur Triplet-Triplet-Annihilierung zweier benachbarter Emitter-Tripletts und ein Photon wird emittieret. Polymer basierte Triplet-Triplet-Annihilierung Upconversion (TTA-UC) ist ein relativ neues Forschungsgebiet. Vor etwa zehn Jahren wurde erstmals ein geeignetes Farbstoffpaar in eine Polymermatix eingebettet davor war dieses Phänomen nur in Lösung bekannt. Seither besteht ein zunehmendes Interesse an Polymer basierte TTA-UC und eine Vielzahl neuer Anwendungen sind mit einem solchen System möglich, wie zum Beispiel hochauflösende optische Mikroskopie, Drug-Delivery, Sauerstoffsensoren und Schichten zur Konvertierung von Sonnenlicht. Die Effizienz der Polymer basierte TTA-UC ist um ein Vielfaches geringer als in Lösung da die Mobilität und Moleküleabstände in festen Polymersystemen ungünstig sind. Zusätzlich kann es zur Aggregation und Phasentrennung der molekular gelösten Farbstoffe. Diese kann umgangen werden indem die Chromophore kovalent an ein Matrixpolymer gebunden werden. Auch sind so unterschiedliche Polymerarchitekturen denkbar, die zu einer Steigerung der Intensität der Emission der TTA-UC führen könnten.

In dieser Arbeit wurden Norbornen-funktionalisierte Perylenebisimid-Derivate und Norbornen-funktionalisierte Pt-Tetraphenyltetrabenzo-*tert*-butly-porphyrine synthetisiert in Absicht diese als Emitter bzw. Sensitizer *via* ringöffnender Metathesepolymerisation (ROMP) zu polymeriserien. Mit dem vielversprechendsten Perylenebisimid-Derivate wurden statistische Copolymer mit unterschiedlichen Emitterkonzentrationen synthetisiert. Ähnlich wurde mit dem Norbornen-funktionalisierte Pt-Tetraphenyltetrabenzo-*tert*-butly-porphrin verfahren. Im nächsten Schritt wurde eine Konzentrationsreihe mit variierendem Sensitizergehalt und den einzelnen Emittercopolymeren erstellt. Der Sensitizer war dabei nicht kovalent gebunden sondern lag gelöst vor. Es sollte systematisch die optimalen Konzentrationen für Sensitizer und Emitter evaluiert werden.

Neben dem Norbornen-funktionalisierter Sensitizer wurde auch ein Acrylat-funktionalisierter Sensitizer hergestellt. Damit war es möglich Endgruppen funktionalisierte Polymere *via* ringöffnender Metathesepolymerisation (ROMP) zu erhalten.

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Abbreviations

$^1E^*$	excited singlet state emitter
$^1S^*$	excited singlet state sensitizer
$^3E^*$	excited triplet state emitter
$^3S^*$	excited triplet state sensitizer
acac	acetyl acetone
APT	Attached Proton Test
ATR-FTI	attenuated total reflection- Fourier transform infrared spectroscopy
b	broad
CH	cyclohexane
COSY	COrrelated SpectroscopY
d	duplet
DABCO	1,4-diazabicyclo[2.2.2]octane
DCC	*N,N'*-Dicyclohexylcarbodiimide
DCM	dichloromethane
DCTB	*trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile
dd	doublet of doublets
DMAP	4-(dimethylamino)-pyridine
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DSC	differential scanning calorimetry
EE	ethyl acetate
EtOH	ethanol
GPC	gel permeation chromatography
GS	ground state
HSQC	Heteronuclear Single Quantum Coherence

ISC	intersystem crossing
m	multiplet
MALDI-TOF	matrix-assisted laser desorption ionization-time of flight
MeOH	methanol
NMR	nuclear magnetic resonance spectroscopy
OAc	acetate
PDi	perylene diiimide
PDI	polydispersity index
PdOEP	Pd-octaethylporphyrin
PdTPTBP	Pd-tetraphenyltetrabenzoporphyrin
PET	photoinduced electron transfer
PTCDA	perylene-3,4,9,10-tetracarboxylic dianhydride
PtOEP	Pt-octaethylporphyrin
PtTPTBP	Pt-tetraphenyltetrabenzoporphyrin
q	quadruplet
ROMP	ring opening metathesis polymerization
s	singlet
t	triplet
T_G	glass transition temperature
THF	tetrahydrofuran
TLC	thin layer chromatography
TPP	*meso*-tetraphenylporphyrin
TTA	triplet triplet annihilation
TTA-UC	triplet triplet annihilation upconversion
TTET	triplet triplet energy transfer
UV	ultraviolet light
UV-Vis	ultraviolet–visible spectroscopy

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1 Theory

1.1 Triplet triplet annihilation upconversion

Optical upconversion is a process that transforms the excitation wavelength into luminescence emission with a shorter wavelength.[1] This so called anti-stokes shifts (Figure 1) means that the emitted photons have higher energy than those absorbed for the excitation. To be not in conflict with the first law of thermodynamic multiple photons were used for the upconversion process.[2]

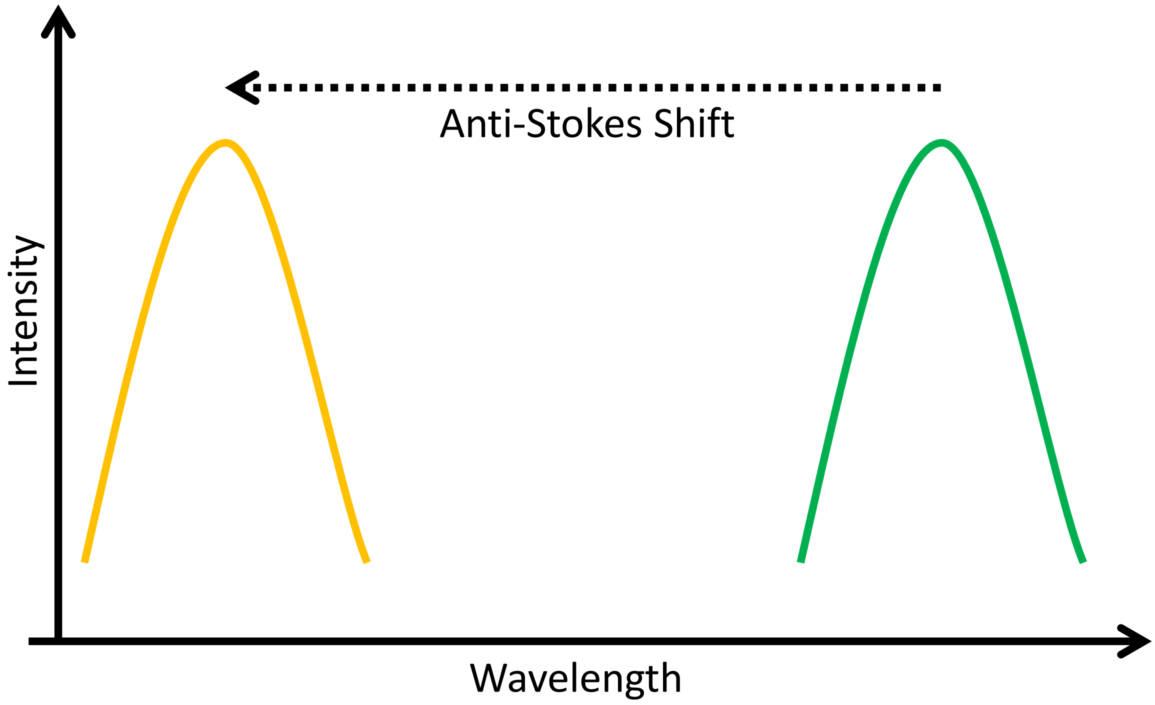


Figure 1. Visualization of the anti-Stokes Shift and energy gain.[3]

Anti-Stokes luminescence based on two-photon absorption and nonlinear-optical progresses such as second and third harmonic generation has been reported multiple times and is well established. These anti-Stokes processes need a pulsed laser and high power densities for excitation. For that reason these effects cannot be applied in many applications where the upconversion of low-power, non-coherent and continuous-wave excitation is required.[1] Low-power upconversion has been known since the 1960s and is realized in Lanthanide-doped or transition-metal-doped materials. The possible processes involved are energy-transfer processes, excited state absorption, cooperative upconversion involving multiple ions, and photon avalanches.[1,2]

In the 1960s Parker and Hatchard[4] reported triplet triplet annihilation (TTA-UC) in a multi-chromophore system for the first time. They used a combination of two organic chromophores, the sensitizer and the emitter. In these early stages phenanthrene/naphthalene or proflavin/anthracene was employed and the emission and absorption was in the ultraviolet (UV) reagion.[2]

The generally accepted mechanisms for the TTA-UC (Figure 2) starts with the excitation of the sensitizer to the first singlet excited state ($^1S^*$) by long-wavelength absorption. The first singlet excited state ($^1S^*$) is converted into a triplet ($^3S^*$) upon intersystem crossing (ISC), followed by the triplet-triplet energy transfer (TTET) to the triplet state of the emitter ($^3E^*$). Triplet triplet annihilation (TTA) can occur and two excited emitters disproportionate to one emitter in the singlet excited state ($^1E^*$) and the second emitter is transitioned into the ground state (GS). Finally the excited state of an emitter ($^1E^*$) decays radiatively to the ground state and leads to delayed fluorescence. Sometimes the emitter is also called annihilator.[1,2]

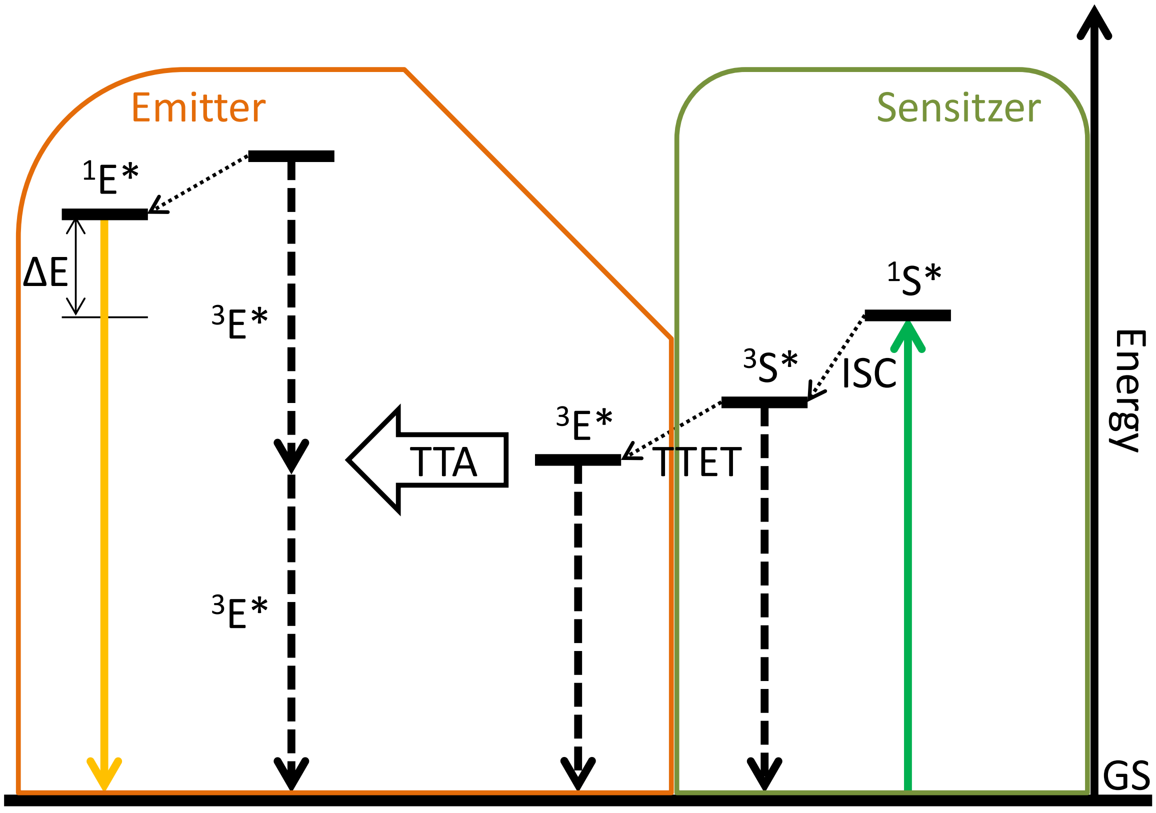


Figure 2. Schematic of the steps involved in the TTA-UC process. The first singlet excited state ($^1S^*$) is converted into a triplet ($^3S^*$) upon intersystem crossing (ISC), followed by the triplet-triplet energy transfer (TTET) to an emitter ($^3E^*$). Triplet-triplet annihilation (TTA) can occur and two excited emitters disproportionate to one emitter in the singlet excited state (1E*) and the second emitter is transitioned into the ground state (GS).[3]

Usually TTA-UC is observed as delayed singlet fluorescence. The emission is anti-Stokes-shifted in comparison to the excitation wavelength. The spectra profile is identical with the spectra of the emitter but the emission lifetime is longer. At lower excitation power density the intensity of the upconversion emission is a quadratic function of the incident excitation and at higher power density the emission intensity shows a linear dependence because the triplet sates of the emitter are saturated then. In time resolved measurements it is shown that the phosphorescence of the sensitizer is quenched when the delayed fluorescence starts. TTA-UC is highly prone to O_2-induced quenching of the upconversion luminescence. There is a energy transfer from the triplets ($^3S^*$) and ($^3E^*$) to molecular oxygen and the TTA-UC is hindered.[1,2,5]

The overall quantum yield Φ_{UC} is the product of the quantum efficiencies for the intersystem crossing Φ_{ISC}, energy transfer Φ_{ET}, triplet triple annihilation Φ_{TTA} and emitter photoluminescence Φ_E (see formula **(1)**). In this process two photons are combined to one photon with higher energy this is expressed with the factor $\frac{1}{2}$. The factor f expresses the probability that the TTA results in a singlet excited state as opposed to a triplet or a quintet excited state.[1]

$$\Phi_{UC} = \frac{1}{2} f \Phi_{ISC} \Phi_{ET} \Phi_{TTA} \Phi_E \qquad \textbf{(1)}$$

In solution Φ_{ISC}, Φ_E, and f mostly depend on the chromophores. Φ_{ET} and Φ_{ET} depend on external factors and can be varied. The concentration of the chromophores which influences the distance between the molecule, the power density of the excitation which is an imported factor amongst others for the concentration of the excited triplet states and the mobility of the chromophores, are the major adjusting tools. The triplet-triplet annihilation is suspected to be the key element of the overall TTA-UC process. In this process an encounter complex of two emitters in the excited triplet state ($^3E^*$) must be formed. The encounter complex disproportionate to one emitter in the singlet excited state ($^1E^*$) and the second emitter is transitioned into the ground state (GS). This process requires a high mobility of the chromophores or exitons can migrate or diffuse efficiently. For the triplet-triplet energy transfer is also a close proximity of at least a few nanometers needed.[1,2]

1.1.1 Chromophores

Sensitizer and emitter have to fulfill numerous requirements in order to obtain efficient TTA-UC. The **emitter** should not absorb at the excitation wavelength and the fluorescence quantum yield should be high. To maximize the anti-Stokes shift the energy level of the first triplet excited state ($^3E^*$) should be close to the triplet excited state of the sensitizer ($^3S^*$). The energy level of the $^3E^*$ is lower than that of the $^3S^*$ but $^3E^*$ should be higher than half of the first singlet excited state ($^1E^*$) and the lifetime of $^3E^*$ should be long enough to enable the TTA process. Furthermore should the normal Stokes shift be small to maximize the anti-Stokes shift.[1,2] Several polycyclic aromatic hydrocarbons have been used as emitter so far because of their wide gap between the $^1E^*$and the relatively low laying $^3E^*$ in relation to their first excited singlet state ($^1E^*$).[1,2,6]

The **sensitizer** should have a high extinction coefficient at the excitiation wavelength and for certain applications, like solar harvesting, the absorption spectrum should be broad. But the fluorescence spectra of the emitter should not overlap with the absorption spectrum of the sensitizer. Otherwise the upconversion emission will be reabsorbed and the overall quantum efficiency will be reduced.[1] The rate of intersystem crossing should be high and the rate of internal conversion should be low in order to populate a large number of triplet states. This manifests among others in a long lifetime of the excited triplet state ($^3S^*$). The energy gap between the excited singlet state ($^1S^*$) and excited triplet state ($^3S^*$) should be small so that a large anti-Stokes shift can be accomplished. It should be noticed that the energy of the TTA-UC emission wavelength cannot be higher than twice the energy of the excitation wavelength.

The most commonly used sensitizers are Pd- or Pt-porphyrin such as Pd-octaethylporphyrin (PdOEP) or Pt-octaethylporphyrin (PTOEP) and Pd-tetraphenyltetrabenzoporphyrin (PdTPTBP) or Pt-tetraphenyltetrabenzoporphyrin (PtTPTBP) because they are efficient triplet generators. This ability is based on the heavy-atom promoted spin-orbit coupling.[1,7] In conjugation with anthracene derivatives or perylene as emitter several groups used these chromophore systems for TTA-UC in polymeric systems. An overview is given in Figure 3.

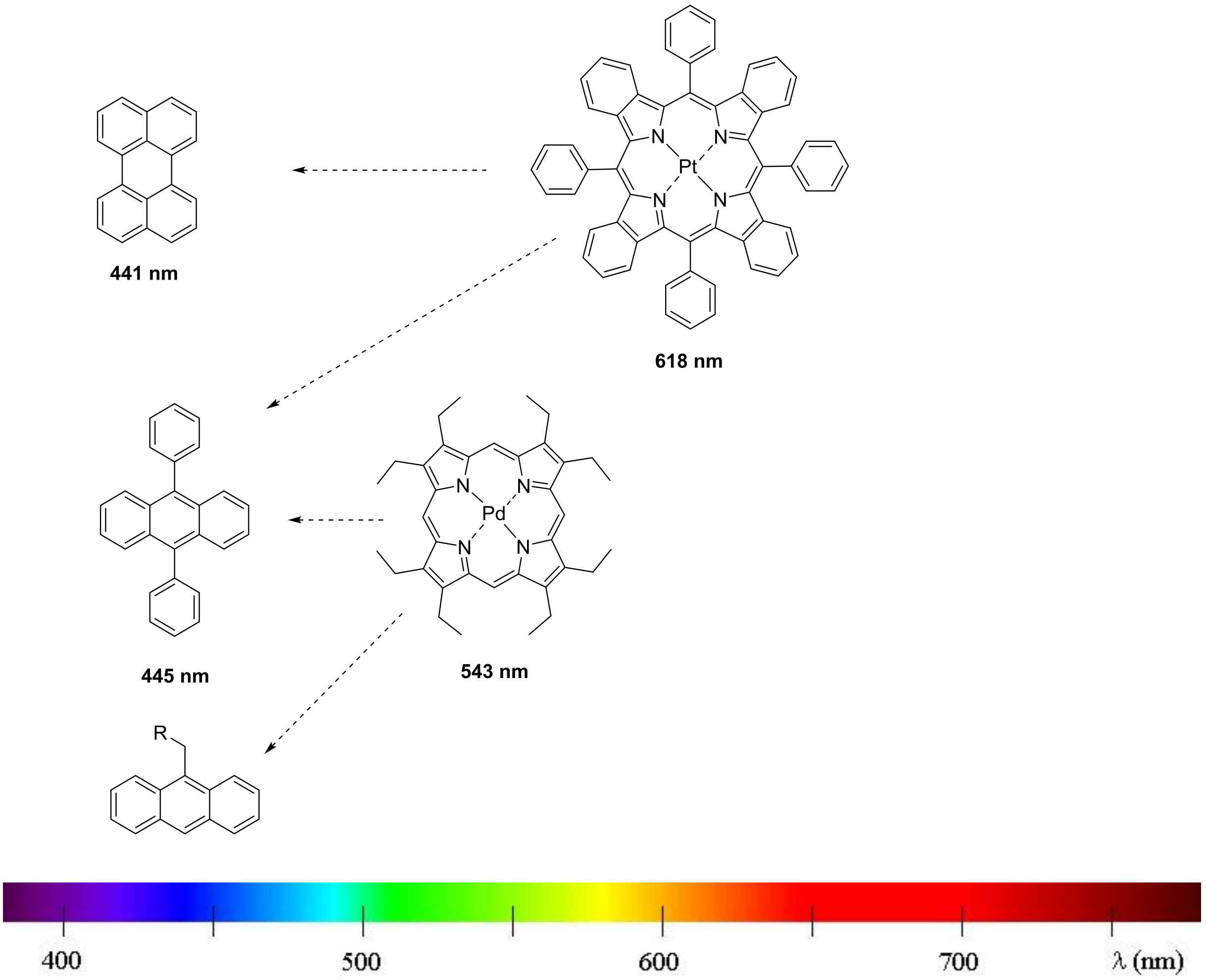


Figure 3. Overview of TTA-UC emitters and sensitizer typically used in polymeric systems.[2,3,8–10]

1.2 TTA-UC in polymers

Very recently, about 10 years ago, TTA-UC was reported in polymeric systems for the first time.[8] There is a growing interest in those systems because the limitations of a liquid system can be overcome and new applications are possible. Potential applications are high-resolution optical microscopy, drug delivery, oxygen sensing and conversion layers for solar harvesting .[1]

The most common way is to blend the sensitizer and the emitter into a polymer matrix. The chromophores are molecularly dissolved in a photophysical inert polymer. As mentioned above the concentration and the mobility of sensitizer and emitter must be high enough so electronic interaction can take place. The solubility of the chromophores in polymers is often limited. If the concentration is above the solubility limit, even under equilibrium conditions phase separation and aggregation appear.[1] The TTA-UC intensity is highly depended on temperature and the glass transition temperature (T_G) of the matrix polymer. The intensity decreases abruptly at temperatures below the T_G.[11] It was suggested that the concentration of the emitter should be maximal to decrease the intermolecular distance and to enable the energy transfer.[8] Different approaches were published for the preparation of polymeric TTA-UC systems and homogenous blends with dye loadings up to 20wt% are possiple.[10] Very recently the group of C. Weder and Y. Simon[3] and the Xinjun Yu *et al.*[12] reported systems with a covalently tethered emitter and the sensitizer was molecularly dissolved. Both groups used chromophore systems with anthracene derivatives as the emitter and PdOEP or PdOEP as the sensitizer (Figure 4). If the chromophores are covalently bound, phase separation and aggregation do not appear and even higher dye concentrations are possible. Especially Xinjun Yu *et al.*[12] studied systematically the effect of the inter-chromophore distances and they observed a sharp maximum of the TTA-UC efficiency as a function of the emitter concentration and the inter-chromophore distance. Interestingly the TTA-UC emission intensity was the highest at moderate concentration (<10 wt% emitter) and drastically decreases at higher dye content.[12] This was in line with the work of the group of C. Weder and Y. Simon. They also could show that with increasing sensitizer concentration (Pd-oktaethyporphyrin) the TTA-UC emission decreases.[3,10]

In summer 2015 the group of C. Weder and Y. Simon reported a systematic study on the composition for statistic copolymers of sensitizer, emitter and a comonomer.[8] More details to the chromophore system is give in Figure 4.

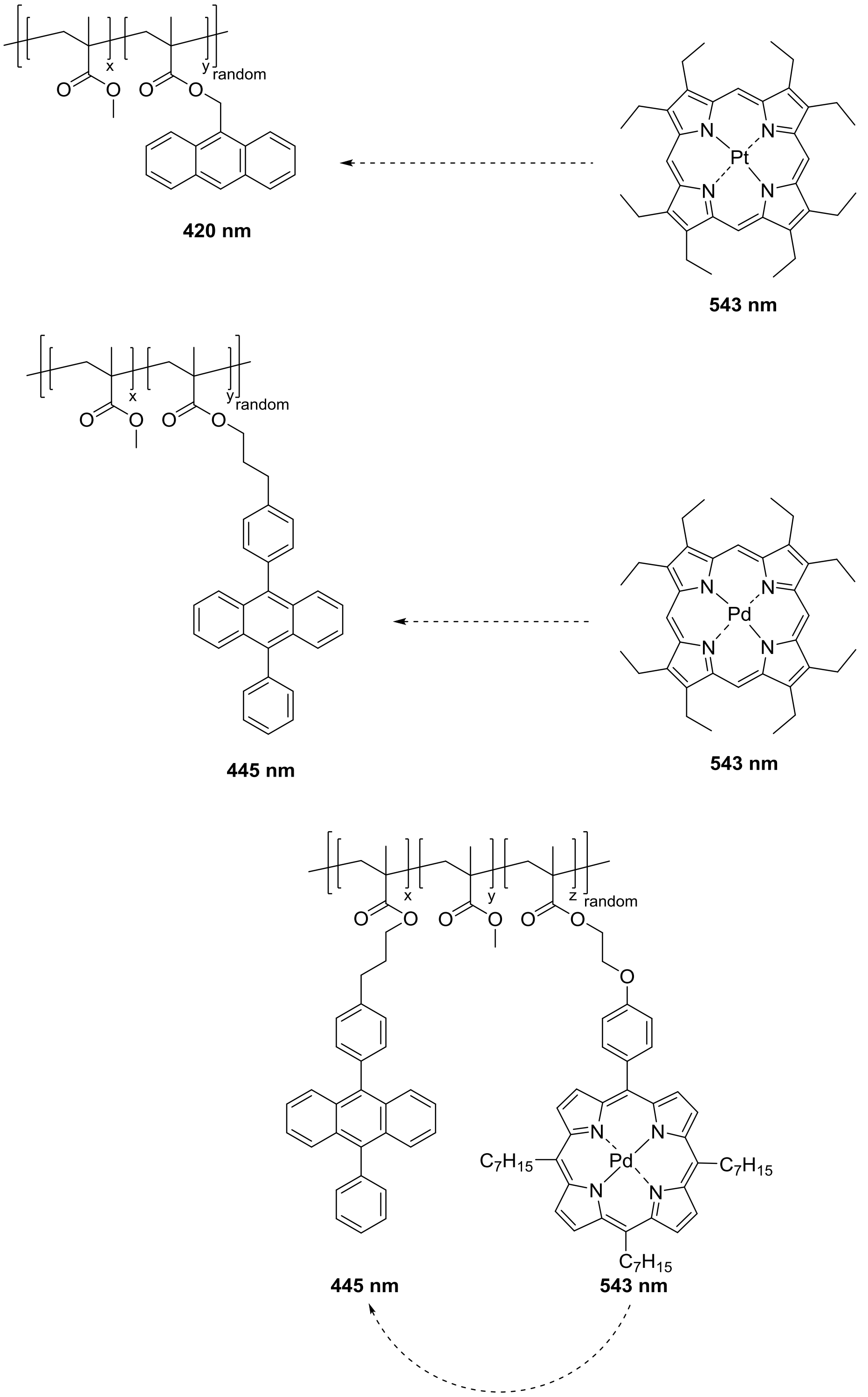


Figure 4. Chromophore systems with covalently attached emitters or sensitizers.[3,8,12]

1.3 Perylene diimide

Perylene-3,4,9,10-tetracarboxylic dianhydride (**PTCDA**), also referred to Pigment Red 224, is well known since the 1910s. Near-unity fluorescence, high photo stability and at strong electron-accepting character make them qualified as a commercially available starting material for large number of optical and electrochemical applications. **PTCDA** is insoluble in most common organic solvents.[13]

In general there are two ways to increase the solubility: Substitution in the bay (position 1,6,7 and 12, Figure 5) or the insertion of a steric demanding imide substituent. If the bay is modified even small substituents, such as chlorine or bromine, the structure of the perlyene scaffold is twisted and the electrical and optical properties are also changed. In contrast to that the imide substituents have hardly any effect on these properties but they affect the solubility and aggregation. In both cases the solubility is enhanced because the face-to-face π – π stacking of the molecules is hindered.[13]

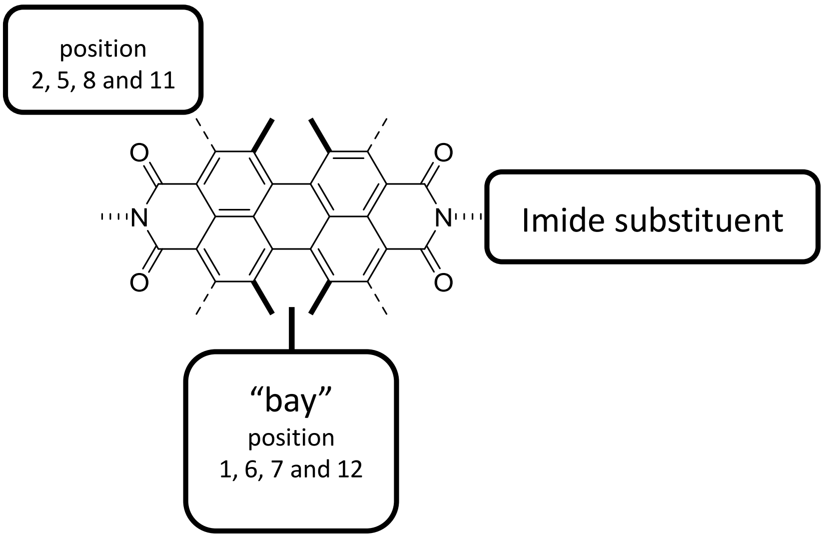


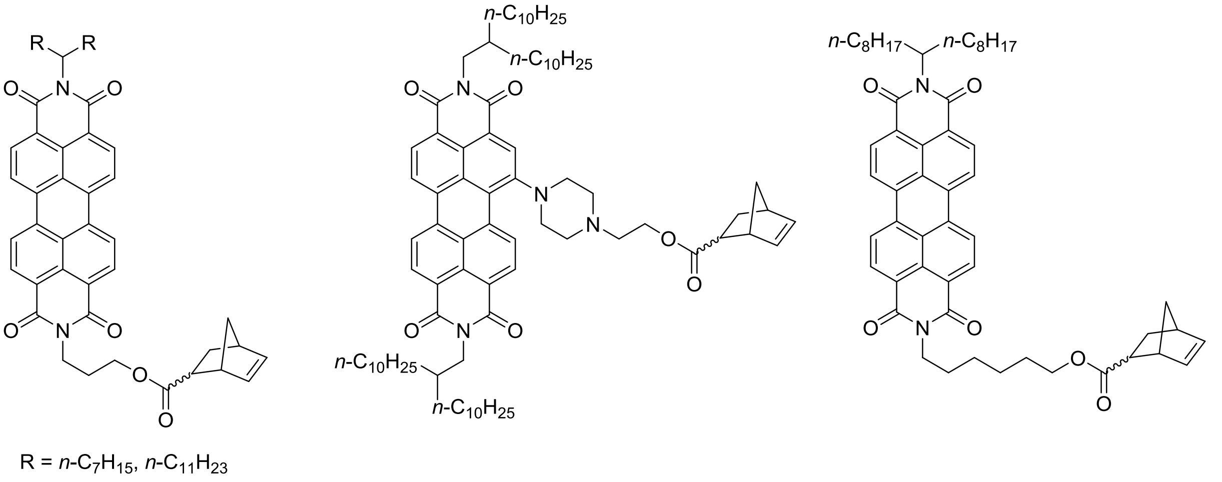
Figure 5. Chemical stucture of PDi and the typical positions for substitution.[13]

Perylene and in particular the perylene-3,4,9,10-tetracarboxylic acid diimide derivatives (**PDi**) are extensively present in research and an enormous variety of structures have been published. The diimide derivatives (**PDi**) are used in multiple optical and electrical applications. The specific physical, optical and electronic properties, especially the ability for reversible reduction make them interesting for applications such as organic field-effect transistors, photovoltaic cells, fluorescent solar collectors, dye lasers, optical power limiters and electrophotographic devices.[13,14]

1.3.1 Perylene diimide covalently bound in ROMP polymers

For these purposes **PDi** was incorporated into the main-chain and also into the side-chain. The morphological stability is potentially higher in polymers and the processing methodologies are better suited for high-throughput fabrication than small molecules.[14] Different approaches were used to include **PDi** into the polymer. On the one hand fully conjugated polymers were synthesized where the perlyene cores were bridged by other π-conjugated units *via* the bay-position or the imide groups.[14–17] On the other hand the **PDi** was bound in the side-chain.[18]

PDi-functionalized polymers based on ring opening metathesis polymerization (ROMP) are a rather new field of research only a few approaches have been published so far. Chun Huang *et al.*[19] reported polynorbornes homopolymers with pendant perylene diimides for organic electronic applications in 2012. The norbornene unit was linkt to the **PDi** either through the imide (**A1**) or the bay-position (**A2**). The structures are given in Figure 6. Linear polymers were synthesized *via* ROMP and the polymers had differed properties. The polymers **A1** showed in solution and in solid state significant aggregation and π-stacking of **PDi** in UV-Vis and powder X-Ray diffraction. These polymers had a weak field-effect transistor behavior. In contrast to that no π-stacking was observed in the polymer **A2,** no field-effect transistor behavior was measured and the UV-Vis spectra in solution and in thin films were monomer-like. **A1** and **A2** were applied in combination with P3HT (poly(3-hexylthiophene) in bulk heterojunction solar cells and power conversion efficiencies up to 0.38% were obtained.[19]

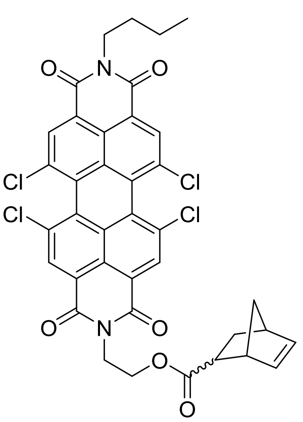


A1 **A2** **A3**

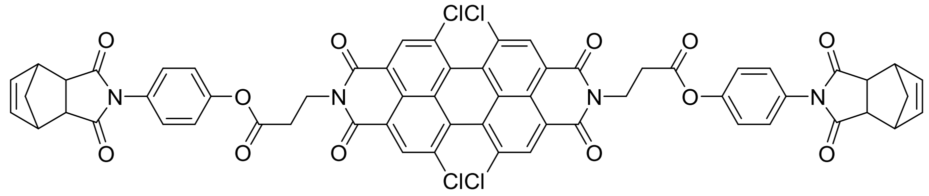
Figure 6. Norbornene-functionalized perylene diimide derivatives for ROMP homopolymers.[19,20]

Glaz *et al.*[20] studied the self-assembly and aggregation of polynorbornenes containing **PDi** as pendant groups (**A3**, Figure 6) dependent on the solvent. They monitored the photophysical properties of that polymer in solution and in thin films. If the polymer backbone is well dissolved, the chromopheres self-assemble into characteristic H-type aggregates (sandwich-like stacking, the absorption spectra is shifted to higher wavelengths – hypsochromic shift)[21,22] and align along the polymer backbone.[20] In contrast a poorly dissolved polymer backbone leads to a collapse into a coiled conformation and the aggregation is hindered and the polymer shows monomer-like photophysics. Thin films of these polymers show similar photophysical properties compared to the fully solvated polymers. Hence the same aggregation of the chromophores appear in those two different systems.[20]

Gallas *et al.*[23] described a modular synthetic approach for optochemical sensors *via* ROMP. The norbornene-functionalized **PDi** (**A4**, Figure 7) was statistically copolymerized with oligo(ethylenglycol)-functionalized norbornenes to ensure water solubility and tertiary-amine or tetramethylpiperidine-1-oxyl bearing monomers in order to allow the detection of pH or ascorbic acid in water. Based on the living character of ROMP also block copolymers were synthesized with the aim to bring the chromophore and the sensing moieties in close proximity to ensure a short distance between the sensing moieties and the fluorophores for efficient photoinduced electron transfer (PET). The fluorescence of the **PDi** is quenched by photoinduced electron transfer (PET) from moieties with free electron pairs. So the polymers with the amine acts as pH probes while the polymers with the tetramethylpiperidine-1-oxyl units can detect radical species, such as ascorbic acid, by recombination.[23,24] The same 1,6,7,12-tetra-chloro perylene scaffold was used by Wei Song *et al.*[25] The **PDi** was functionalized at both imide units with norbornene moieties (**A5**, Figure 7). The polymer was amorphous and showed ladder-like self-assembly behavior. The perylene moieties were aligned between the two polynorborne strands but they did not show π-stacking.[25]



A4

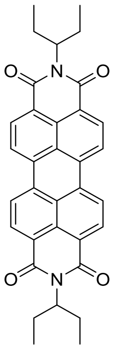


A5

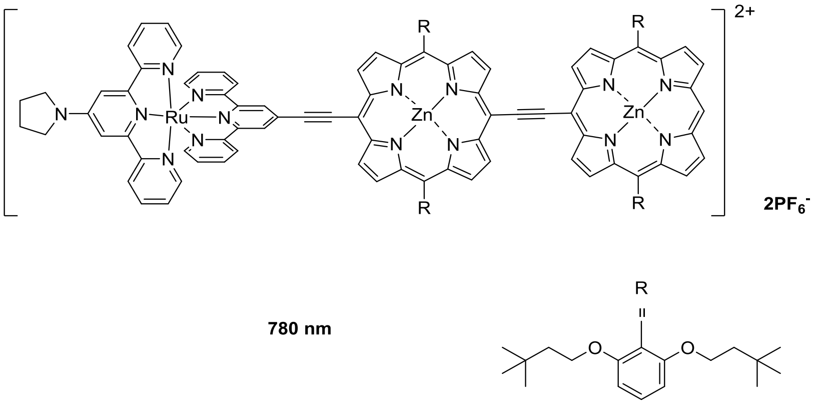
Figure 7. 1,6,7,12-tetrachloroperylene-3:9,10-bis(dicarboximide) derivatives for fluorescent pH and ascorbic acid sensors (A4) and for ladder-like self-assembling ROMP polymers (A5).[23,25]

1.3.2 Perylene diimide – as emitter for TTA-UC

The derivatives of perylene-3,4,9,10-tetracarboxylicdiimide (**PDi**) are very promising emitter chromophores for near-infrared (NIR) TTA-UC systems. In comparison to the ordinary perylene the first excited triplet state of **PDi** (^{3}**PDi*** = 1.15 – 1.2 eV) is 0.3 eV lower than that of the perylene (^{3}perylene* = 1.53 eV). For efficient TTA-UC the energy of the excited triplet state of the emitter (^{3}E*) must be close to that of the triplet state of the sensitizer (^{3}S*). Sensitizers which were excited in the NIR have usually a lower triplet state. **PDi** has similar energy levels as the higher acene homologenes but **PDi** has a better photo stability and near-unity fluorescence.[1,26,27]



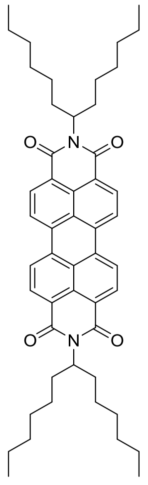
541 nm



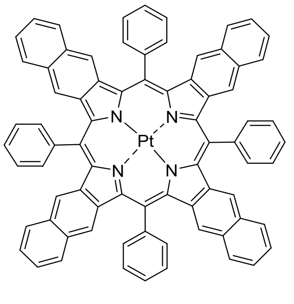
780 nm

Figure 8. The supermoleculare sensitizer complex was excited with laser light at 780 nm, the maximum of the TTA-UC emission was at 541 nm.[27]

PDi was used in a TTA-UC chromophore system by Singh-Rachford *et al.*[27] for the first time in 2010. *N*,*N*-bis(ethylpropyl)perylene-3,4,9,10-tetracarboxylicdiimide was combined with a conjugated supermoleculare sensitizer complex (Figure 8). A solution of sensitizer and emitter was excited with laser light (780 nm) and gave TTA-UC emission at 541 nm. The TTA process was confirmed and the first studies on the kinetics of TTA process involving ^{3}PDi* was done. The maximum quantum yield of upconverted emission was Φ_{UC} = 0.75 ± 0.02%.[27]



580 nm



690 nm

Figure 9. Structures of TTA-UC chromophore combination. The sensitizer Pt-tetraphenyltetranaphthol[2,3]porphyrin was excited at 690 nm and the emission maximum was at 580 nm.[28]

Fan Deng *et al.*[28] reported a Pt-tetraphenyltetranaphtho[2,3]porphyrin sensitizer coupled with perylene diimide as the emitter. The structures are given in Figure 9. They displayed TTA-UC in solution with a maximum quantum yield of $\Phi_{UC} = 6.0 \pm 0.5\%$. The excitation wavelength was 690 nm and the maximum of the emission was at 580 nm. With this system a remarkable photostability was obtained. In contrast to a Pt-tetraphenyltetranaphtho[2,3]porphyrin – rubrene system exibits a slightly higher upconversion efficiency but it was not long-term-stable.[28]

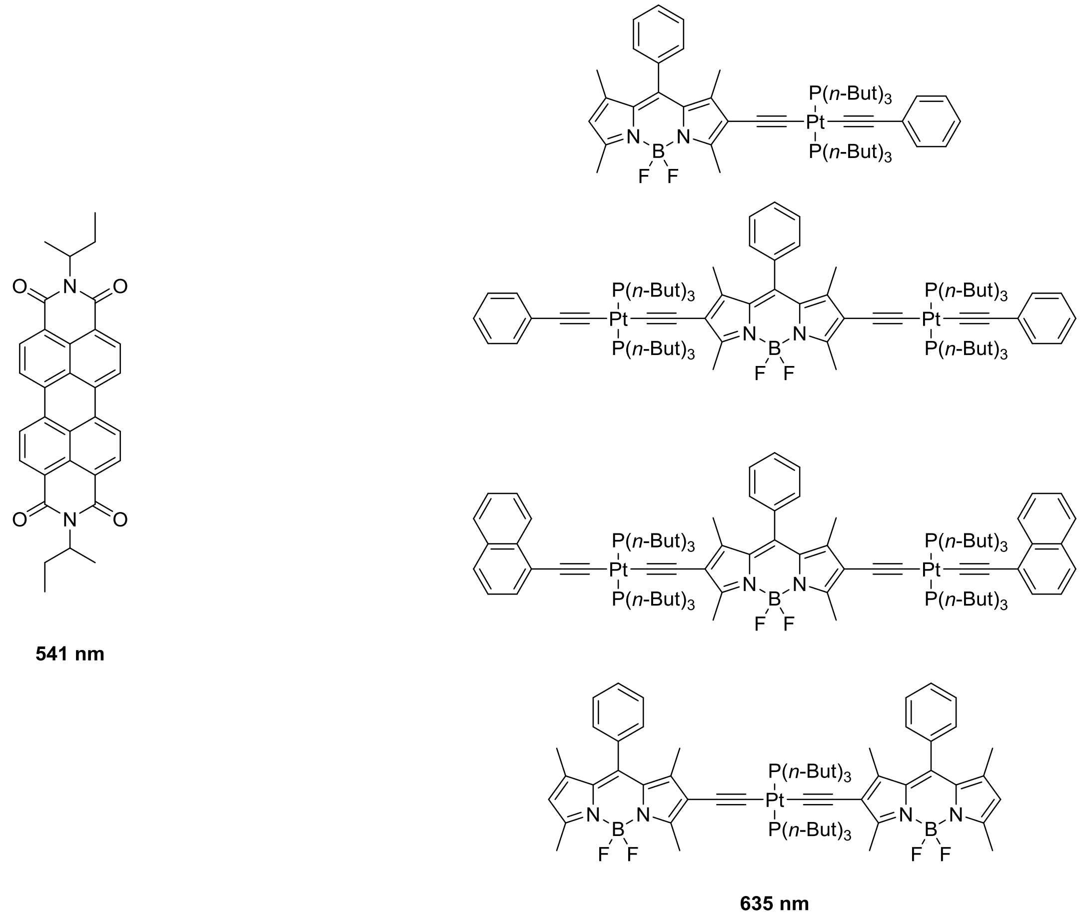
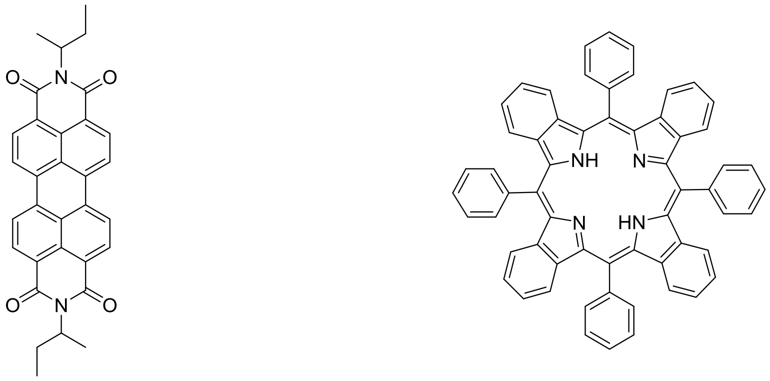


Figure 10. Red-light absorbing (excitation wavelength: 635 nm) TTA-UC photo sensitizers with light-harvesting antennas.[29]

Wanhua Wu *et al.*[29] developed a whole set of sensitizers for TTA-UC. This Pt(II)-bis(aryleneethynylene) bis(trialkylphosphine) complexes had light-harvesting antennae attached to the Pt(II) centers and absorb strongly in the range of 570 – 603 nm (Figure 10). The complexes were excitable with red-light and in conbination with perylene or **PDi** TTA-UC emission was observed. **PDi** was betters suited for the red-shifted complexes with two Pt(II) centers than perylene. The maximum quantum yield in solution was $\Phi_{UC} = 7.1\%$.[29]

In the later works all the sensitizers which were combined with **PDi** contained a rare heavy metal atom such as Pd- or Pt. Xiaoneg Cui *et al.*[30] demonstrated TTA-UC was also possible with the free base tetraphenyltertrabenzoporphyrin (H_2TPTBP) in combination with **PDi** (Figure 11), although the maximum quantum yield of upconverted emission was only Φ_{UC} = 0.08%.[30]



541 nm **654 nm**

Figure 11. Structure of H_2TPTBP as the sensitizer and PDi as the emitter. The excitation wavelength was 654 nm.[30]

1.4 Porphyrin – as sensitizer for TTA-UC

Porphyrin is one of the most extensively studied off all known macrocyclic ring systems.[31] The structure is formed by a tetrapyrrolic macrocycle and occurs naturally i.e. in the plant photosynthetic system or in the protein complex of hemoglobin. Porphyrin has multiple biological functions and it is a attractive metal-complexing ligand. It has a rigid and planar geometry with inherent symmetry and a high tolerance for temperature and pH variation. Further properties are among others: easily tunable electronic and redox properties and outstanding photosensitization.[31,32]

Porphyrins are interesting sensitizers for the TTA-UC because of their photophysical properties. Porphyrin has usually a strong molar absorption in the visible and NIR region of the spectra. The absorption spectra has complex structure. The spectra can be divided into two sections: the high-energy Soret-band and the low-energy Q-band. The Q-band is normally excited for TTA-UC but this band is in the most cases very defined. Porphyrin complexes containing heavy-metals such as Pd or Pt are highly effective triplet generators because of the heavy-atom promoted spin-orbit coupling.[9]

Porphyrin is a well-established sensitizer in differed TTA-UC chromophore systems in solution and in polymers.[9,33] The most common sensitizers to study polymer-based TTA-UC are Pd- or Pt-porphyrin such as Pd-octaethylporphyrin (PdOEP) or Pt-octaethylporphyrin (PTOEP) and Pd-tetraphenyltetrabenzoporphyrin (PdTPTBP) or Pt-tetraphenyltetrabenzoporphyrin (PtTpTBP) (Figure 3). Many systematic studies were performed on these systems in order to understand the underlying TTA-UC process in polymers. Usually in all these works the sensitizer was molecularly dissolved in a polymer matrix. In summer 2015 the group of C. Weder and Y. Simon reported a covalently bound porphyin in that context for the first time.[8,9]

Myles *et al.*[34] reported random copolymers of photochromic phenoxynaphthacenequinone and *meso*-tetraphenylporphyrin (H_2TPP) bearing ROMP polymers with photoswitchable luminescence. Photochromic phenoxynaphthacenequinone can change reversibly between two isomers (Figure 12. **B1a** and **B2b**) by irritation with UV-Vis light. The state **B1a** is a better electron acceptor and quenches the fluorescence of H_2TPP.[24,34]

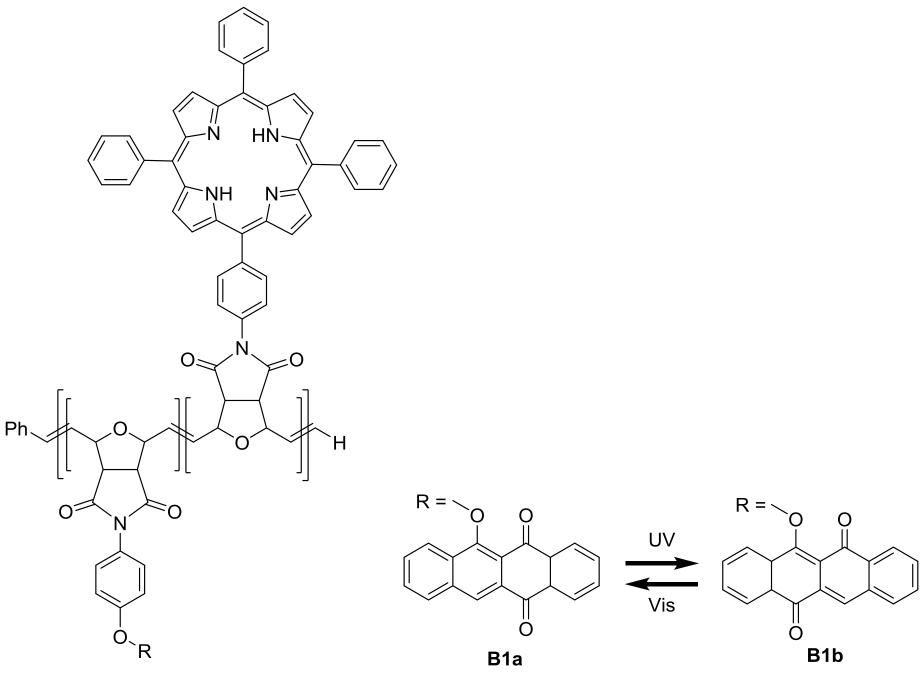
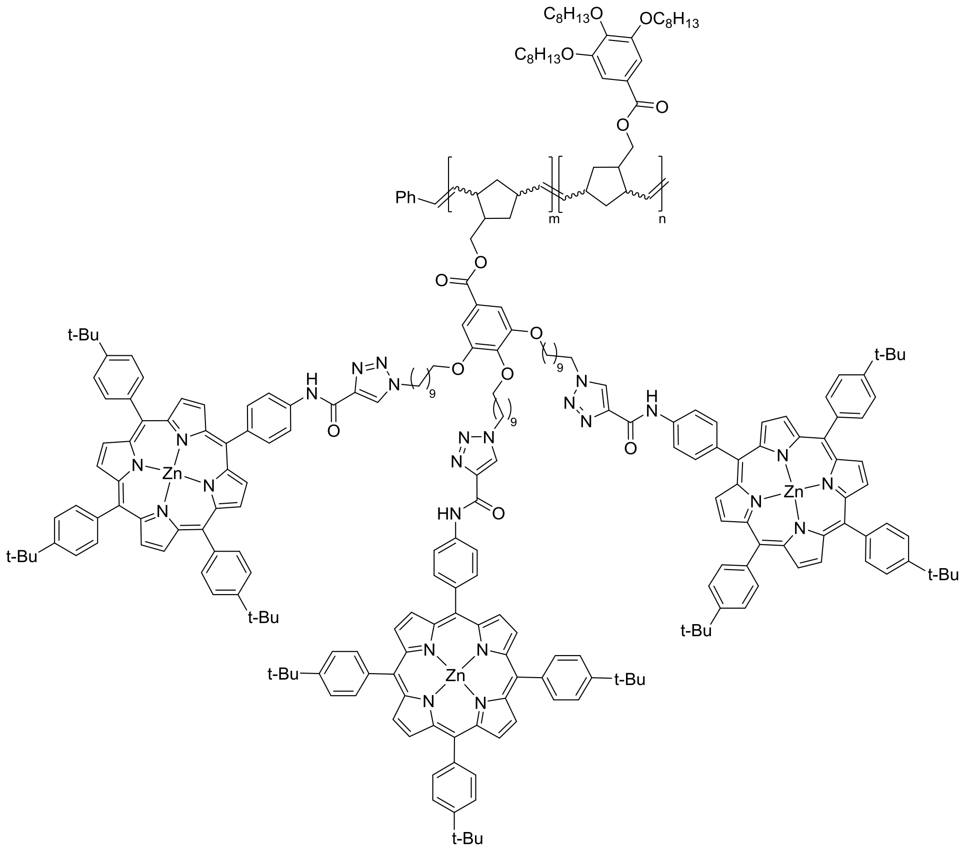


Figure 12. Photoswitchable fluorescent ROMP-polymer, B1a quenches the luminescence while B1b does not.[34]

Fiset and Morin[35] synthesized dendronized diblock copolymers by ROMP and functionalized one block after the polymerization with Zn-*meso*-tetrametylphenylporphyrin using copper-catalized “click chemistry” (Figure 13). Fullerene-functionalized diblock copolymers were synthesized in a similar way. These polymers were used as polymeric accepter-donor materials for photovoltaic applications.[35]



B2

Figure 13. Polyborbornene diblock copolymer B2 was functionalized after the polymerization with Zn-meso-tetrametylphenylporphyrin using copper-catalized "click chemistry". [35]

Hsien-Wen Wang *et al.*[36] studied supramolecular porpyhrin-arrays in single- and double-stranded polynorbornes (Figure 14. **B3** and **B4**). Between the Zn-porphyrin was DABCO (1,4-diazabicyclo[2.2.2]octane) coordinated. The porphyrin was functionalized with either one or two opposing monomers. In the polymers were the Zn-porphyrin aligned along the polymer backbone and DABCO coordinated in between.[36] Nai-Ti Lin *et al.*[37] demonstrated later with **B3** that there was no need of DABCO for orientation. The orientation of the chromophores was related to the stiffness of the polymeric backbone. In polynorbornenes this depends on the rate of Z-bonds.[37]

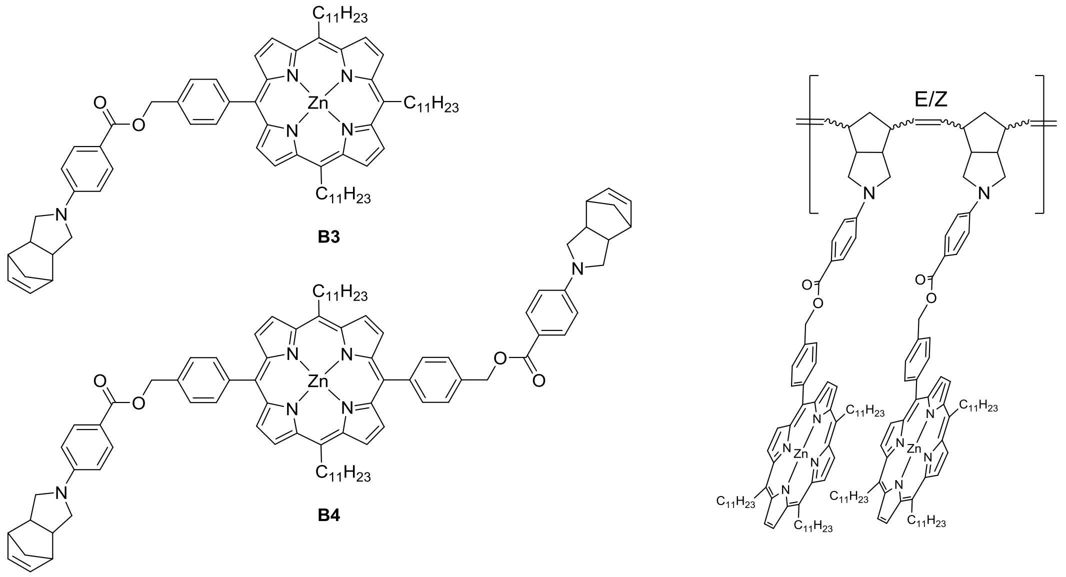
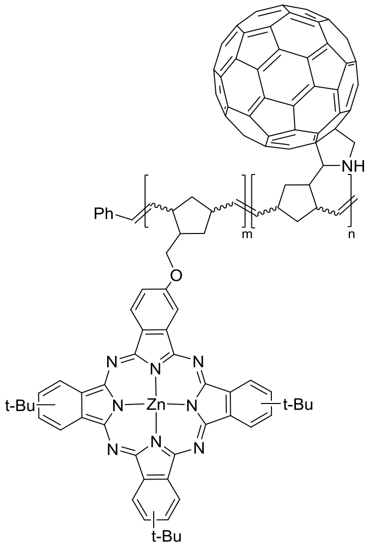
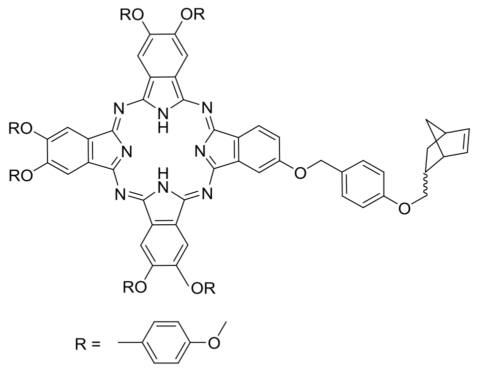


Figure 14. Zn-porphyrin functionalized with either one or two opposing monomers for single- and double-stranded polynorbornes (B3 and B4). The degree of orientation is related to percentage of Z-bounds.[36,37]

Phthalocyanine has a related structure (Figure 15) and they are also a promising sensitizer for TTA-UC. De la Escosura *et al*.[38] synthesized polynorbornene random copolymers **B5** with pendant phthalocyanine and C_{60} fullerene moieties for photovoltaic applications. The system had enhanced fluorescence quenching abilities in comparison to blend systems but only moderate conversion efficiencies were achieved.[24,38] A similar norbornene functionalized phthalocyanine **B6** was reported by the group of McGrath. The polymer was used for ROMP-capture-release synthesis of asymmetric porphyrazines and was a method for the isolation of asymmetric products without chromatographic purification. For that reason the chromophore was cleaved of in acidic conditions after the polymerization.[39]



B5



B6

Figure 15. Random polynorbornene copolymers with pendant phthalocyanine and C_{60} fullerene moieties for photovoltaic applications (B5). Norbornene-functionalized phthalocyanine for the ROMP-capture-release method of asymmetric porphyrazines (B6).[38,39]

2 Discussion and results

2.1 Aim and scope of the thesis

The aim of this master thesis is to synthesize an appropriate combination of polymerizable sensitizer and emitter chromophores with norbornene ester side groups and to statistically copolymerize sensitizer and emitter with various monomers *via* ring-opening metathesis polymerization (ROMP) to give defined polymers, which show photon upconversion *via* sensitized triplet triplet annihilation (TTA-UC) in solution and in thin films as well. Since about ten years this effect is knowen also to occur in polymers. Hence a new field of applications is possible by overcoming the limitations of liquid solutions. In many cases the solubility of the chromophores, phase separation and aggregation are limiting for homogeneous and stable layers.[1] These problems can be solved by integrating these species covalently into the polymeric structure. Nevertheless the typical efficiency of TTA-UC is much lower in polymers than in liquid solutions because of the reduced mobility of the chromophores.[1] By the beginning of this master thesis (December 2014), statistic copolymers of sensitizer, emitter and a comonomer has not been reported yet. Generally there are only very few groups working on covalently bound TTA-UC chromophores. A key figure is the group of Weder and Simon.[3,8–11]

The chromophores should be functionalized with norbornene ester side groups. Norbornene and ROMP are preferred due to their straightforward synthetic availability and and excellent film-forming behaviour and is also competible to a wide range of functional groups.[40] The living character of ROMP makes multiple polymer architectures possible.

Another important topic was to optimise the concentration and distribution of sensitizer, emitter and comonomer in order to increase TTA-UC efficiency. To make the transition from a liquid system to thin films the following combinations were investigated:

- sensitizer and emitter in liquid solution
- either sensitizer or emitter covalently bound to the polymer and in solution
- either sensitizer or emitter covalently bound to the polymer but in thin film
- sensitizer and emitter covalently bound to the polymer and in solution
- sensitizer and emitter covalently bound to the polymer and in thin film.

Perylendiimide derivates were introduced as emitter and benzoporhyrine as sensitizer. Similar combination were reported and show overall efficiencies up to 7 % and remarkable photostability.[28]

2.2 Perylene as an emitter dye

Starting from **PTCDA** (perylene-3,4,9,10-tetracarboxylic dianhydride) two different groups of perylene derivates with norbornene ester side groups were synthesized (Figure 16). On the one hand a steric demanding imide substituent was inserted to increase the solubility (**4**). Substituents at these positions showed hardly any differences in the absorption and emission spectra but synthesis of asymmetric derivates is more complex. On the other hand the bay (position 1,6,7 and 12) was substituted with chlorine (**9**, **11)**. This forced the perylene to a twisted structure and also to a change in the optical and electronic properties.

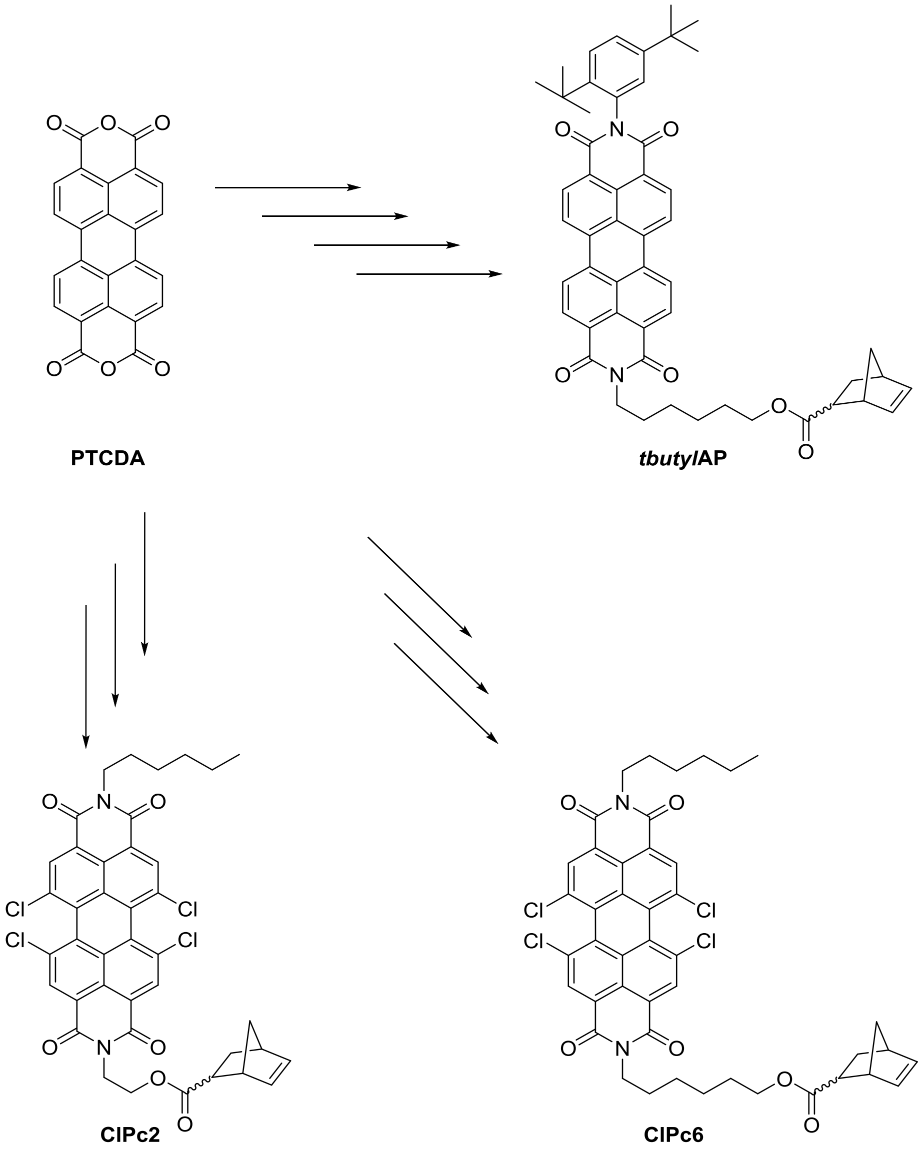


Figure 16. Overview of the norbornene-functionalized perylene derivatives.

2.2.1 ***tbutyl*AP**

Asymmetrical perylene diimide with a steric demanding imide substituent could not be obtained *via* straightforward synthesis, see Figure 17. First experiments, according to the general reaction procedure with imidazole as solvent and $Zn(OAc)_2$ as catalyst, showed that, simultaneous addition of ethanolamine and 2,5-*tert*-butylaniline just as simultaneous addition of hexylamine and ethanolamine did not lead to statistically distributed products. Based on the different reactivity of the amines, the dominant species were the symmetrical products. This was in line with the literature.[41] Another set of first experiments was to obtain perylene monoanhydride monoimide directly from **PTCDA.** The primary aimine was 2,5-*tert*-butylaniline. Even if 2,5-*tert*-butylaniline was limiting and the asymmetric product was expected, the diimide was favored, probable because of the increasing solubility by imidization associated with an increasing reactivity.

Tröster *et al*.[42] suggested a smart procedure to synthesize **2**. **PTCDA** was dissolved in an aqueous solution of KOH. The solution was acidified and **1** was precipitated below pH 5. At very low pH also **PTCDA** is formed again. Langhals[43] *et al*. optimized the synthesis by using acetic acid for precipitating **1**. This simplifies finding the right pH range for precipitation. According to Pasaogullari[44] *et al*. also H_3PO_4 can be used and a similar yield was obtained. Finally **1** is condensed with aqueous ammonia to **2**. The substances **1** and **2** were insoluble in all common organic solvents so the product was characterized with ATR-FTIR spectroscopy. This limitation made it difficult to monitor the reaction progress and to purify the products.

The condensation of **2** with 2,5-*tert*-butylaniline was done with molten imidazole as solvent and $Zn(OAc)_2$ as catalyst. The yield could be enhanced by rising the temperature to 180 °C and the reaction time to 8 hours. In a set of first experiments it was tried to condense 2,5-*tert*-butylaniline directly with **1** but no reaction was observed.

4 was received *via* Diels-Alder reaction of cyclopentadiene and acryloyl chloride in dry DCM and subsequent esterification with 5-bromohexanol *via* the Einhorn modification of the Schotten-Baumann reaction. ***tbutyl*AP** was synthesized *via* a S_N2 reaction of **3** and **4** in DMF in slightly basic conditions. DMF seemed to be an ideal solvent for this kind of reaction, but also made purification and drying difficult. Moving to another polar aprotic solvent may simplifies the workup.

In future condensing **1** with a primary amine like ethanolamine or 6-aminohexanol in aqueous solution may reduce the amount of steps and increase the overall yield. Usually it is not possible to insert a steric demanding imide substituent under these conditions.[43] The imide will be inserted afterwards according to the general procedure followed by the coupling with the monomer group.

The absorption spectra showed the typical structure of perylene diimide (Figure 18): three maxima at 458 nm, 488 nm and 525 nm with increasing absorption coefficients. The emission spectra, excited at 460 nm, showed three peaks with maxima at 538 nm, 578 nm and 625 nm with decreasing intensity.The Stokes shift was with 13 nm relatively small. All spectra were recorded in DCM.

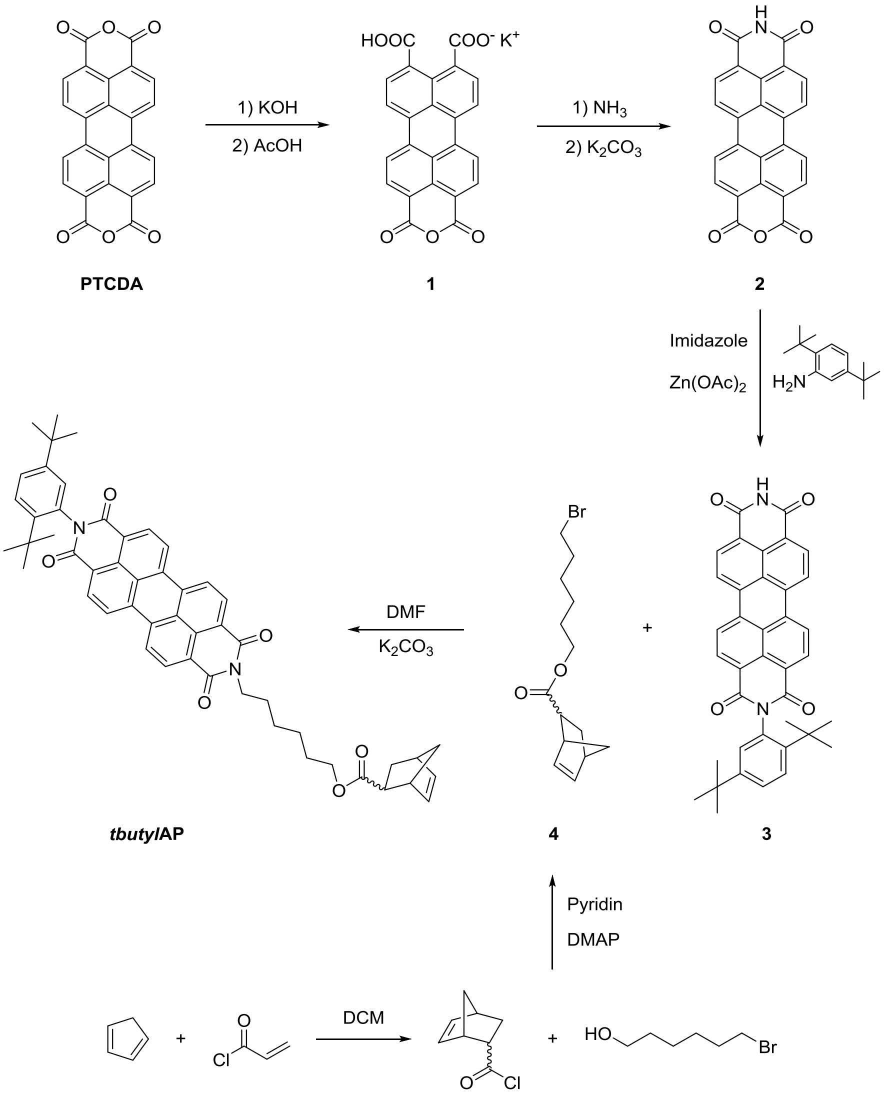


Figure 17. Reaction scheme for the synthesis of *tbutyl*AP.

2.2.2 ClPc2 and ClPc6

The reaction of **PTCDA**, chlorosulfuric acid and iodine leaded to **7**.[45] The overview on the reaction is given in Figure 19. At the positions 1, 6, 7 and 12 chlorine was introduced. Even these rather small substituents like chlorine increase the solubility drastically. They lead to a twisted structure and so face-to-face $\pi - \pi$ stacking is prevented. [13] High yields of **7** and a pure product was obtained. The crude product was used without any further purification steps. **7** was dissolved in THF and the equimolar amount of hexylamine and ethanolamine or hexylamine and 6-aminohexanol was added at once.[23] The products were isolated *via* column chromatography. The separation was straightforward, because all species had different polarities. All these aliphatic primary amines showed similar reactivity and the two symmetric imides and the asymmetric imide (**8** and **10**) were equally distributed. To increase the ratio of **8** one equivalent of each amine was added one after the other but it was not possible to overcome the statistical distribution of the products **8** and **10** and showed reasonable solubility in organic solvents. The solubility of **8** was expectably a bit lower. **11** was synthesized *via* a Diels-Alder reaction of freshly distilled cyclopentadiene and acryloyl chloride in dry DCM and was subsequently used to receive **ClPc2** and **ClPc6** *via* the Einhorn modification of the Schotten-Baumann reaction. The ^{1}H-NMR spectrum were in line with the literature.[23] The products were bright orange powders.

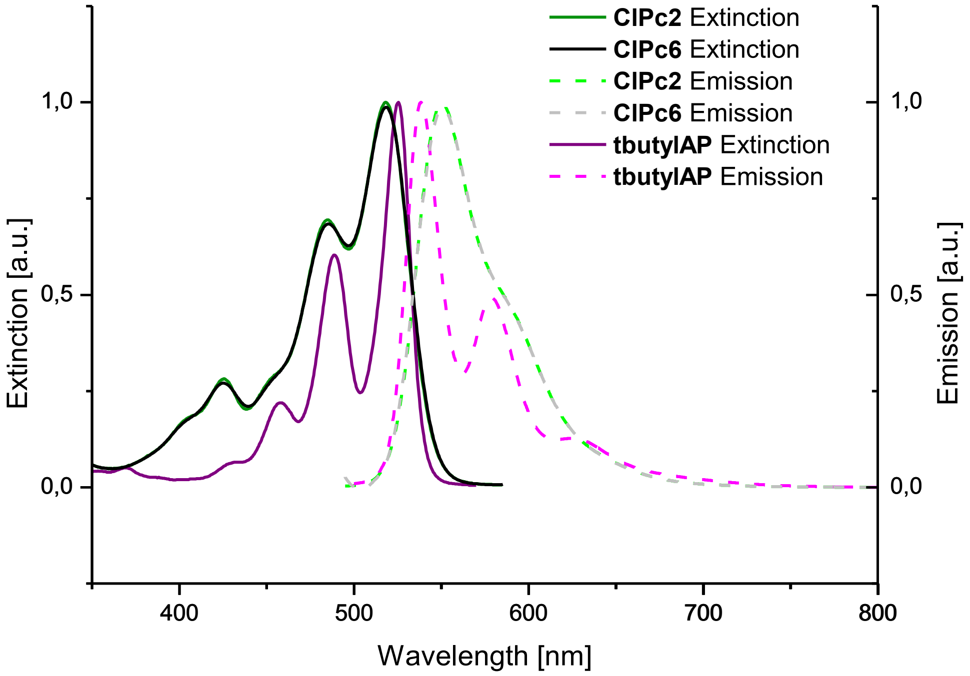


Figure 18. UV-Vis spectroscopy of the polymers ClPc2, ClPc6 and *tbutyl*AP dissolved in DCM. ClPc2 and ClPc6 were excited at 425 nm and *tbutyl*AP was excited at 457 nm.

The absorption spectra and the emission spectra of **ClPc2** and **ClPc6** showed hardly any difference (Figure 18). The absorption spectra showed the three maxima at 426 nm, 484 nm and 518 nm with increasing absorption coefficients. In comparison to ***tbutyl*AP** the maxima are shifted to lower wavelengths. Especially the first peak at 426 nm was shifted 32 nm offset the maximum. The emission spectra, excited at 425 nm, showed one, rather broad peak with maximum at 550 nm and a shoulder around 584 nm. The Stokes shift was 32 nm. All spectra were recorded in DCM.

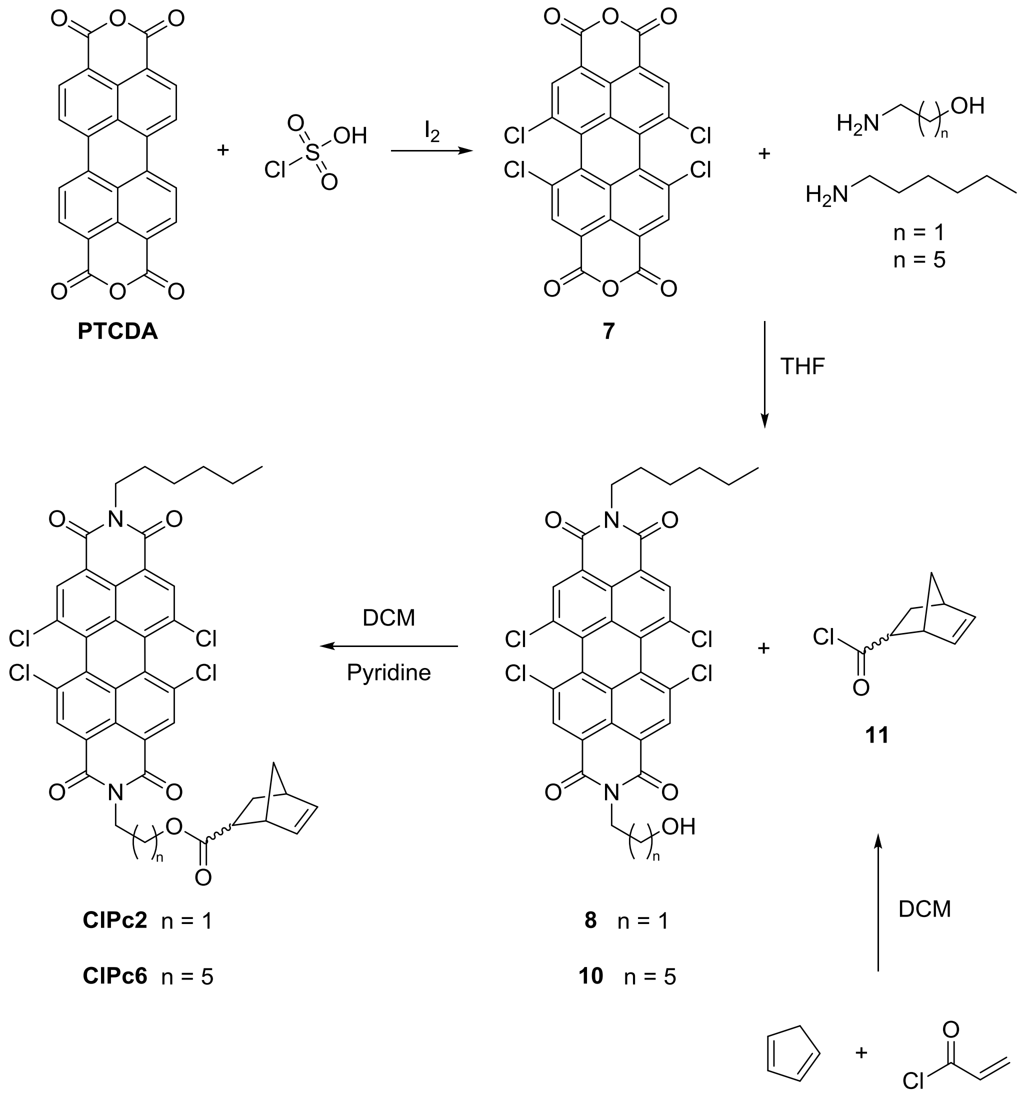


Figure 19. Reaction scheme for the synthesis of ClPc2 and ClPc6.

2.3 Pt-Tetraphenyltetrabenzo-*tert*-butyl-porphyrin (PtTPTB*tbut*P) as a sensitizer

TPTB*tbut*PBr was synthesized according to the template method introduced by Hutter *et al.*[46] This method usually gives higher yields at lower reaction temperature than comparable approaches with phthalimide instead of phthalonitrile.[46,47] All these starting material are commercially available and have a reasonable price. Another well-established procedure is the Lindsey method[48,49], which gives good yields and pure products but the starting materials are not commercially available and the synthesis of them is a multi-step reaction. The template method was the favored synthetic pathway because of its relative cost efficiency and in-house experience. In this procedure phenylacetic acid, zinc-di(2-(4-bromophenyl)acetat and 4-*tert*-butylphthalonitrile were condensed at 280 °C and **16** was obtained (Figure 20). The purification of the product was challenging but Hutter *et al.* developed a sophisticated procedure, a combination of precipitation and column chromatography, for the product isolation. Only small changes were needed to consider the reduced polarity because of the *tert*-butyl groups. This method leaded to a mixture of products with different degree of bromo-substitution. The products were too similar in polarity for column chromatography separation at this stage. *Tert*-butyl groups were introduced *via* 4-*tert*-butylphthalonitrile to the porpyhrin to increase the solubility. Due to the mono-functionalized dicyanobenzene several different isomers were formed but no difference in their properties could be observed. All the porphyrins were highly soluble in DCM and acetone. In comparisons to the non-functionalized benzoporphyrins reported in literature[46] they showed slightly more hydrophobic properties in thin layer chromatography and column chromatography. The central Zn-atom of **16** was removed in strong acid conditions and after washing with aqueous $NaHCO_3$ solution to deprotonate the formed intermediate H_4TPTB*tbut*PBr^{2+} the free ligand **17** was isolated. ZnTPTBP and the free ligand H_2TPTBP were not appropriate TTA sensitizers in combination with perylene diimide derivates. TTA-UC was measured with these combinations but these investigations were done in solution and the upconversion quantum yields reported were quite low (<0.35%).[30] In polymer thin films upconversion quantum yields were usually by orders of magnitudes smaller.[1] There was also a stability problem with **16** and **17** in solution especially in DCM, if they were exposed to light for a longer period of time.

The next step was the platination also according to method given by Hutter *et al.*[46] The metalation was done in cumene using the precursor complex $Pt(C_6H_5CN)_2Cl_2$. Nitrogen was bubbled constantly through the refluxing reaction mixture to remove HCl from the equilibrium to reach higher yields and to prevent the formation of H_4TPTB*tbut*PBr^{2+}. The product **18** was purified *via* column chromatography and the remaining starting material was collected and reused. The yield was 50%. This was in line with the literature.[46] Another promising approach was the microwave assisted platination. It has been shown by Dean at al. that microwave assisted synthesis could decrease the reaction time for platination of *meso*-tetraphenylporphyrin (TPP) drastically with a minimum of synthetic effort and high yields.[50] **17** and Pt(acac)$_2$ was dissolved in benzonitril and heated in the microwave to 250°C for 20 minutes. **18** was formed under this conditions. The reaction progress was monitored *via* thin layer chromatograpy and UV-Vis spectroscopy. No starting material could be monitored and there were only very little side products. The product was precipitated in a mixture of EtOH and deionized water. This procedure led to pure **18** with a yield of 54% but this could only be seen as a first try. There is plenty of space for further optimization. A lot of fine dispersed elementary platin was formed. It was suggested that the reaction conditions were too harsh and also the recycled educt **17** was contaminated and so led to reduction of the platin salt. The excess of Pt(acac)$_2$ was only 1.5 equivalents. The next step will be to replace benzonitril as the solvent with cumene. In a preliminary test TPP was platinated in cumene without the use of the microwave. The reaction speed was reduced in comparison to benzonitril possibly due to the lower boiling point of cumene (152°C) but the solvent could be removed under reduced pressure easily and in the microwave synthesis the boiling point would be not limiting.

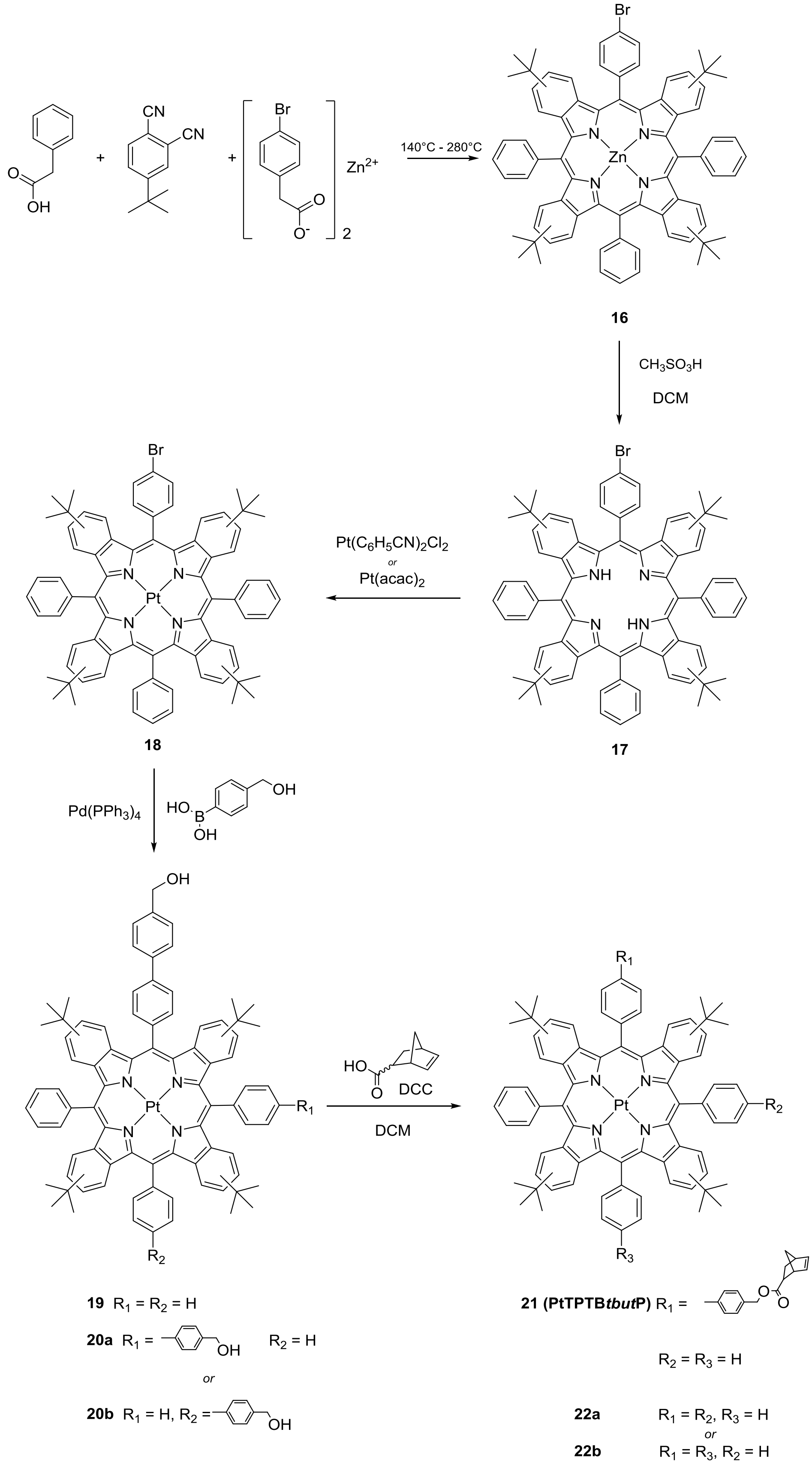
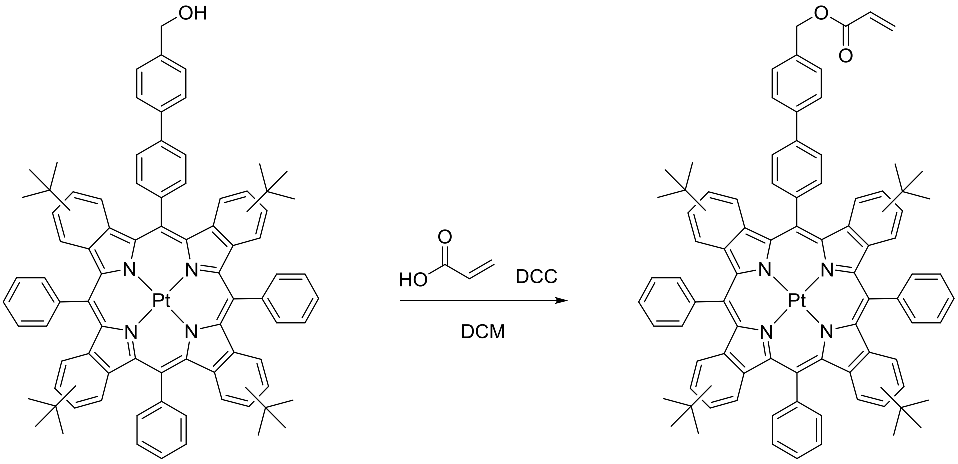


Figure 20. Reaction scheme for the norbornene-functionalized Pt-Tetraphenyltetrabenzo-*tert*-butly-porphyrin.

A hydroxyl group was introduced *via* a Suzuki coupling reaction. **18** was coupled with (4-(hydroxymethyl)phenyl) boronic acid dissolved in a mixture of toluene and MeOH, K_2CO_3 and $Pd(PPh_3)_4$ as catalyst. Due to the fact that **18** was a mixture of products with different degree of bromo-substitution, mono functionalized **19** and difunctionalized **20** was synthesized. **20a** and **20b** were the two possible isomers but they could not be separated. At this stage it was possible to isolate the products *via* column chromatography due to the difference in polarity. The reaction gave insufficient yields so the solvent mixture was varied and the yield could be improved to 37% for **19** and 16% for **20**. One reason for the low reactivity was that the coupling side of the porpyhrin was difficult to access because of the steric hindrance by the *tert*-butyl groups. Meanwhile in our group the same coupling reaction was done with PtTPPBr, with the same solvent as for the synthesis of **19** and **20** no reaction occurred. By using DMF as the solvent the reaction was almost quantitative.[51] It was assumed that these results could be transferred to **PtTPTB*tbut*PBr** and the yields could be improved significantly.

The norbornene-functionalized porpyhins **21** and **22** and also the acrylic acid functionalized **23** was synthesized. **23** was a terminating agent for ROMP so that well defined end group functionalized polymers could be received. This porphyrin derivative could also be used as a monomer for other polymerization technics. **21** and **22** were tried to synthesize *via* the Einhorn modification of the Schotten-Baumann reaction according to the general procedure used to functionalize the perylene derivatives but a very polar unidentified side product with similar properties in UV-Vis spectroscopy was the dominant product. The same effect occurred for the synthesis of **23**. The problem was solved by using dicyclohexylcarbomide (DCC) activated esterification and 5-norbornene-2-carboxylic acid or acrylic acid, see Figure 21.[52] The reaction was carried out in dry DCM at room temperature and was catalyzed with DMAP. In contrast to the literature the carboxylic acid was added in excess. Nevertheless high yields were obtained. The products were purified *via* column chromatography and characterized with ^{1}H-NMR spectroscopy and MALDI-TOF mass spectrometry. ^{1}H-NMR spectroscopy and especially was not an appropriate method to characterize all these porphyrins. The aromatic region showed multiple splitting and coupling promoted through the twisted structure reported in the literature[48] for similar PtTPTBP and mixture of isomers referred to the *tert*-butyl groups. In ^{13}C-NMR spectroscopy the TPT*butly*BP showed multiple overlapping signals in the aromatic region with low intensity even when concentrated probes were measured. However, the products **19**, **20**, **21**, **22** and **23** were clearly identified *via* MALDI-TOF mass spectroscopy.



19

23

(endgroupPtTPTB*tbut*P)

Figure 21. Synthesis of the termination-reagenz *via* dicyclohexylcarbomide (DCC) activated esterification.

16, **17** and **18** showed characteristic absorptions spectra and so the reaction progress was monitored *via* UV-Vis spectroscopy. The Soret peak of **16** was at 460 nm and was the most intensive peak (Figure 22). There were two more peaks in the Q-region at 606 nm and 652 nm. The Soret peak of the free ligand **17** was at 462 nm there were three more peaks in the Q-region at 592 nm, 642 nm and 696 nm. There were hardly any differences in the spectra of **18**, **19**, **20**, **21**, **22** and **23**. When another phenyl group was introduced *via* the Suzuki reaction the absorption spectra hardly changed at all. The same was true for further functionalization. The modification was too far outside the π-conjugated core of the prophyrin to affect the photophysical properties significantly.[7,46] As mentioned before further functionalization of this position had very little effect on the photophysical properties. **18** and any other products based on **18** showed a Soret peak at 426 nm and two peaks in the Q-region at 564nm and 616 nm.

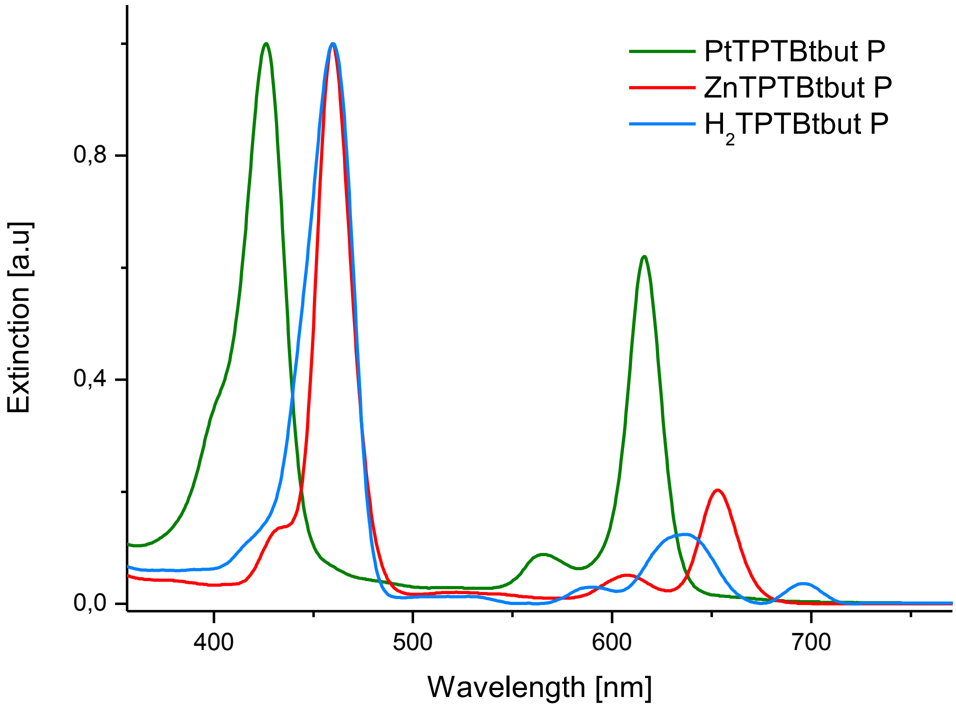


Figure 22. UV-Vis spectroscopy of the intermediates in the synthesis of Pt-Tetraphenyltetrabenzo-*tert*-butyl-porphyrin. the spectra were recorded in DCM.

2.4 Matrixmonomers

Two norbornene derivatives with different moieties in position 2 and 3 were synthesized. The structures were selected in order to have to contrary glass-transition temperature (T_G) and to retrieve information about the effect of the glass-transition temperature on TTA-UC with covalently bound chromophores.

The synthesis of **13** and **14** was straightforward *via* Diels-Alder reaction as reported several times in literature (see Figure 23). The dienophil was in both chases the trans-isomer to obtain only exo,endo-norbornene. The [4+2] cycloaddition reaction of cyclopentadiene of dimethyl fumarate gave **13**[53] and the reaction of cyclopentadiene and trans-1,4-diphenyl-2-butene-1-dione gave **14**[54]. **poly14** has a highest T_G (T_G = 146.6 °C, M_n = 61600 g/mol), then **poly13** (T_G = 90.5, M_n = 77100 g/mol).[55]

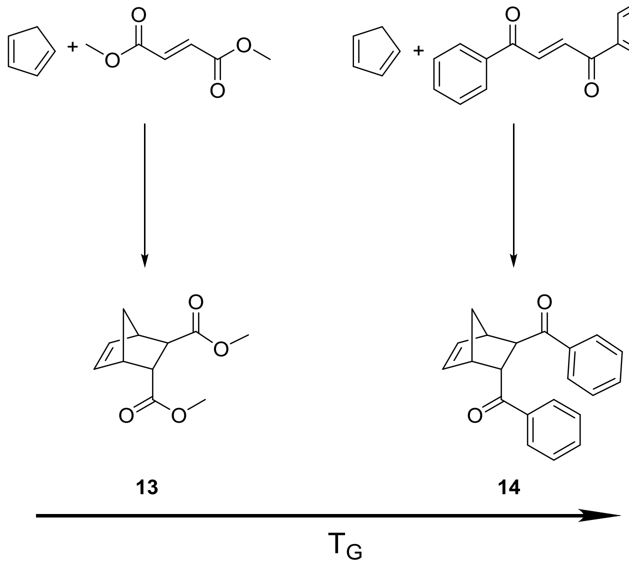


Figure 23. Reaction scheme for the predation of the matrixmonomers and the trend of the glass transition temperature (T_G).

2.5 Polymers

Statistic polymers with a varying dye concentration were synthesized in order to study the effect of the inter-chromophore distance and to receive information about the optimum ratio between sensitizer and emitter. In this set of experiments the TTA-UC was measured in solution and either the sensitizer or the emitter was covalently bound to the polymer. A similar approach was done by Xinjun Yu *et al*[12]. with different chromophores (Pt-octaethylporphyin was the sensitizer and the emitter was anthrylmethyl functionalized on a PMMA-polymer (Figure 4)). They reported a sharp maximum of the TTA-UC efficiency as a function of the emitter concentration and the inter-chromophore distance. They also suggested that self-quenching of the excited singlet state became significant at high dye concentrations.

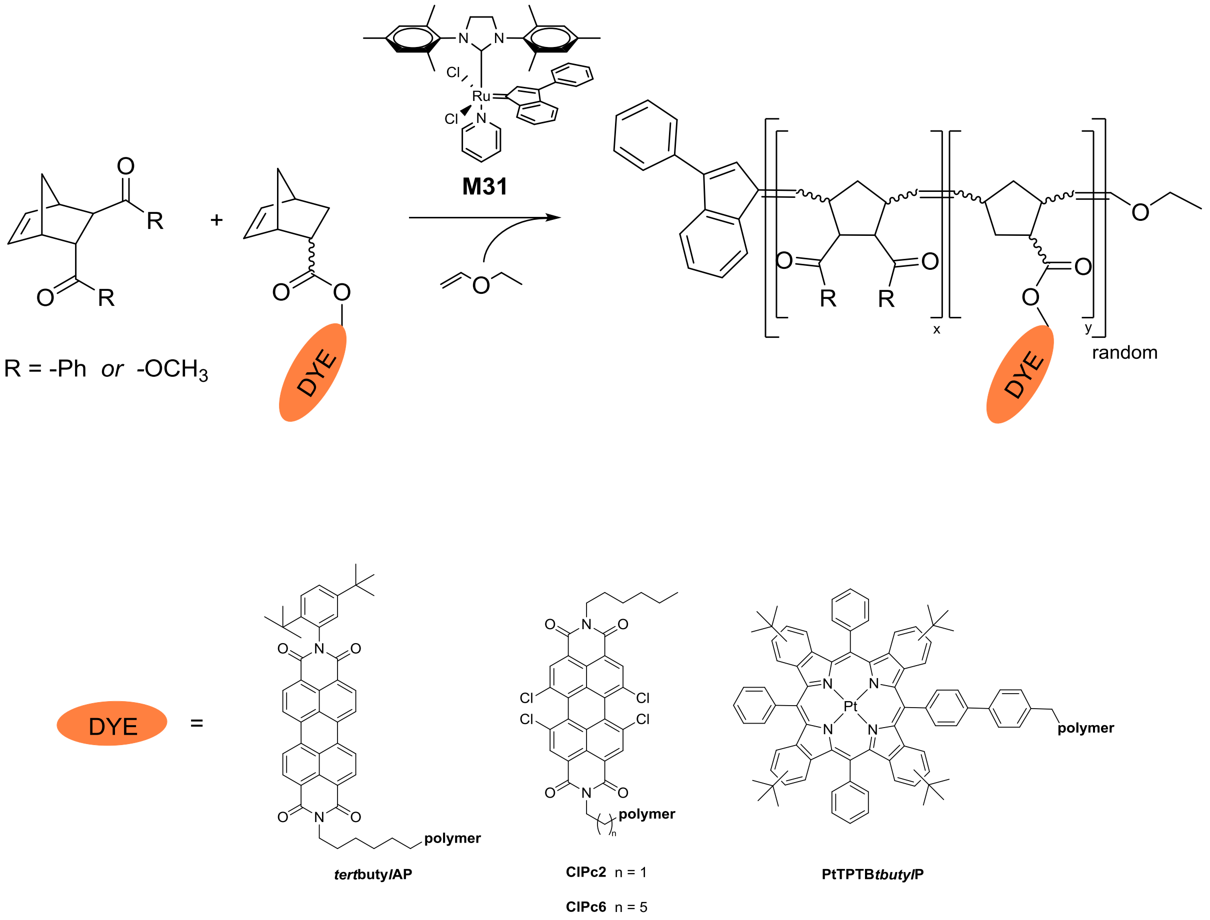


Figure 24. Overview over the synthesis of dye-functionalized polymers *via* ROMP. The ration monomer:catalyst was 1000:1.

Similar self-quenching was observed with our first polymers **poly14-tbutylAP-0.65wt%**[1] and **poly14-tbutylAP-6.5wt%** in solution and in thin film as well. The intensity of the

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[1] The name of polymers composes of the used **matrixmonomer** – the **chromophore** – and the **concentration** of the chromophore. The prefix **poly** indicates the polymer.

fluorescence was mainly influenced by the dye loading of the polymer and not by the dye concentration of the solution. There was a need to optimize the inter-chromophore distance for the chosen chromophore combination to quantify the optimal concentration range for futher statistical copolymers of sensitizer, emitter and copolymer.

2.5.1 Statistic copolymers of emitter and matrixmonomer

From preliminary optical investigations carried out at the Joanneum Researchter, it was decided that ***tbuyl*AP** was the most promising emitter in combination with **PtTPTB*tertb*PBr.** The comonomer was **13** because of the mid-level T_G, straightforward synthesis and the low price. To cover a wide range seven polymers with a emitter content of 1 wt%, 2 wt%, 4 wt%, 10 wt%, 20 wt%, 30 wt% and 40 wt%, respectively 0.26 mol%, 0.52 mol% , 1.04 mol%, 2.56 mol% 5.00 mol%, 7.32 mol% and 9.52 mol% were prepared according the general procedure for ROMP given in 3.5.1. To **13** the corresponding amount of ***tbutyl*AP** and **M31** was added and the polymerization was terminated with an excess of ethyl-vinyl ether. The theoretical chain length was 1000 monomer units. The polymers were characterized *via* ^{1}H-NMR spectroscopy, GPC and DSC.

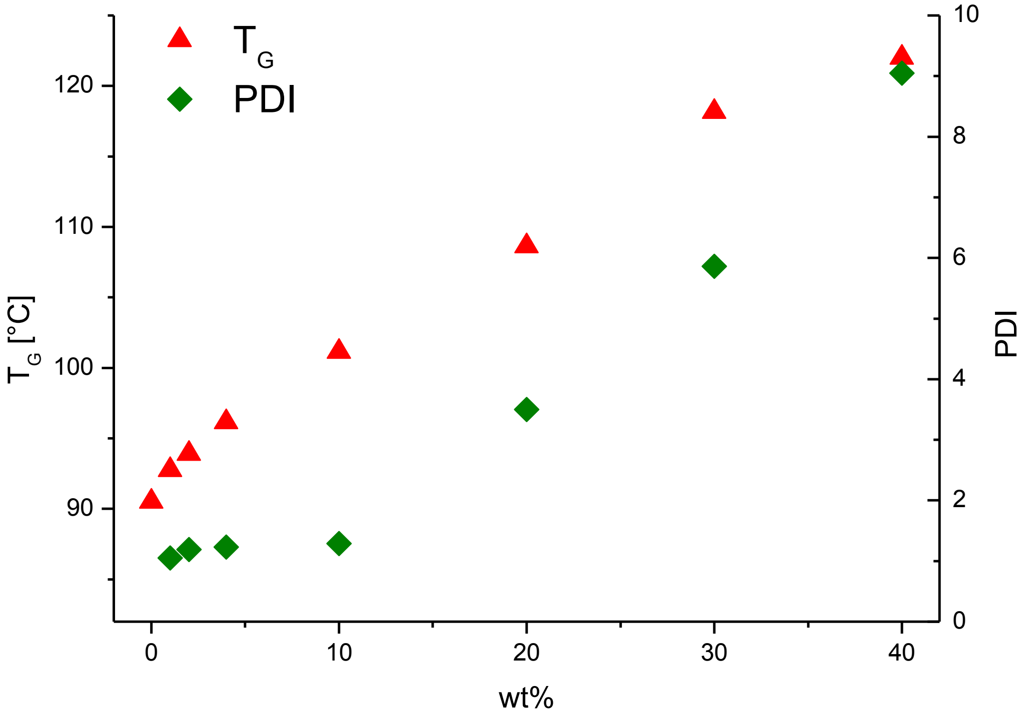

Figure 25. Characterization of the polymers poly13-*tbutyl*AP-*X*wt%. The T_G and the PDI as function of the *tbutyl*AP concentration.

Up to 10wt% of ***tbutyl*AP** polymers with a narrow molar mass distribution were obtained. At higher dye content the PDI increases dramatically up to PDI 9.05. The rising PDI with increasing chromophore concentration was noticed in almost any other polymers with a high-dye-content as well (i.e. **poly13-PtTPTB*tbut*P-5wt%** and **poly13-ClPc6-20wt%)**. It was suggested that the different reaction rate of **13** and the monomer functionalized chromophore in ROMP, which was observed with TLC, was leading to increasing PDI. In further experiments it should be tried to add the comonomer and the monomer functionalized chromophore dropwise to the polymerization so well defined polymers and the chromophore will be better distributed over the whole polymer chain.

Polynorbornes with pentad perylene diimide moieties are well known for self assempling.[19,20,25] Glaz *et al*.[20] systematically studied the effect of the solvent on these systems. The aggregation and conformation of the polymers is depended of the solvent. It was assumed that **poly13-*tbutyl*AP-*X*wt%** aggregated when the dye concentration was increased. In the same way changed the conformation respectively the coiling. The M_n of the polymers with a low ***tbutyl*AP** content (≤10 wt%) was usually approximately double the theoretical molar mass. In contrast to that corelated the M_n of the polymers with a ***tbutyl*AP** content >10 wt% with the theoretical molar mass. It is suggested that the coiling of the synthesized polymers changed as a function of the chromophore concentration relative to the used polystyrene calibration standard. The GPC was performed in THF.

The concentrations of the chromophore in the polymers were proven *via* ^{1}H-NMR spectroscopy. The integral, associated with the 2,5-*tert*-butylaniline was referenced to the integral of the polymer backbone (Figure 26). The calculated values were in line with the experimental data. All the chromophores in the polymerization were bound to the polymer. The peaks related to the perylene scaffold showed broadening of the peak at dye concentrations higher than 4 wt%. This was caused by aggregation of the perylene molecules.

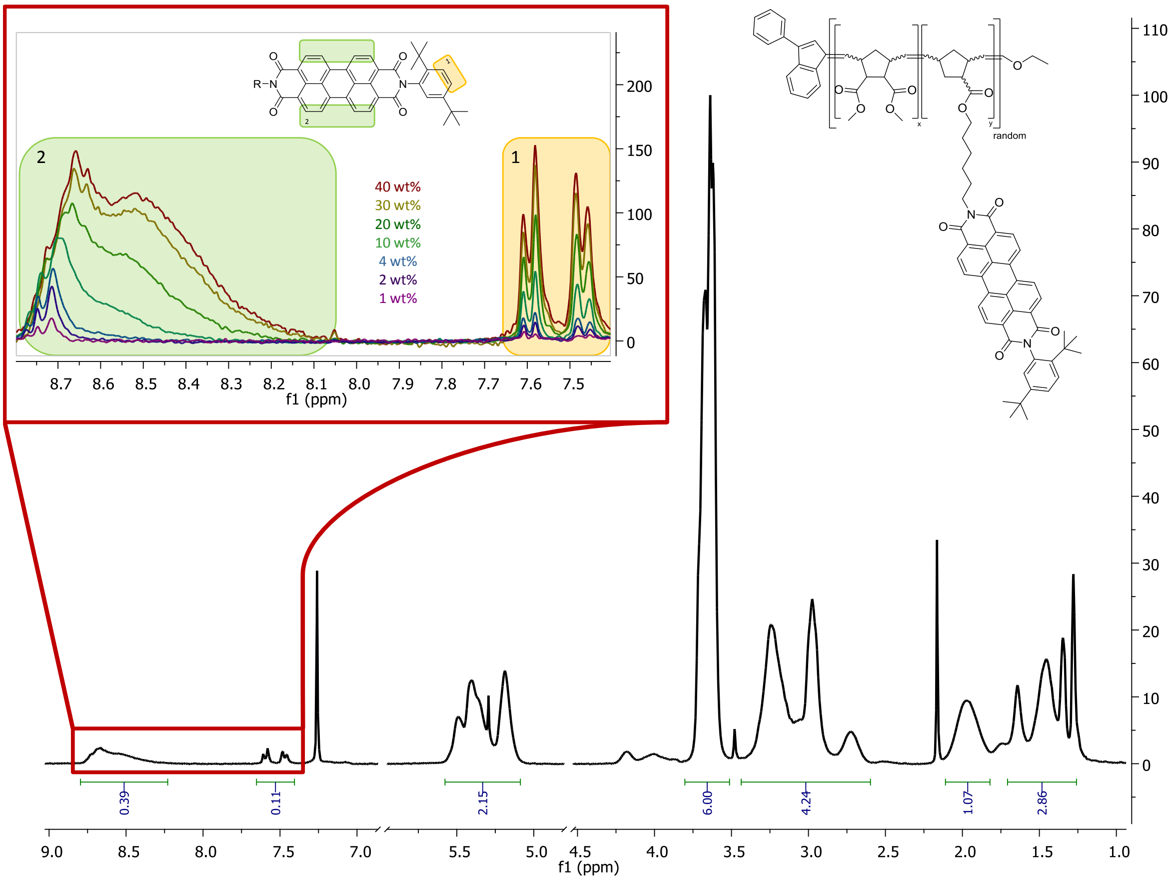

Figure 26. ^{1}H-NMR spectroscopy of poly13-*tbutyl*AP-*X*wt% in CDCl$_3$. The peaks of the perylene scaffold were broadened due to aggregation of the perylene molecules.

The absorption spectra of **poly13-*tbutyl*AP-1wt%**, **poly13-*tbutyl*AP-20wt%** and **poly13-*tbutyl*AP-40wt%** were not changing with the increasing dye content. The same was true for the pattern of the emission spectra. However the fluorescence intensity dropped obviously at higher dye concentrations due to self-quenching of the excited singlet state. The UV-Vis spectra and the aggregation of dye loaded polymers were highly dependent of the used solvent.[20] If the polymer backbone is well dissolved, the chromopheres self-assemble into characteristic H-type aggregates and align along the polymer backbone. In contrast leads a poor solvent for the polymer backbone to a coiled conformation, the aggregation is hindered and the polymer shows monomer-like photophysics.[20] DCM was a good solvent for ***tbutyl*AP** but a pore solvent for the comonomer so the aggregation was minimal.

The T_G was measured *via* differential scanning calorimetry (DSC). The scanning speed was 20°C/min and always the second cycle was analyzed. The T_G increased almost linearly by increasing ***tbutyl*AP** concentration and was another reference for covalently bound chromophores. Pure Poly13 had a T$_G$ of 90.5°C[55] and **poly13-*tbutyl*AP-40wt%** had a T$_G$ of 122.0°C. The increasing T$_G$ is an evidence for interchain interaction and aggregation. To gain further information about the influence of ***tbutyl*AP** onto the T$_G$ it was tried to polymerize pure ***tbutyl*AP.** Only a small amount of a shiny dark insoluble product was obtained, to little for further investigations.

The results of the copolymers **poly13-*tbutyl*AP-*20*wt%** were compared with the copolymers **poly13-ClPc2-20wt%** and **poly13-ClPc6-20wt%.** The matrix monomer of these polymers was **13** and the chromophores were **ClPc2** and **ClPc6.** The polymers were characterized identical to previous copolymers. The results were summarized in Table 1. In contrast to **poly13-*tbutyl*AP-*20*wt%** these polymers did not show peak broadening due to aggregation and the reduced intensity of the fluorescence was not as visible as for the **poly13-*tbutyl*AP-*20*wt%.** The T$_G$ of **poly13-ClPc2-20wt%** and **poly13-ClPc6-20wt%** was lower than pure poly13. This is in completely in contrast to **poly13-*tbutyl*AP-*20*wt%.** It was suggested that the twisted structure of **ClPc2** and **ClPc6** suppressed the aggregation. By now no difference based on a shorter or longer spacer could be noticed.

Table 1. Comparison of the polymers containing 20wt% of *tbutyl*AP, ClPc2 and ClPc6.

	poly13-*tbutyl*AP-*20*wt%	**poly13-ClPc2-20wt%**	**poly13-ClPc6-20wt%**
matrix:dye	19:1	18:1	20:1
PDI	3.50	4.21	3.73
T$_G$	108.63	81.94	81.91

2.5.1 Statistic copolymers of sensitizer and matrixmonomer

In the same manner four polymers with a sensitizer **PtTPTB*tertb*P** content of 0.005 wt%, 0.05 wt%, 0.5 wt% and 5 wt%, respectively 0.000764 mol%, 0.00721 mol% , 0.0721 mol% and 0.7160 mol% were prepared according to the general procedure given in 3.5.1. The polymers were characterized *via* ^{1}H-NMR spectroscopy, GPC and DSC.

With ^{1}H-NMR spectroscopy only the polymer backbone could be examined. The concentrations of **PtTPTB*tertb*P** were too low for ^{1}H-NMR spectroscopy. As mentioned before **PtTPTB*tertb*P** showed multiple overlapping signals in the aromatic region with low intensity and even the polymer with the highest sensitizer content was not concentrated enough.

2.5.2 Endgroup-functionalization

Another very promising approach was the end-group functionalizitation of the polymer chain with a single sensitizer molecule at the end, see Figure 27. Due to the living character of ROMP the active carbenoid species was still residing on the polymer chain and was reactive. Alkene-, vinylether- and acrylate- functionalized dyes could be used as terminating reagents. Vinylether- functionalized dyes leaded to quantitatively dye-labeled polymer chains, but the synthesis of vinylethers is more complex.[24] For the synthesis of acrylate-functionalized **endgroupPtTPTB*tertb*P** no major changes were needed. A drawback of the acrylate-functionalized terminating reagents was that beside the dye-functionalized polymers also methylene terminated polymers were formed as byproduct.[24,56] **13** was polymerized with the general ROMP procedure. The theoretical chain length was 500 monomer units. When the monomer was consumed as monitored by TLC **endgroupPtTPTB*tertb*P** was added in excess. After another 2 hours the reaction was finished. **poly13-endgroupPtTPTB*tbut*P** was characterized *via* UV-Vis spectroscopy, DSC and GPC. The solid polymer was pale green but when the polymer was dissolved the solution was hardly colored. With UV-Vis spectroscopy and the reported molar absorptions coefficient ε of the similar **PtTPTB** it was tried to estimate the amount of dye-functionalized polymer but the concentration was too low, respectively the polymer quantity was not big enough.

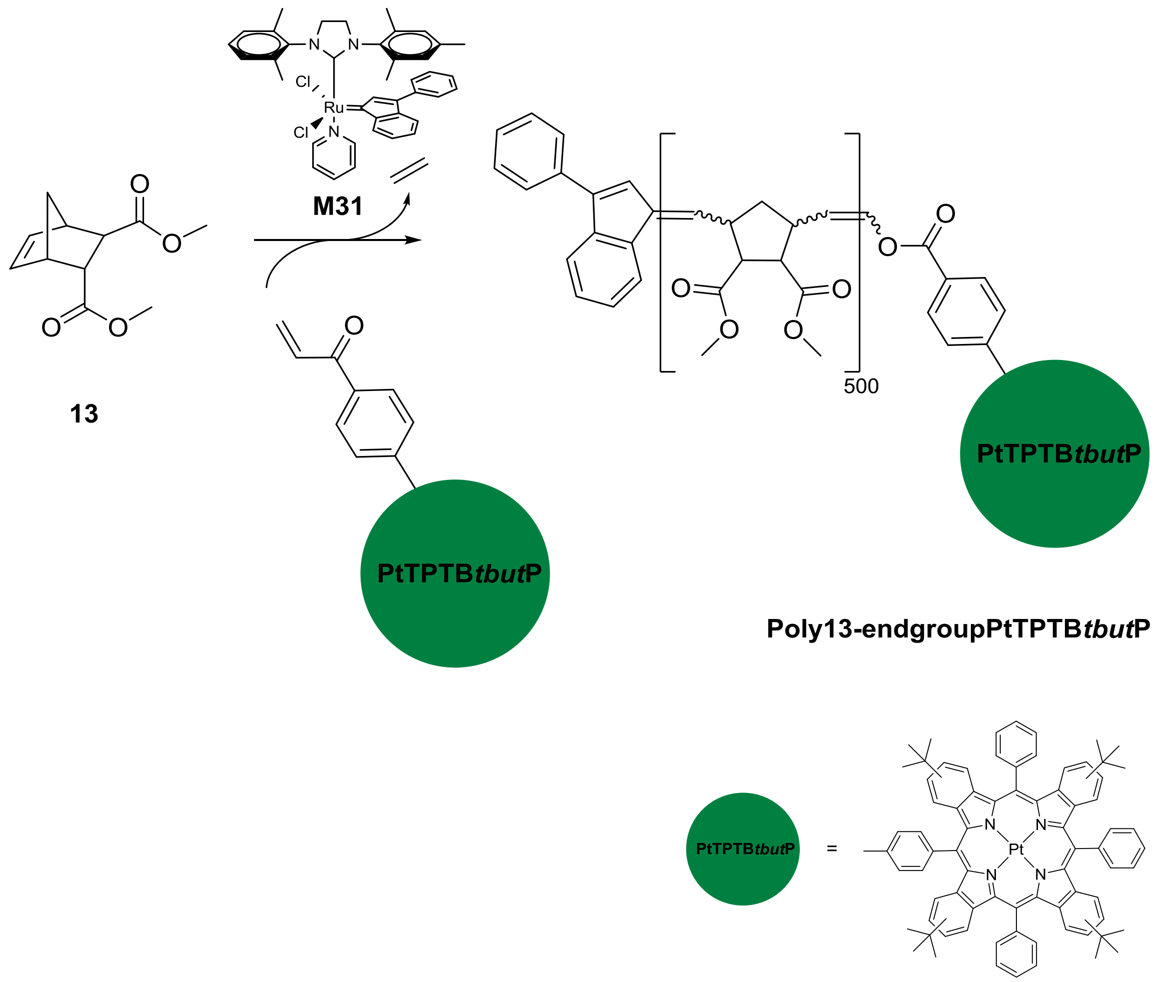

Figure 27. The endgroup- functionalized polymers were synthesized be terminating the ROM-polymerisation with a dye-bearing acylate.

2.6 TTA-UC measurement

Upconversion *via* sensitized triplet- triplet annihilation was measured in cooperation with Materials, Institute for Surface Technologies and Photonics, Joanneum Research, Weiz, Austria.

On purpose to evaluate systematically the optimal concentration of the chromophores a concentration series with four sensitizer concentration and **poly13-tbutylAP-*X*wt%** was made. The concentrations were selected by purpose to give reasonable combinations in solution and in films. For that reason the approaches of Xinjun Yu *et al.*[12] and Soo Hyon Lee *et al.*[10] were combined. Both groups worked with a different sensitizer and emitter combination but they gave a suggestion for the order of magnitude. 28 samples covered a wide range of rations between sensitizer and emitter (Figure 28). Some samples had the same rations but with different inter-chromophore distance. The copolymers **poly13-*tbutyl*AP-*X*wt%** were blended with 0.005 wt%, 0.05 wt%, 0.5 wt% and 5 wt% **18** (revered to the copolymers). 10 mg to 15 mg of each polymer dissolved in DCM and the corresponding amount of **18** was added. The solvent was removed and dried *in vacuo*. These 28 sampels were named **poly13-*tbutyl*AP-*X*wt%_PtTPTB*tbut*PBr -*Y*wt%**[2] and the samples were handed to the cooperation partners of Joanneum Research for the photo physical characterization and the TTA-UC measurements. The samples were redissolved in 1.0 mL DMF for the photo physical characterization and the TTA-UC measurements at the Joanneum Research. The solutions were deoxygenized before each measurement. For that reason was nitrogen bubbled through the solution for 1 minute. The setup for measuring the TTA-UC emission was continuously developed.

In the first experiments it was tried to excite and measure the TTA-UC luminescence on a RF-5301PC spectrofluorophotometer from Shimadzu without any further modifications. The monochromator of this spectrometer was a concave, blazed holographic grating. Related to the design there was always a significant percentage of polychromic light in the excitation beam due to overlap of higher order diffraction af the grating.[57,58] With this setup the emitter was directly excited. The luminescence was not quenched by oxygen, for this reason it was suggested that the fluorescence was not the result of TTA-UC.

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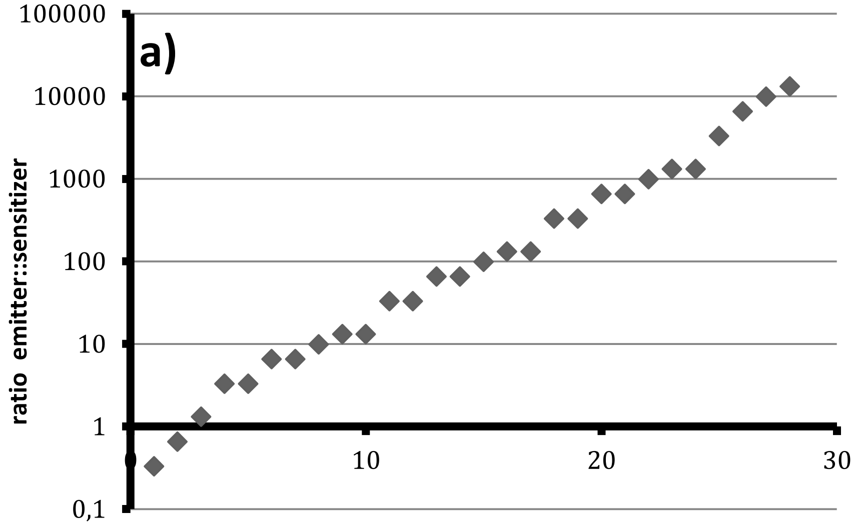
[2] The name of polymers blends composes of the used **matrixmonomer** – the **emitter** – the **concentration** of the pedant chromophore_ the **sensitizer** – and the **concentration** of the sensitizer. The prefix **poly** indicates the polymer and the underscore character signals that the emitter is moleculary dissolved and not covalent bound.



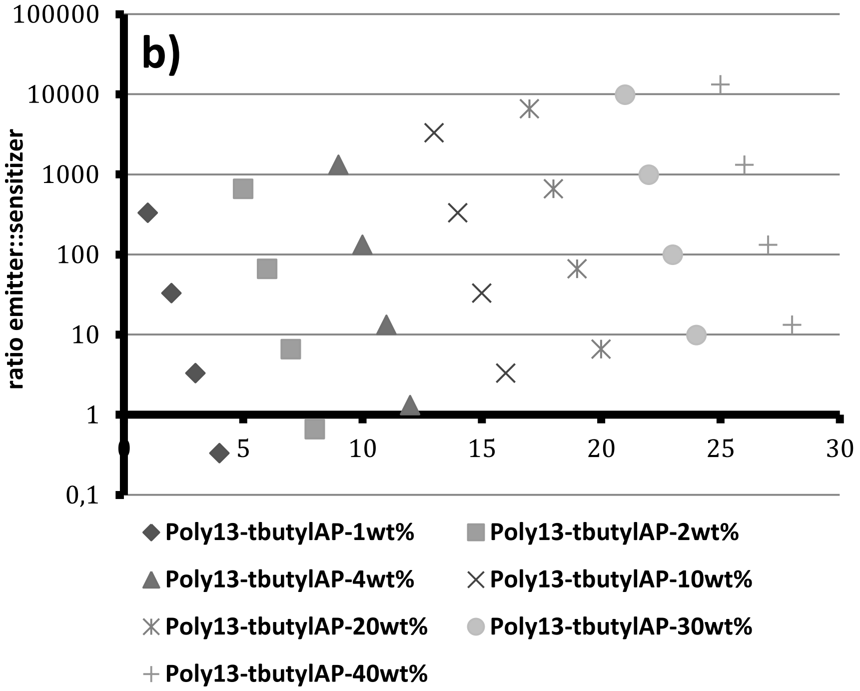


Figure 28. The polymers poly13-*tbutyl*AP-*X*wt% were blended with 0.005 wt%, 0.05 wt%, 0.5 wt% and 5 wt% sensitizer (revered to the copolymers). a) A wide range of emitter to sensitizer ratios was screened. b) Further information could be gained because some probes had the same ratio of emitter to sensitizer but different dye inter-chromophore distances in the polymer.

The next step was to use a monochromatic light source for the excitation. For this purpose the laser beam of a red 635 nm laser was guided by two mirrors into the housing of the spectrofluorophotometer and the sample was radiated at an angel of 90 degrees to the detection plane. With this setup it was not possible to excite either the triplet state of the sensitizer (no phosphorescence occurred) or the TTA-UC. The wavelength of the laser was too far of the peaks in the Q-band (564 nm, 616 nm) for efficient excitation. At 635 nm **PtTPT*tbut*B** hardly absorbs any light. This was in line with the literature.[5]

Next a red high Power LED (~ 618 nm) was used for the excitation. The LED was mounted directly onto the sample holder to ensure a high power density despite the wide beam angle of the LED. The LED had the strongest intensity at 618 nm but the maximum was rather wide and the emitter was excited as well again. The TTA-UC could not be proven.

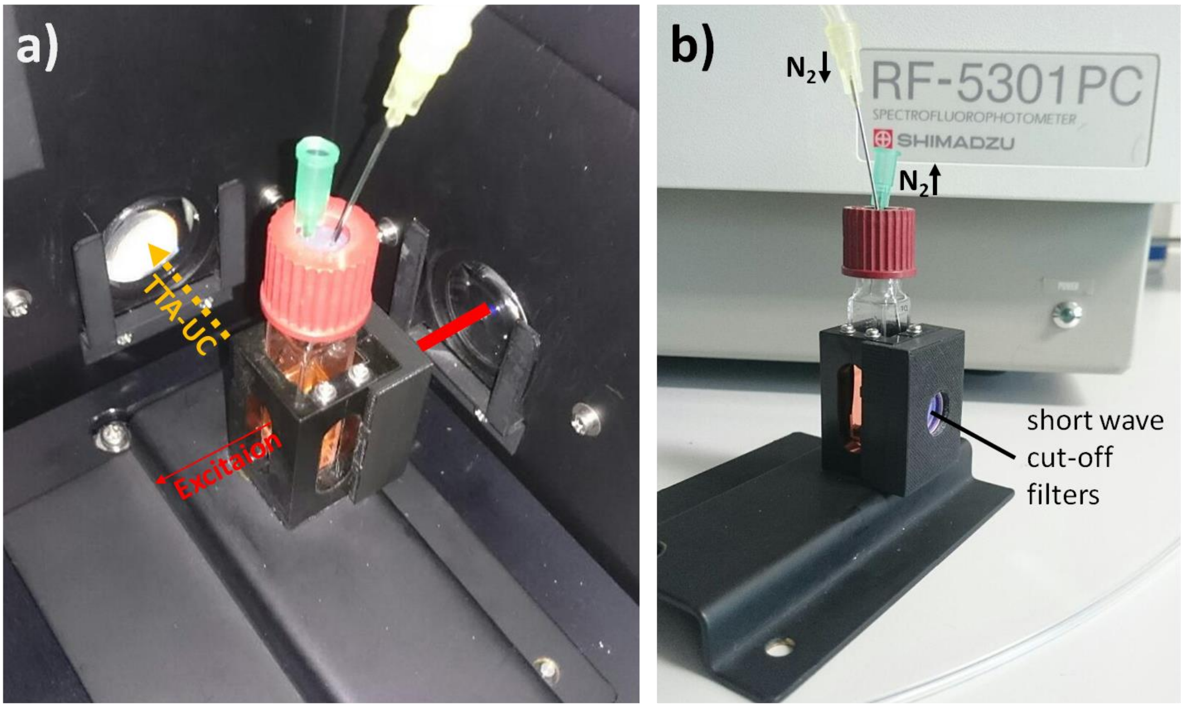


Figure 29. The final setup for the TTA-UC emission measurement. a) the emission is detected analogous to normal fluorescence. The excitation wavelength was 618 nm. b) The sample holder was equipped with a 3D-printed holder for the two short wave cut-off filters. The quartz cuvette was sealed with a screw-cap equipped with a septum and two syringe needle, one for the N2-inlet and one for the outlet. The pictures were taken by Martin Tscherner.

Finally the samples were excited with the build in Xenon lamp and the monochromator of the RF-5301PC spectrofluorophotometer from Shimadzu (Figure 29). The excitation wavelength was 618 nm and varying slit width. In order to eliminate the polychromic light below 600 two short wave cut-off filters were place in the in front of the probe. The filters were held by 3D-printed holder. For the measurement was a solution of the emitter and sensitizer placed in a quartz cuvette with a screw-cap equipped with a septum and two syringe needle, one for the N_2-inlet and one for the outlet. N_2 was bubbled through the solution in the cuvette to deoxygenise the solution. During the measurement only the heat space was flushed with nitrogen. In the first set of experiments was the concentration, in comparison to similar chromophore systems reported in the literature, in orders of magnitudes too high.[26,28] The concentration was stepwise reduced but by now not TTA-UC was observed with the samples.

3 Experimental

3.1 Materials and Methods

All chemicals for the synthesis and characterization of sensitizer and emitter dyes and matrix monomers were purchased from commercial sources (Sigma Aldrich, TCI, ABCR, Alfar Aesar, Fluka, VWR chemicals, Fischer chemicals, euriso-top). All products were used without additional purification, otherwise the procedure is specified.

Thin layer chromatography

Silica gel 60 F_{254} and aluminum oxide 60 F_{254} on aluminum sheets were use for thin layer chromatography. They were purchased from Merk. Visualization was done under UV light and dipping into an aqueous solution of $KMnO_4$ (0.1 wt%).

^{1}H-NMR and ^{13}C NMR spectroscopy

Characterization *via* NMR spectroscopy (^{1}H, ^{13}C, APT, COSY, HSQC) was peformed on a Brucker Avance 300 MHz spectrometer. Deuterated solvents (Chlorofrom-d, DMSO-d^6) were purchased from euriso-top. NMR chemical shifts of solvents was referenced according to the literature[59]. Peak shapes are identified as follows: s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quadruplet) and m (multiplet).

Mass spectrometry

MALDI-TOF mass spectrometry was performed on Micomass TofSpec 2E Time-of-Flight Mass Spectrometer. The instrument was equipped with a nitrogen laser (λ = 337 nm, operated at a frequency of 5 Hz) and a time lag focusing unit. Ions were generated just above the threshold laser power. Positive ion spectra were recorded in reflection mode with an accelerating voltage of 20 kV. The Spectra was externally calibrated with a polyethylene glycol standard. Analysis of data was done with MassLynx-Software V3.5 (Micromass/Waters, Manchester, UK). The best ten shots were averaged to a spectrum. Samples were dissolved in acetone (c = 1 mg/mL). Solutions were mixed in the cap of 1 µL: 10 µL. The resulting mixture (0,5 µL) was spotted onto the target and allowed to air dry. The matrix was *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)

UV-Vis spectroscopy

Absorptions spectra were recorded on a Shimadzu spectrophotometer UV-1800. The emission was measured on a Hitachi F-7000 fluorescence spectrometer equipped with a red-sensitive photomuliplier R928 from Hamamatsu.

TTA-UC

Upconversion *via* sensitized triplet- triplet annihilation was measured in cooperation with Materials, Institute for Surface Technologies and Photonics, Joanneum Research, Weiz, Austria.

The upconversion emission was measured on a RF-5301PC spectrofluorophotometer from Shimadzu. The excitation was done with the build in Xenon lamp at 618 nm and varying slit width. Related to the design of the monochromator there is always a significant percentage of poly polychromic light in the excitation beam. In order to eliminate the polychromic light below 600 two shot wave cut-off filters were place in front of the probe. The filters were held by 3D-printed sample holder. For the measurement a solution of the emitter and sensitizer was placed in a quartz cuvette with a screw-cap equipped with a septum and two syringe needles, one for the N_2-inlet and one for the outlet. N_2 was bubbled through the solution in the cuvette to deoxygenise the solution. During the measurement only the heat space was flushed with nitrogen.

ATR-FTIR spectroscopy

FT-IR spectra were recorded on a Brucker Alpha-P infrared spectrometer, equipped with an attended total reflection (ATR) accessory using a diamond crystal.

GPC spectroscopy

Molecular weights and the polydispersity index (PDI) of polymers were determined *via* gel permeation chromatography (GPC). Measurements were carried out in chloroform with the following instrument set up: Merk hitachi L6000 (pump); Polymere Standards Service, 5 µm grade size (separation columns); Wyatt Technology (refractive index detector).

DSC

The T_G was measured on a PerkinElmer Differntial Scanning Calorimeter with HyperDSC DSC 8500. Two isothermal cycles were executed and the second scan was analyzed. The scanning speed for cooling and heating was 20 °C/sec.

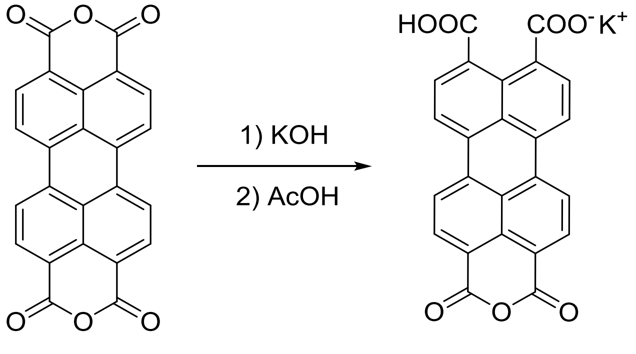
Microwave

The microwave assisted platination was performed in Biotage Initiator EXP EU. The temperature was 250 °C and the temperature was held for 20 minutes at this temperature while the reaction mixture was stirred permanently. The absorption rate was set to high.

3.2 TTA-UC Emitters

3.2.1 Synthesis of the potassium salt of perylene-3,4,9,10-tetracarboxylic monoanhydride

Literature: [43]



PTCDA **1**

Perylene-3,4,9,10-tetracarboxylic dianhydride (10.16 g, 0.0259 mol) and KOH (54 g, 0.96 mol) was dissolved in 500 mL deionized water and heated to reflux. Acetic acid (99%) was added drop wise over the reflux condenser. A brown precipitate was formed. The addition was continued until pH 5 was reached and the remaining solution shows only very little fluorescence in the spot test. For the spot test the reaction solution was dropped onto a filter paper and the spreading aqueous phase was observed. The reaction mixture was cooled to room temperature and the precipitate was filtered off. The precipitate was washed twice with deionized water. The product was dried at 120 °C in an oven over night.

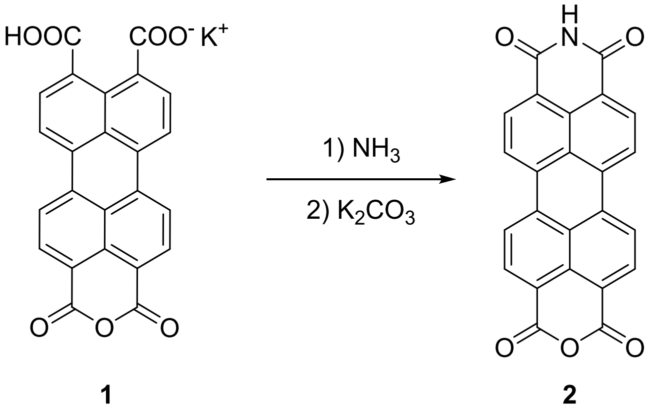
Yield: 11.87g (97%)

The product was insoluble in all common organic solvents and used without any further characterization.

ATR-FTIR spectroscopy (cm^{-1}): 3067 (m), 1797 (s), 1719 (s), 1612 (s), 1590 (b), 1508 (b), 1440 (b), 1367 (b), 1341 (b), 1313 (b), 1300 (b), 1229 (s), 1209 (s), 1180 (w), 1147 (s), 1119 (m), 1003 (b), 929 (b), 852 (s), 807 (m), 738 (b), 612 (s).

3.2.2 Synthesis of perylene-3,4,9,10-tetra-carboxylic-3,4-anhydrid-9,10-imide

Literature: [43]



The potassium salt of perylene-3,4,9,10-tetracarboxylic-3,4- anhydride-9,10 (11.00 g, 0.0245 mol) was added into 150 mL of cold ammonia solution (3%) and was stirred for 30 minutes at 0°C. Then the solution was heated to 90°C for 2 hours. Brown precipitate was formed. 100 mL of K_2CO_3 solution (8.8 g, 0.064 mol) was added and kept at 90°C for an hour. The precipitate was filtered off and washed with 100 mL K_2CO_3 solution (2%) three times. The precipitate was dissolved in KOH solution (10%, 500 mL) at 90°C. The hot solution was filtered off, and HCl (2N) was added until pH 5 was reached. The precipitate was filtered off and was washed with deionized water twice. The product, a dark-brown powder, was dried in an oven at 120°C over night.

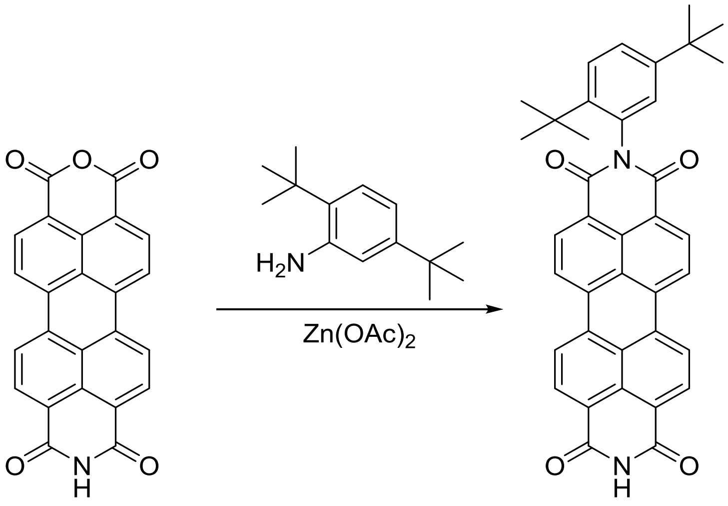
Yield: 5.26 g (55%)

The product was insoluble in all common organic solvents. Therefore ATR-FTIR spectroscopy was used for charaterisation.

ATR-FTIR spectroscopy (cm^{-1}): 3058 (m), 1768 (s), 1753 (s), 1728 (s), 1616 (s), 1591 (b), 1505 (b), 1439 (b), 1423 (b), 1405 (m), 1300 (b), 1266 (s), 1234 (b), 1148 (b), 1120 (m), 1014 (b), 857 (s), 810 (m), 731 (m), 640 (m).

3.2.3 Synthesis of N^1-(2,5-di-tert-butylphenyl)-perylene-3,4,9,10-tetracarboxylicdiimide

Literature: [60]



2 **3**

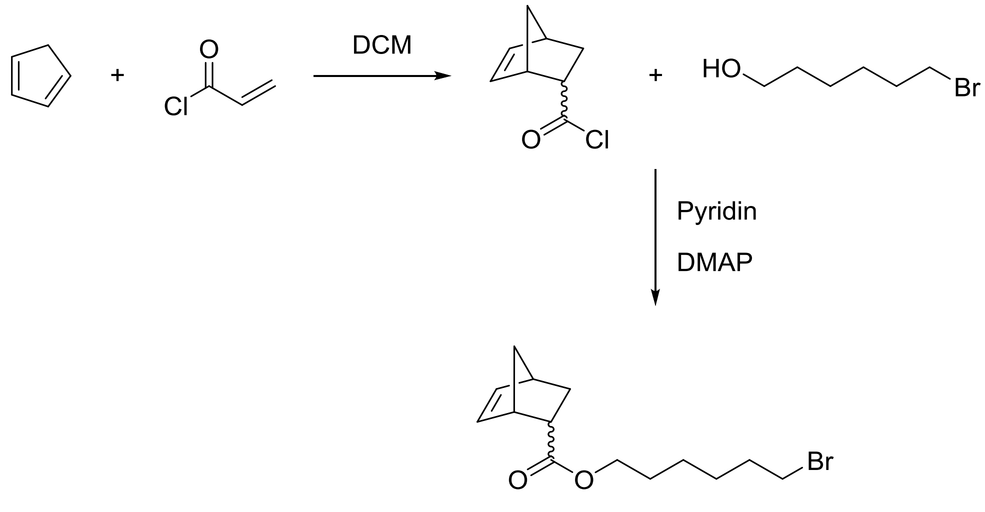
A mixture of **2** (5.23 g, 0.0135mol), 2,5-di-*tert*-butylaniline (3.85 g, 0.0188 mol), Zn(OAc)$_2$ (2.21 g, 0.010 mol), and imidazole were stirred under inert atmosphere at 160°C for 3 hours. The cold mixture was dissolved in a minimum of THF and precipitated in mixture of 2N HCl/MeOH 2:1 (500 mL). Deionized water (500 mL) was added for better precipitation. The precipitate was filtered and washed several times with 2N HCl, deionized water and MeOH. The product was dried in an oven at 120°C over night. The crude product was purified by column chromatography (silica gel, DCM/MeOH 20:1) and dried *in vacuo*. A red powder was obtained.

Yield: 2.89g (37%)

$R_f = 0.32$ (DCM/MeOH 20:1)

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): δ 8.83 – 8.60 (m, 8H, $\mathbf{H}_{\mathrm{Perylene}}$), 7.61 (d, J = 8.5 Hz, 1H, C**H**-CH-C(CH_3)$_3$), 7.48 (d, J = 8.6 Hz, 1H, C**H**-CH-C(CH_3)$_3$), 7.07 (s, 1H, C-C**H**-C(CH_3)$_3$), 1.34 (s, 9H, (C$\mathbf{H_3}$)$_3$), 1.30 (s, 9H, (C$\mathbf{H_3}$)$_3$).

3.2.4 6-Bromohexyl(1R,4R)-bicyclo[2.2.1]hept-5-ene-carboxylate



4

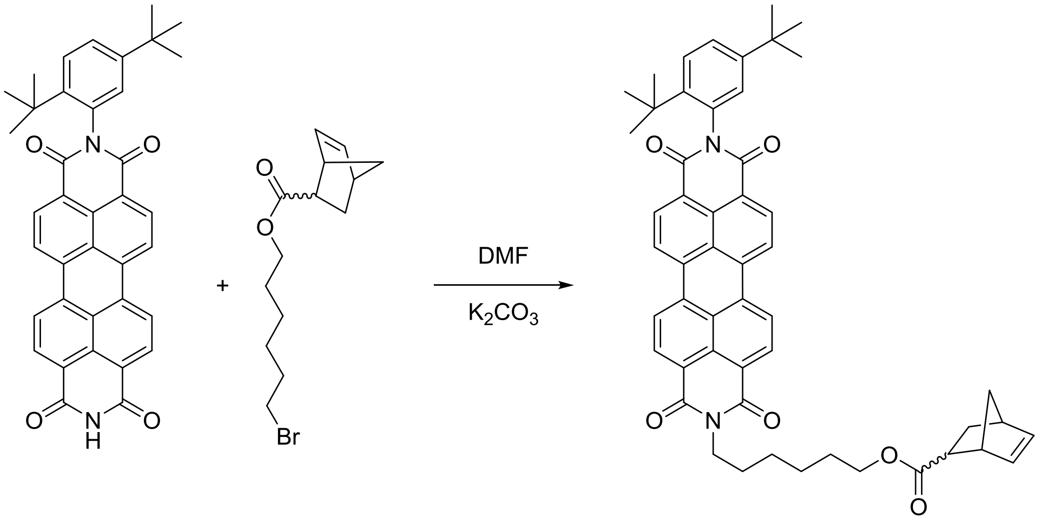
Fresh distilled cyclopentadiene (0.835 mL, 0.00993 mol) and acryloyl chloride (0.322 mL, 0.00397 mol) were added under stirring and inert atmosphere to dry, ice-cooled DCM. The reaction mixture was stirred for 3 hours at room temperature. The solution was cooled with ice again and 6-bromo-1-hexanol (0.725 mL, 0.00552 mol), pyridine (0.25 mL, 0.0030 mol) and DMAP (catalytic amount) was added. After stirring at room temperature over night the reaction was quenched with deionized water. The organic phase was collected and was washed with HCl (2N, 30 mL) and K_2CO_3 (2%, 30 mL) twice. The product was dried over Na_2SO_4 filtered of and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, CH/EE 5:1) and dried *in vacuo*. A colorless oil was obtained.

Yield: 1.152 g (96%)

R_f = 0.73 (CH/EE 5:1)

3.2.5 Synthesis of N^1- 6-hexyl (1R,4R)-bicyclo[2.2.1]hept-5-ene-2-carboxylate -N^2-(2,5-di-tert-butylphenyl)-perylene-3,4,9,10-tetracarboxylicdiimide

Literature: [61]



3 **4** ***tbutyl*AP**

A mixture of **4** (1.12 g, 0.00194 mol), 6-bromohexyl (1R,4R)-bicyclo[2.2.1]hept-5-ene-2-carboxylate (1.15 g, 0.00382 mol) and K_2CO_3 (0.792 g, 0.00573 mol) were refluxed in DMF (25 mL) for 4 hours and afterwards stirred at room temperature for 24 hours. Deionized water (60 mL) and HCl (2N, 150 mL) was added to the reaction mixture and the emulsion was stirred for 1 hour. DCM (100 mL) was added and the collected organic phase was washed twice with HCl (0.5 M, 100 mL). The solution was dried over Na_2SO_4 over night. After filtration the solvent was removed under reduced pressure and dried in an oven at 80°C for three hours. The crude product was purified by column chromatography (silica gel, DCM/MeOH 200:1) and dried *in vacuo*. A red powder was obtained.

Yield: 0.673 g (60%)

R_f = 0.69 DCM/MeOH 20:1)

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): δ 8.63 (d, *J* = 8.0 Hz, 2H, $\mathbf{H}_{\text{Perylene}}$), 8.38 (dd, *J* = 7.9, 4.8 Hz, 4H, $\mathbf{H}_{\text{Perylene}}$), 8.25 (d, *J* = 8.1 Hz, 2H, $\mathbf{H}_{\text{Perylene}}$), 7.61 (d, *J* = 8.6 Hz, 1H, C**H**-CH-$C(CH_3)_3$), 7.49 (dd, *J* = 8.5, 2.0 Hz, 1H, CH-C**H**-$C(CH_3)_3$), 7.43 (d, *J* = 1.9 Hz, 1H, C-C**H**-$C(CH_3)_3$), 6.17 (dd, *J* = 5.4, 3.1 Hz, 1H, C**H**=CH), 5.91 (dd, *J* = 5.3, 2.6 Hz, 1H, CH=C**H**), 4.16 (t, *J* = 7.2 Hz, 2H, C$\mathbf{H_2}$-N), 4.00 (dd, *J* = 6.3, 4.6 Hz, 2H, C$\mathbf{H_2}$-O), 3.19 (bs, 1H, CH-CH_2-C**H**), 2.98 – 2.84 (m, 2H, C**H**-CH, CH-CH_2-C**H**), 1.98 – 1.82 (m, 2H, C$\mathbf{H_2}$-CH), 1.78 –

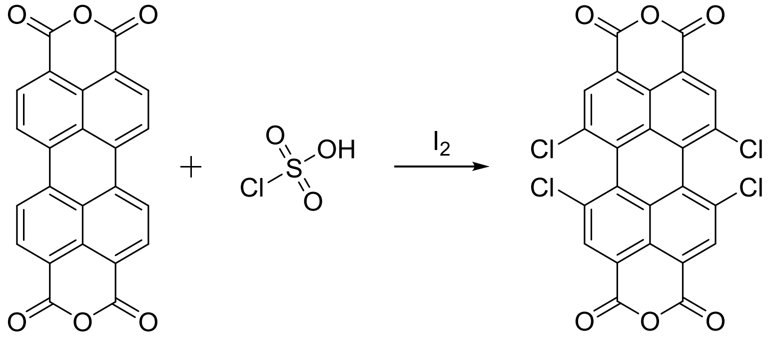
1.54 (m, 4H, O-CH_2-C**H_2**, N-CH_2-C**H_2**), 1.47 – 1.21 (m, 28H, CH-C**HH**-CH, CH_2-(C**H_2**)$_4$-CH_2, (C**H_3**)$_3$.

^{13}C-NMR (δ, 20°C, $CDCl_3$, 75 MHz): 174.92 (**C**OO), 164.25 (N-**C**O-C), 163.07 (N-**C**O-C), 150.40 (**C**(CH_3)$_3$), 143.78 (**C**(CH_3)$_3$), 138.11 (**C**H=CH), 134.41 (**C**), 134.03 (**C**), 132.82(**C**), 132.50 (**C**H=CH), 131.53 (**C**H), 130.87 (**C**H), 129.72 (**C**), 128.86 (**C**), 128.73 (**C**H), 128.31 (**C**H), 126.36 (**C**H), 126.16 (**C**), 125.90 (**C**), 123.73 (**C**), 123.10 (**C**H), 122.93 (**C**H), 64.31 (**C**H_2), 49.72 (**C**H_2), 46.72 (**C**H), 46.47 (**C**H_2), 45.82 (**C**H), 43.47 (**C**H), 43.30 (**C**H), 42.63 (**C**H), 40.65 (**C**H_2), 35.60 (**C**H_2), 34.49 (**C**H_2), 31.85 (**C**H_3), 31.38 (**C**H_3), 30.43 (**C**H_2), 29.31 (**C**H_2), 28.71 (**C**H_2), 28.14 (**C**H_2), 26.88 (**C**H_2), 25.91 (**C**H_2), 25.75 (**C**H_2).

UV-Vis (DCM) λ_{max}, *nm (rel. in.)*: 458 (0.22), 488 (0.60), 525 (1)

3.2.6 Synthesis of 1,6,7,12-tetrachloro-perylene-3,4,9,10-tetracarboxylic acid dianhydride

Literature: [45]



PTCDA **7**

Perylene-3,4,9,10-tetracarboxylic dianhydride (3.75 g, 0.0096 mol) and iodine were dissolved in chloro-sulfuric acid (25 mL, 0.376 mol). The mixture was stirred at 70°C for 20 hours subsequently cooled to room temperature and dropped onto ice-water. The precipitate was filtered off and washed with deionized water. The product was dried in an oven at 120 °C over night. The crude product was used without any further purification steps.

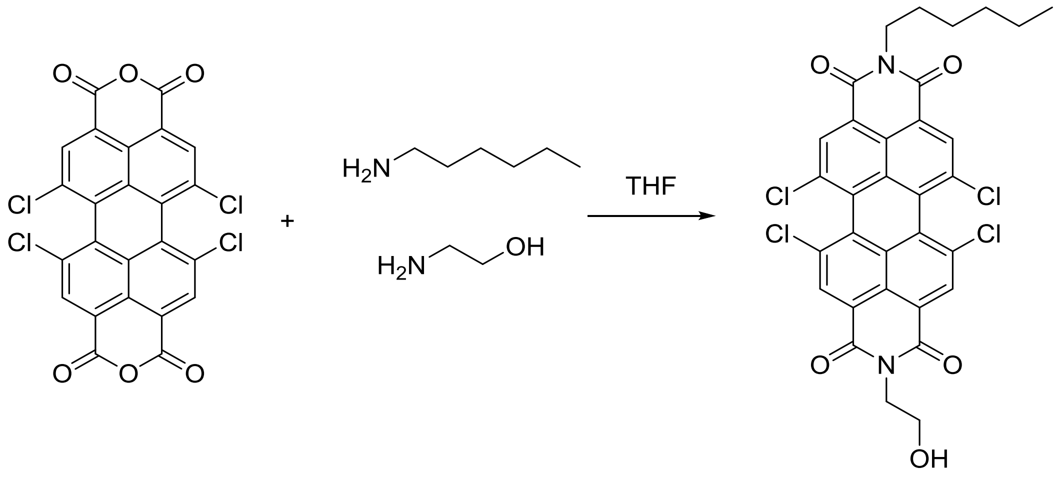
Yield: 4.91 g (97%)

R_f = 0.86 (acetone)

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 8.75 (s, 4H, **H**$_{Perylene}$).

3.2.7 Synthesis of N^1-hexyl-N^2-2-hydroxyethyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylicdiimide

Literature: [23]



7 **8**

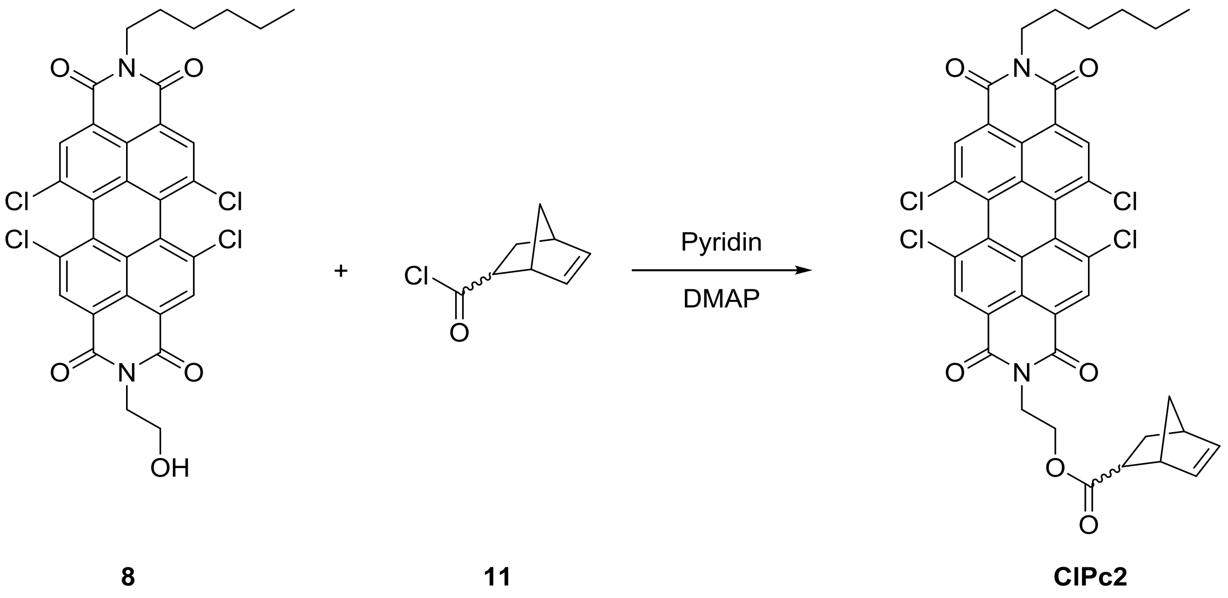
A mixture of **7** (0.498 g, 0.000939 mol), 2-aminoethan-1-ol (0.115 mL , 0.00188 mol) and hexylamine (0.248 mL, 0.00188 mol) dissolved in THF (100 mL) were heated to reflux for 24 hours. The solvent was removed under reduced pressure. The product was isolated by column chromatography (silica gel, DCM/acetone 30:1).

Yield: 0.184 g (30%)

R_f = 0.39 (DCM/MeOH 20:1)

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 8.69 (d, *J* = 4.0 Hz, 4H, $\mathbf{H}_{\text{Perylene}}$), 4.50 (t, *J* = 5.1 Hz, 2H, O-CH_2-C$\mathbf{H_2}$-N), 4.28 – 4.10 (m, 2H, C$\mathbf{H_2}$-N), 3.99 (t, *J* = 9.9 Hz, 2H, O-C$\mathbf{H_2}$-CH_2-N), 1.80 – 1.67 (m, 2H, C$\mathbf{H_2}$-CH_2-N), 1.51 – 1.21 (m, 6H, (C$\mathbf{H_2}$)$_3$-CH_3), 0.91 (t, *J* = 6.8 Hz, 3H, C$\mathbf{H_3}$).

3.2.8 Synthesis of N¹-hexyl-N²-2-ethyl-(1R,4R)-bicyclo[2.2.1]hept-5-ene-2-carboxylate-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylicdiimide



A mixture of **8** (0.475 g, 0.000726 mol), pyridine (0,13 mL 0,00160 mol) and DMAP (catalytic amount, spatula tip) was dissolved in dry DCM (100 mL). Freshly prepared **11** (0.250 g, 0.00160 mol) dissolved in dry DCM (25 mL) was added slowly. The reaction mixture was stirred at room temperature for 18 hours. The reaction was quenched with deionized water (10 mL). The organic phase was washed with HCl (5%, 60 mL) and K_2CO_3 (2%, 100 mL) twice. The organic phase was dried on Na_2SO_4. The crude product was purified by column chromatography (silica gel, DCM) and dried *in vacuo*.

Yield: 0.417 g (74%)

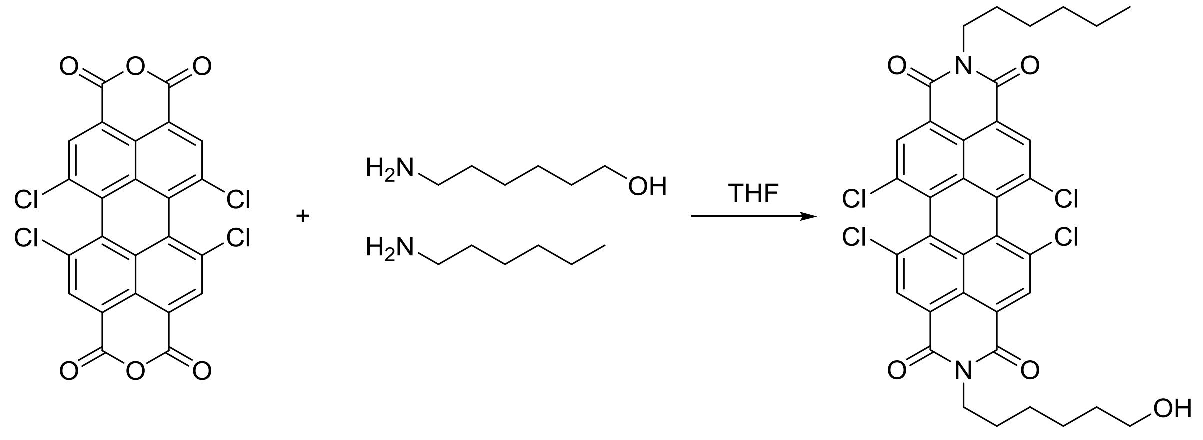
R_f = 0.65 (DCM/MeOH 100:1)

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 8.68 (d, *J* = 1.5 Hz, 4H, $\mathbf{H}_{Perylene}$), 6.21 (dd, *J* = 5.4, 2.9 Hz, 1H, C**H**=CH), 5.99 (dd, *J* = 5.4, 2.7 Hz, 1H CH=C**H**), 4.57 – 4.47 (m, 2H, O-C$\mathbf{H}_2$), 4.48 – 4.33 (m, 2H, N-C$\mathbf{H}_2$-CH_2-O), 4.26 – 4.12 (m, 2H, N-C$\mathbf{H}_2$), 3.23 (bs, 1H, CH-CH_2-C**H**), 3.04 – 2.95 (m, 2H, C$\mathbf{H}_2$-CH), 2.86 (bs, 1H, CH-CH_2-C**H**), 1.98 -1.87 (m, 1H, C**H**-CH_2), 1.80 – 1.66 (m, 2H, CH-C**HH**-CH), 1.53 – 1.17 (m, 10H, -(C$\mathbf{H}_2$)$_5$-CH_3), 0.90 (t, *J* = 6.7 Hz, 3H, C$\mathbf{H}_3$).

^{13}C-NMR (δ, 20°C, CDCl$_3$, 75 MHz): 162.45 (N-**C**O-C), 138.05 (**C**H=CH), 137.89 (**C**H=CH), 135.62 (**C**$_{\text{Perylene}}$), 135.51 (**C**$_{\text{Perylene}}$), 133.17 (H **C**$_{\text{Perylene}}$), 133.09 (H **C**$_{\text{Perylene}}$), 132.54 (**C**H=CH), 128.97 (**C**$_{\text{Perylene}}$), 128.66 (**C**$_{\text{Perylene}}$), 123.49 (**C**$_{\text{Perylene}}$), 123.12 (**C**$_{\text{Perylene}}$), 61.47 (**C**H$_2$), 49.87 (**C**H$_2$), 49.74 (**C**H$_2$), 45.84 (**C**H), 45.75 (**C**H), 45.70 (**C**H), 43.35 (**C**H), 43.21 (**C**H), 42.69 (**C**H), 42.65 (**C**H), 41.14 (**C**H$_2$), 39.99 (**C**H$_2$), 31.65 (**C**H$_2$), 29.51 (**C**H$_2$), 29.29 (**C**H$_2$), 28.19 (**C**H$_2$), 26.87 (**C**H$_2$), 22.69 (**C**H$_2$), 14.19 (**C**H$_3$).

UV-Vis (DCM) λ_{max}, *nm (rel. in.)*: 426 (0.28), 484 (0.69), 518 (1)

3.2.9 Synthesis of N^1-hexyl-N^2-6-hydroxyhexyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylicdiimide



7 **10**

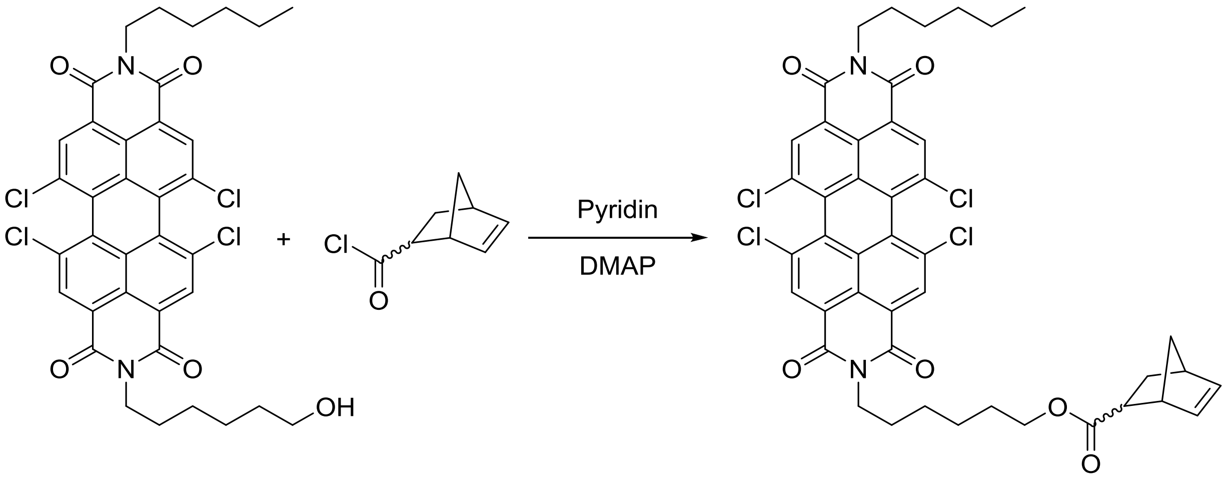
A mixture of **7** (1.114 g, 0.0021 mol), 6-aminohexan-1-ol (0.495 g, 0.0042 mol) and hexylamine (0.555 mL, 0.0042 mol) dissolved in THF (100 mL) were heated to reflux for 24 hours. The solvent was removed under reduced pressure. The product was isolated by column chromatography (silica gel, DCM/acetone 30:1).

Yield: 0.634 g (42%)

R$_f$ = 0.56 (DCM/MeOH 20:1)

^{1}H-NMR (δ, 20°C, CDCl$_3$, 300 MHz): 8.68 (s, 4H, **H**$_{\text{Perylene}}$), 4.27 – 4.15 (m, 4H, N-C**H$_2$**), 3.67 (t, *J* = 6.3 Hz, 2H, O-C**H$_2$**), 1.86 – 1.13 (m, 16H, **-**(C**H$_2$**)$_4$-CH$_3$, O-CH$_2$-(C**H$_2$**)$_4$), 0.91 (t, *J* = 6.5 Hz, 3H, C**H$_3$**).

3.2.10 Synthesis of N^1-hexyl-N^2-6-hexyl-(1R,4R)-bicyclo[2.2.1]hept-5-ene-2-carboxylate-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylicdiimide



10 **11** **ClPc6**

A mixture of **10** (0.634 g, 0.000890 mol), pyridine (0.14 mL, 0.00169 mol) and DMAP (catalytic amount, spatula tip) was dissolved in dry DCM (100 mL). Freshly prepared **12** (0.503 g, 0.00321 mol) dissolved in dry DCM (25 mL) was added slowly. The reaction mixture was stirred at room temperature for 18 hours. The reaction was quenched with deionized water (10 mL) and the organic phase was washed with HCl (1M, 60 mL) and K_2CO_3-solution (2%, 100 mL) twice. The organic phase was dried over Na_2SO_4. After filtration was the solvent removed under reduced pressure and the crude product was purified by column chromatography (silica gel, DCM) and dried *in vacuo*.

Yield: 0.496 g (66%)

R_f = 0.6 (DCM/MeOH 100:1)

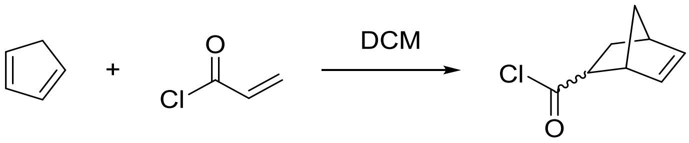
^{1}H-NMR (δ, 20°C, CDCl$_3$, 300 MHz): 8.67 (s, 4H, **H**$_{\text{Perylene}}$), 6.17 (dd, *J* = 5.3, 3.0 Hz, 1H, C**H**=CH), 5.91 (dd, *J* = 5.4, 2.6 Hz, 1H, C**H**=CH), 4.21 (t, *J* = 9.1 Hz, 2H, N-C**H**$_2$,), 4.05 – 3.98 (m, 2H, O-C**H**$_2$), 3.22 (bs, 1H, CH-CH$_2$-C**H**), 2.98 – 2.85 (m, 1H, C**H**-CH), 2.45 (bs, 1H, CH-CH$_2$-C**H**), 2.01 – 1.88 (m, 2H, C**H**$_2$-CH), 1.67 – 1.57 (m, 6H, N-CH$_2$-C**H**$_2$-, C**H**$_2$-CH$_2$-O), 1.53 – 1.20 (m, 12H, -C**H**$_2$-C**H**$_2$-C**H**$_2$-CH$_3$, CH$_2$-C**H**$_2$-C**H**$_2$-CH$_2$, CH-C**HH**-CH), 0.90 (t, *J* = 6.6 Hz, 3H, C**H**$_3$).

^{13}C-NMR (δ, 20°C, $CDCl_3$, 75 MHz): 162.36 (N-**C**O-C), 137.87 (**C**H=CH), 135.52 ($\mathbf{C}_{\text{Perylene}}$), 135.49 ($\mathbf{C}_{\text{Perylene}}$), 133.06 (H $\mathbf{C}_{\text{Perylene}}$), 132.51 (**C**H=CH), 131.57 ($\mathbf{C}_{\text{Perylene}}$), 128.77 ($\mathbf{C}_{\text{Perylene}}$), 128.69 ($\mathbf{C}_{\text{Perylene}}$), 123.42 ($\mathbf{C}_{\text{Perylene}}$), 123.33 ($\mathbf{C}_{\text{Perylene}}$), 77.58 ($\mathbf{C}H_2$), 77.16 ($\mathbf{C}H_2$), 76.74 ($\mathbf{C}H_2$), 64.51 ($\mathbf{C}H_2$), 64.28 ($\mathbf{C}H_2$), 49.76 ($\mathbf{C}H_2$), 46.50 ($\mathbf{C}H_2$), 45.85 (**C**H), 43.50(**C**H), 43.34 (**C**H), 42.67 (**C**H), 41.77 ($\mathbf{C}H_2$), 41.11 ($\mathbf{C}H_2$), 40.91 (**C**H), 38.23 ($\mathbf{C}H_2$), 38.02 ($\mathbf{C}H_2$), 36.59 (**C**H), 34.58 ($\mathbf{C}H_2$), 31.64 ($\mathbf{C}H_2$), 30.46 ($\mathbf{C}H_2$), 29.34 ($\mathbf{C}H_2$), 28.71 ($\mathbf{C}H_2$), 28.18 ($\mathbf{C}H_2$), 28.13 ($\mathbf{C}H_2$), 26.86 ($\mathbf{C}H_2$), 26.80 ($\mathbf{C}H_2$), 25.87 ($\mathbf{C}H_2$), 22.68 ($\mathbf{C}H_2$), 14.18 ($\mathbf{C}H_3$).

UV-Vis (DCM) λ_{max}, *nm (rel. in.)*: 426 (0.28), 484 (0.69), 518 (1)

3.3 Matrix monomers

3.3.1 Synthesis of 5-chlorocarbonylbicyclo[2.2.1]hept-2-ene



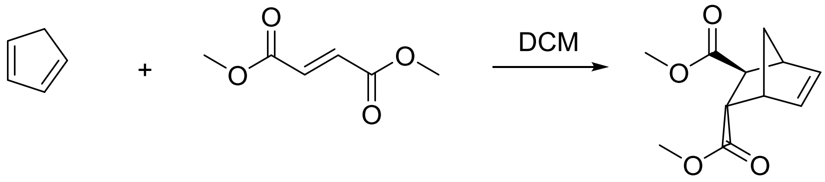
11

Fresh distilled cyclopentadiene (0.835 mL, 0.00993 mol) was dissolved in dry, ice-cooled DCM (25 mL). Acryloyl chloride (0.322 mL, 0.00397 mol) was added drop wise. The reaction mixture was stirred at room temperature for 3 hours. The progress of the reaction was monitored *via* TLC. The reaction mixture was used without any purification for further steps.

R_f = 0.59 (CH/EE 5:1)

3.3.2 Synthesis of dimethylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate

Literature:[53]



13

Dimethyl fumarate (10.01 g, 0.0679 mol) was dissolved in ice-cooled DCM (75 mL). Fresh distilled cyclopentadiene (6.43 mL, 0.0764 mol) was added slowly and the reaction mixture was stirred at room temperature for 15 hours. The solvent was removed under reduced pressure and crystallisation was initiated by adding a seed crystal. The product was dried *in vacuo* and was used without any further purification steps.

Yied: 12.47 g (87%)

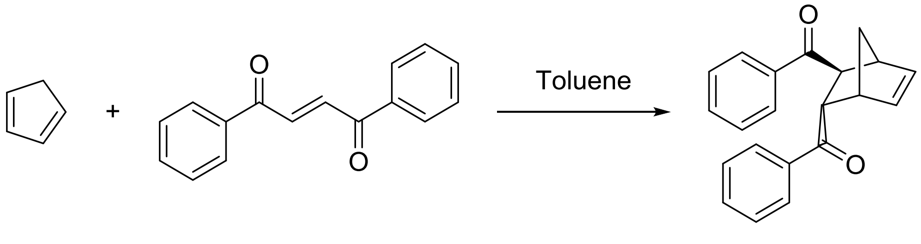
R_f = 0.19 (CH/EE 10:1)

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 6.24 (dd, *J* = 5.4, 3.1 Hz, 1H, C**H**=CH), 6.04 (dd, *J* = 5.5, 2.7 Hz, 1H, CH=C**H**), 3.68 (s, 3H, C**H_3**), 3.61 (s, 3H, C**H_3**), 3.34 (t, *J* = 4.1 Hz, 1H, OOC-C**H**), 3.23 (bs, 1H, CH-C**H**-CH), 3.09 (bs, 1H, CH-C**H**-CH), 2.65 (dd, *J* = 4.3, 1.4 Hz, 1H, OOC-C**H**), 1.58 (d, *J* = 8.8 Hz, 1H, CH-C**H**H-CH), 1.43 (dd, *J* = 8.8, 1.5 Hz, 1H, CH-CH**H**-CH).

^{13}C-NMR (δ, 20°C, $CDCl_3$, 75 MHz): 175.08 (**C**OO), 173.85 (**C**OO), 137.69 (**C**H=CH), 135.27 (CH=**C**H), 52.16 (**C**H_3), 51.88 (**C**H_3), 47.94 (OOC-**C**H-CH), 47.71 (OOC-**C**H-CH), 47.40 (CH-**C**H_2-CH), 47.17 (**C**H-CH), 45.70 (**C**H-CH)

3.3.3 Synthesis of bicyclo[2.2.1]hept-5-ene-2,3-diylbis(1-phenyl-methanone)

Literature:[54]



14

(E)-1,4-diphenylbut-2-ene-1,4-dione (4.9 g, 0.021 mol) was dissolved in toluene (75 mL). Fresh distilled cyclopentadiene (2.0 mL, 0.024 mol) was added slowly and the reaction mixture was stirred at room temperature for 15 hours. The solvent was removed under reduced pressure. The product was recrystallized from MeOH three times. The product was dried *in vacuo*.

Yield: 2.56 g (40%)

R_f = 0.78 (CH/EE 5:1)

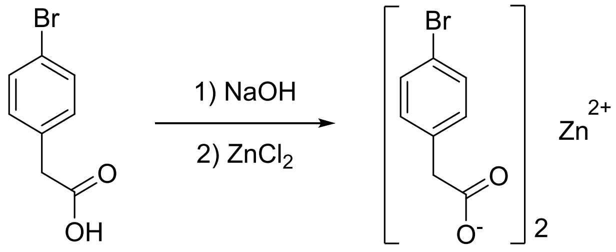
^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 8.12 – 7.91 (m, 4H, *o*-**H**$_{Ar}$), 7.55 (t, *J* = 7.2 Hz, 2H, *p*-**H**$_{Ar}$), 7.45 (dd, *J* = 10.8, 4.2 Hz, 4H, *m*-**H**$_{Ar}$), 6.43 (dd, *J* = 5.3, 3.1 Hz, 1H, C**H**=CH), 5.95 (dd, *J* = 5.4, 2.7 Hz, 1H, CH=C**H**), 4.51 (t, *J* = 4.0 Hz, 1H, OC-C**H**), 4.03 – 3.87 (m, 1H, OC-C**H**), 3.35 (bs, 1H, CH-C**H**-CH), 3.15 (bs, 1H, CH-C**H**-CH), 1.90 (d, *J* = 8.6 Hz, 1H, CH-C**H**H-CH), 1.49 (dd, *J* = 8.6, 1.3 Hz, 1H, CH-CH**H**-CH).

^{13}C-NMR (δ, 20°C, $CDCl_3$, 75 MHz): 200.96 (**C**O), 199.69 (**C**O), 137.27 (**C**=C), 137.07 (**C**-CO), 136.78 (**C**-CO), 134.73 (**C**=C), 133.23 (**C**H_{Ar}), 133.07 (**C**H_{Ar}), 128.76 (**C**H_{Ar}), 128.73 (**C**H_{Ar}), 128.71 (**C**H_{Ar}), 128.49 (**C**H_{Ar}), 50.70 (CO-**C**H), 48.87 (**C**H-CH_2), 48.10 (CO-**C**H) , 47.48 (**C**H-CH_2), (CH-**C**H_2-CH).

3.4 TTA-UC Sensitizer

3.4.1 Synthesis of Zn-4-bromophenylacetate

Literature:[47]



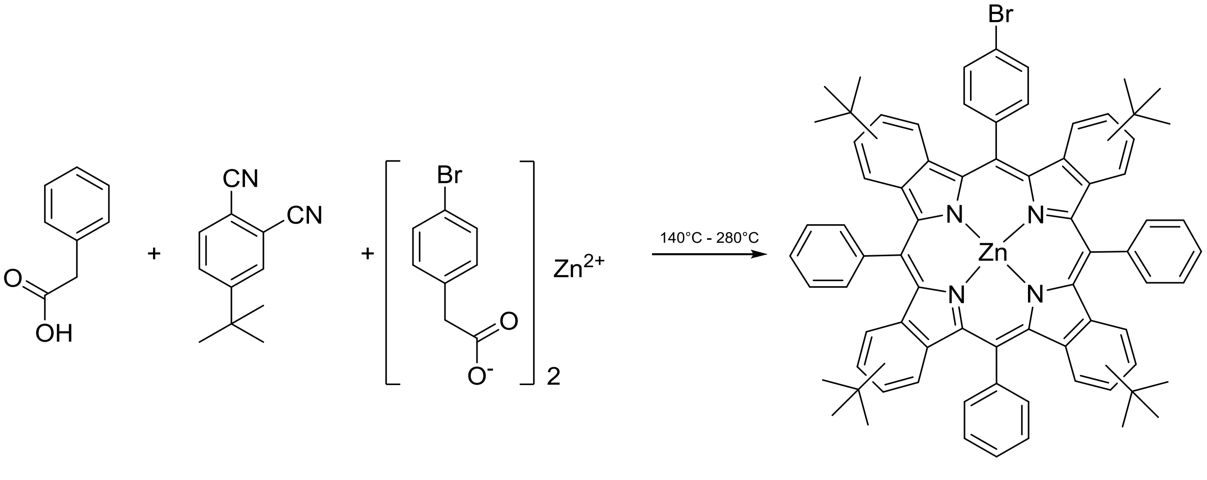
15

4-bromophenylacetic acid (20.0 g, 0.093 mol) was dissolved in a solution of NaOH (4.21 g, 0.11 mol) and deionized water (350 mL) at room temperature overnight. The remaining precipitate was filtered off. $ZnCl_2$ (6.51 g, 0.048 mol) dissolved in deionized water (25 mL) was added at once and a white precipitate was formed. For better crystallization the mixture was kept at 4 °C for 3 hours. The precipitate was filtered off and was washed twice with cold deionized water (75 mL). The product was dried in a vacuum drying oven *in vacuo* at 70 °C overnight.

Yield: 20.9 g (91%)

3.4.2 Zn-5-(4-bromphenyl)-10,15,20-tri(phenyl)-tetrabenzo-*tert*-butyl-porphyrin

Literature:[46]



16

Phenyl acetic acid (17.59 g, 0.129 mol), Zn-4-bromophenylacetate (7.98 g, 0.0162 mol) and 4-(*tert*-butyl)phthalonitrile (11.90 g, 0.0646 mol) were mixed and homogenized using a mortar. Portions of about 1 g each were put in into 4 ml vials, compressed with a glass rod and sealed with a metal screw cap. The vials were placed into a preheated metal block at 140°C. Immediately after the reaction start the temperature was increased to 280°C. The reaction progress was monitored *via* UV-Vis spectroscopy and thin layer chromatography. After 40 minutes the reaction was stopped and left to cool. The dark solid was dissolved in acetone (750 mL). The solvent was removed under reduced pressure. The product was precipitated from EtOH: The residue was redissolved in EtOH (500 mL). H_2O/sat. $NaHCO_3$ (4:1, 150 mL) was added drop wise under constant stirring. A green precipitate was formed. The precipitate was filtered off and dissolved in acetone. The solvent was removed under reduced pressure. The precipitation was repeated twice. The product was additionally purified by column chromatography (Al_2O_3, DCM) and dried *in vacuo*.

Yield: 1.27 g (6%)

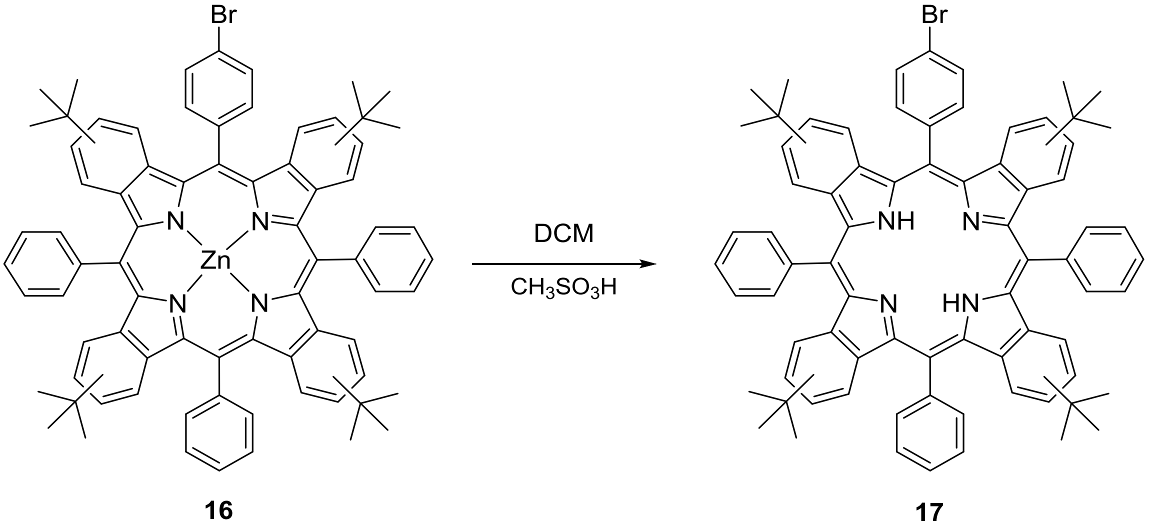
$R_f = 0.8$ (CH/EE 5:1)

UV-Vis (acetone) λ_{max}, *nm (rel. in.)*: 460 (1), 606 (0,05), 652 (0,20)

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 8.49 – 6.88 (m, 31H, $\mathbf{H}_{\text{Porphyrin}}$, $\mathbf{H}_{\text{Ar}}$), 1.40 – 1.12 (m, 36H, $(C\mathbf{H_3})_3$).

3.4.3 5-(4-bromphenyl)-10,15,20-tri(phenyl)-tetrabenzo-*tert*-butyl-porphyrin

Literature:[46]



A mixture of **16** (0.400 g, 0.339 mmol) and methanesulfonic acid (1.5 mL, 0.0231 mol) was dissolved in acetone (5 mL). The mixture was stirred for 0.5 hour. Subsequently DCM (100 mL) was added. The mixture was washed several times with H_2O/sat.$NaHCO_3$ (2:1, 100 mL) until the characteristic band of the protonated ligand (500 nm, acetone) was not observed any more *via* UV-Vis spectroscopy. The product was dried on Na_2SO_4 and the solvent was removed under reduced pressure.

Yield: 0.389 g (99%)

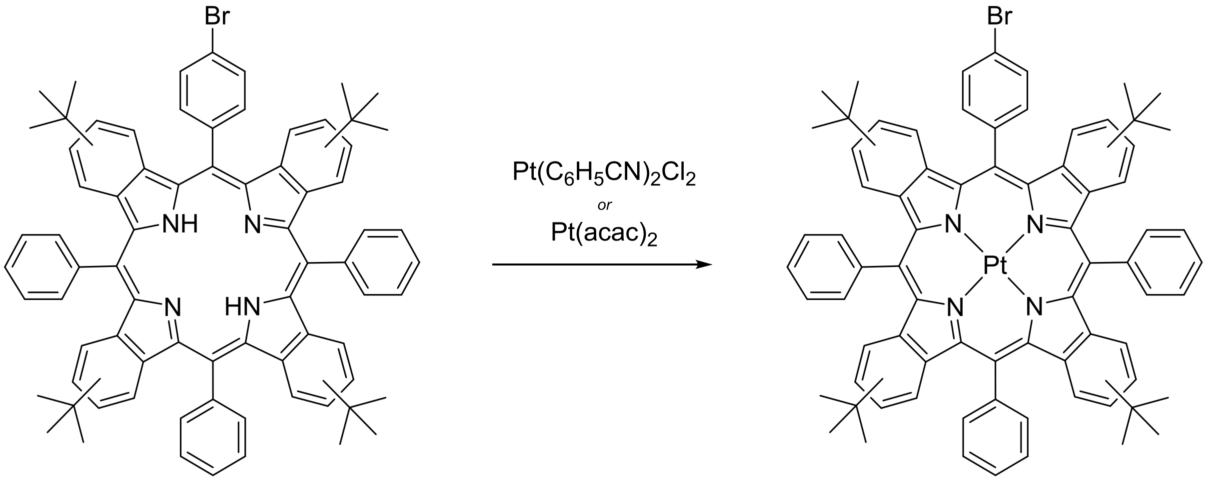
R_f = 0.47 (CH/DCM 2:1)

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 8.41– 6.90 (m, 31H, $\mathbf{H}_{\text{Porphyrin}}$, $\mathbf{H}_{\text{Ar}}$), 1.36 – 1.13 (m, 36H, $(C\mathbf{H_3})_3$), -1,4 (bs, 2H, N**H**).

UV-Vis (acetone) λ_{max}, *nm (rel. in.)*: 464 (1), 592 (0,05), 642 (0,17), 696 (0,06)

3.4.4 Pt(II)-5-(4-bromphenyl)-10,15,20-tri(phenyl)-tetrabenzo-*tert*-butyl-porphyrin

Literature:[46,50]



17 **18 (PtTPTB*tbut*P)**

Method A

The free ligand **17** (0.550 g, 0.492 mmol) was dissolved in cumene (200 mL) and heated to reflux. N_2 was bubbled through the reaction mixture. $Pt(C_6H_5CN)_2Cl_2$ (0.562 g, 1.19 mmol) was suspended in cumene (200 mL) and added in portions of 3 mL over 10 hours. The reaction progress was monitored *via* UV-Vis spectroscopy and thin layer chromatography. The solution was decanted of and the solvent was removed under reduced pressure. The product was purified by column chromatography (SiO_2, CH/DCM 3:1) and dried *in vacuo*.

Yield: 0.335 g (50%)

Method B

The free ligand **17** (30 mg, 0.0336 mmol) and $Pt(acac)_2$ (20.8 mg, 0.0529 mmol) was dissolved in benzonitrile (2 mL) and put into a 5 mL microwave vial. The glass tube was sealed with a septum and was placed in the microwave according to the device specific procedure. The reaction was heated from room temperature to 250 °C was held for 20 minutes at this temperature while the reaction mixture was stirred permanently. The reaction mixture was decanted and predicated from EtOH: The mixture was poured into EtOH (100 mL). Under stirring H_2O/brine (1:1, 100 mL) was added. The precipitate was filtered off and washed with deionized water (50 mL). The precipitate was redissolved in acetone (25 mL) and the solvent was removed under reduced pressure.

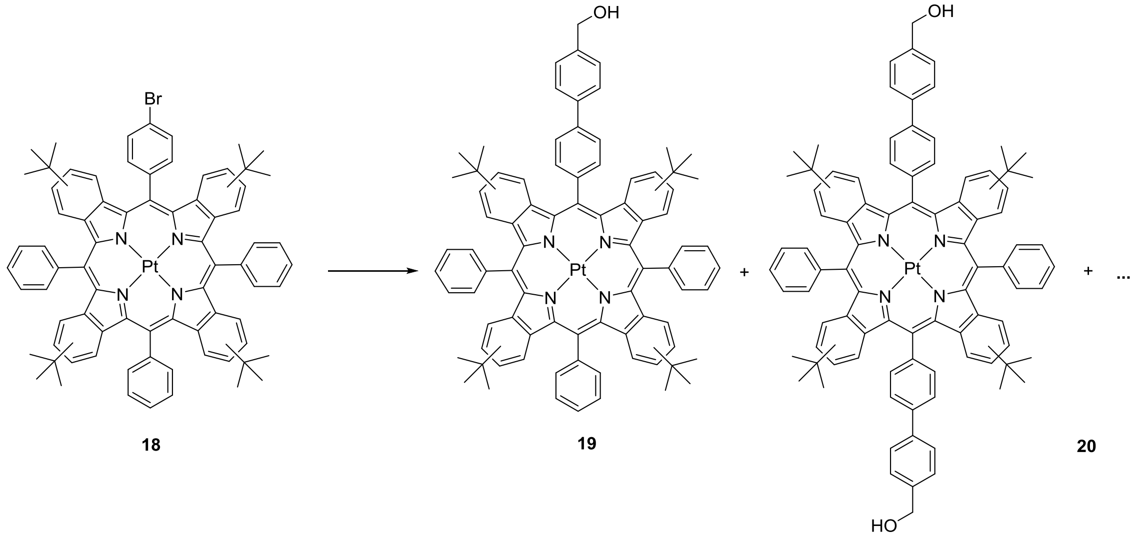
Yield: 24 mg (54%)

R_f = 0.80 (CH/DCM 2:1)

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 8.45– 6.80 (m, 31H, $\mathbf{H}_{Porphyrin}$, $\mathbf{H}_{Ar}$), 1.19 – 1.01 (m, 36H, $(C\mathbf{H_3})_3$).

UV-Vis (acetone) λ_{max}, *nm (rel. in.)*: 426 (1), 564 (0,09), 616 (0,62)

3.4.5 Pt(II)-5-((4-hydroxymethyl)-biphenyl)-10,15,20-tri(phenyl)-tetrabenzo-*tert*-butyl-porphyrin and Pt(II)-di((4-hydroxymethyl)-biphenyl)-di(phenyl)-tetrabenzo-*tert*-butyl-porphyrin



A mixture of **18** (0.300 g, 0.229 mmol) was dissolved in toluene (15 mL) and MeOH (5 mL). The solution was deoxygenised for 30 minutes. Subsequently the 4-(Hydroxymethl)-pheyl-boronic acid (0.126 g, 0.826 mmol) and $Pd(PPh_3)_4$ (16 mg, 5 mol%) was added. The reaction mixture war stirred under inert atmosphere at 65 °C for 72 hours. DCM (50 mL) was added and the organic phase was washed with H_2O (25 mL) and sat. $NaHSO_4$-solution (25 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure. The products were isolated by column chromatography (SiO_2). **19** was eluted with CH/EE 10:1 and **20** was eluted CH/EE 1:1.

Yield **19**: 0.115 g (37%)

R_f **19** = 0.14 (CH/EE 5:1)

^{1}H-NMR (δ, 20°C, DMSO, 300 MHz) **19**: 8.35 – 6.81 (m, 35H, $\mathbf{H}_{Porphyrin}$, $\mathbf{H}_{Ar}$), 5.34 (dd, J = 8.9, 5.1 Hz, 1H, O**H**), 4.62 (d, J = 5.4 Hz, 2H, C$\mathbf{H_2}$-OH), 1.20 – 1.01 (m, 36H, $(C\mathbf{H_3})_3$).

MS (MALDI-TOF) *m/z*: 1337.6288 (calcd for $C_{83}H_{74}N_4OPt$, $[M]^+$ 1337.5516)

Yield **20**: 0.065 g (16%)

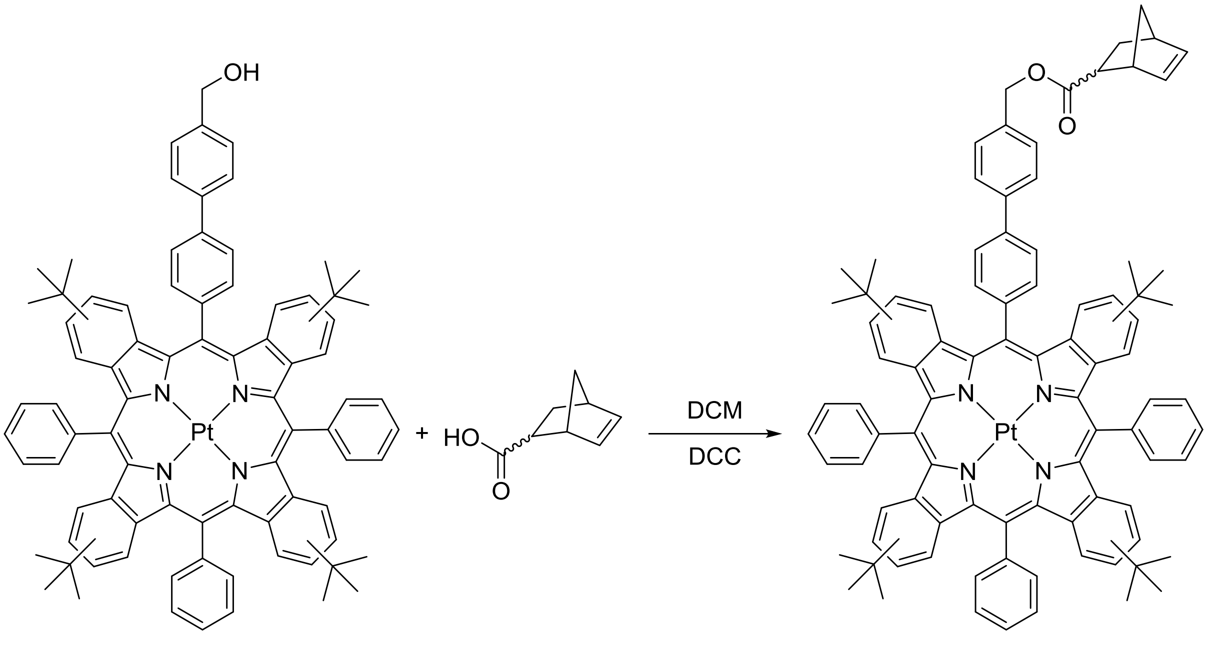
R_f **20** = 0.75 (CH/EE 1:1)

^{1}H-NMR (δ, 20°C, DMSO, 300 MHz) **20**: 8.36 – 6.72 (m, 38H, $\mathbf{H}_{Porphyrin}$, $\mathbf{H}_{Ar}$), 5.37 – 5.28 (m, 2H, O**H**), 4.61 (d, *J* = 5.4 Hz, 4H, C$\mathbf{H_2}$-OH), 1.22 – 1.03 (m, 36H, (C$\mathbf{H_3}$)$_3$).

MS (MALDI-TOF) *m/z*: 1443.5814 (calcd for $C_{90}H_{80}N_4O_2Pt$, $[M]^+$ 1443.5935

3.4.6 Pt(II)-5-(biphenyl -4-metyl-((1R,4R)-bicyclo[2.2.1]hept-5-ene-2-carboxylate)-10,15,20-tri(phenyl)-tetrabenzo-*tert*-butyl-porphyrin

Literature:[52]



19 **21 (PtTPTB*tbut*P)**

A mixture of **19** (0.340 g, 0.0822 mmol), 5-norborne-2-carboxylic acid (0.224 g, 1.62 mmol) and DMAP (catalytic amount, spatula tip) were dissolved in dry, ice-cooled DCM (15 mL). DCC (0.342 g, 1.58 mmol) was added and after 5 minutes the reaction mixture was allowed to warm to room temperature and the mixture was stirred for 24 hours. The precipitate was filtered off and the solvent was removed under reduced pressure. The product was purified by column chromatography (SiO_2, CH/DCM 1:1) and dried *in vacuo*.

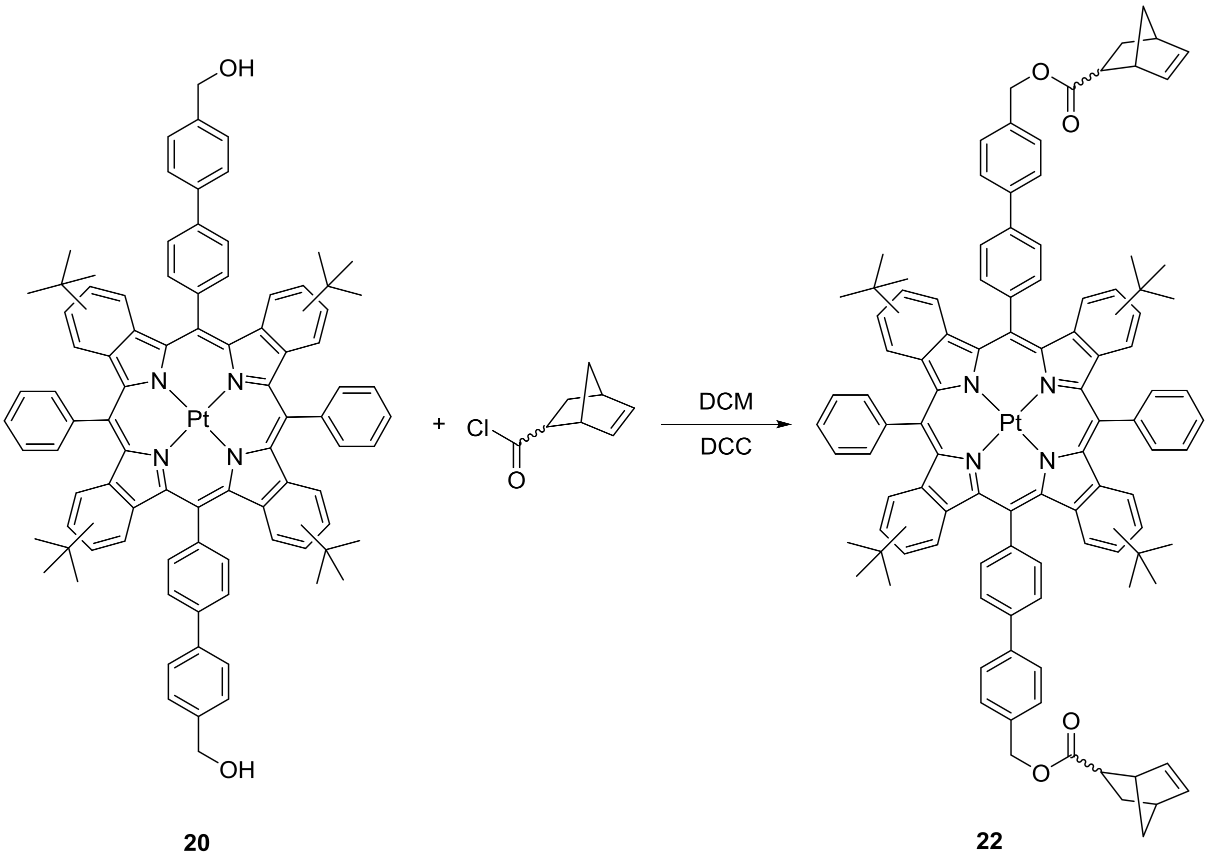
Yield: 0.106 g (88%)

R_f = 0.56 (CH/EE 5:1)

^{1}H-NMR (δ, 20°C $CDCl_3$, 300 MHz): 8.46 – 6.90 (m, 35H, $\mathbf{H}_{\text{Porphyrin}}$, $\mathbf{H}_{\text{Ar}}$), 6.28 (dd, *J* = 5.1, 3.0 Hz, 1H, C**H**=CH), 6.06 – 5.98 (m, 1H, C**H**=CH), 5.25 (s, 2H, O-C$\mathbf{H_2}$), 3.35 (bs, 1H, C**H**-CH_2-CH), 3.11 (dd, *J* = 9.2, 3.7 Hz, 1H, CO-C**H**), 2.99 (bs, 1H, C**H**-CH_2-CH), 2.11 – 1.88 (m, 2H, C$\mathbf{H_2}$-CH), 1.62 – 1.11 (m, 38H, CH-C$\mathbf{H_2}$-CH, (C$\mathbf{H_3}$)$_3$).

MS (MALDI-TOF) *m/z*: 1457.7949 (calcd for $C_{90}H_{82}N_4O_2Pt$, $[M]^+$ 1457.6091)

3.4.7 Pt(II)-di(biphenyl -4-metyl-((1R,4R)-bicyclo[2.2.1]hept-5-ene-2-carboxylate) -di(phenyl)-tetrabenzo-*tert*-butyl-porphyrin



20

22

A mixture of **20** (0.065 g, 0.0450 mmol), 5-norborne-2-carboxylic acid (0.289 g, 2.09 mmol) and DMAP (catalytic amount, spatula tip) were dissolved in dry, ice-cooled DCM (15 mL). DCC (0.408 g, 1.98 mmol) was added and after 5 minutes the reaction mixture was allowed to warm to room temperature and the mixture was stirred for 24 hours. The precipitate was filtered off and the solvent war removed under reduced pressure. The product was purified by column chromatography (SiO_2, CH/EE 5:1) and dried *in vacuo*.

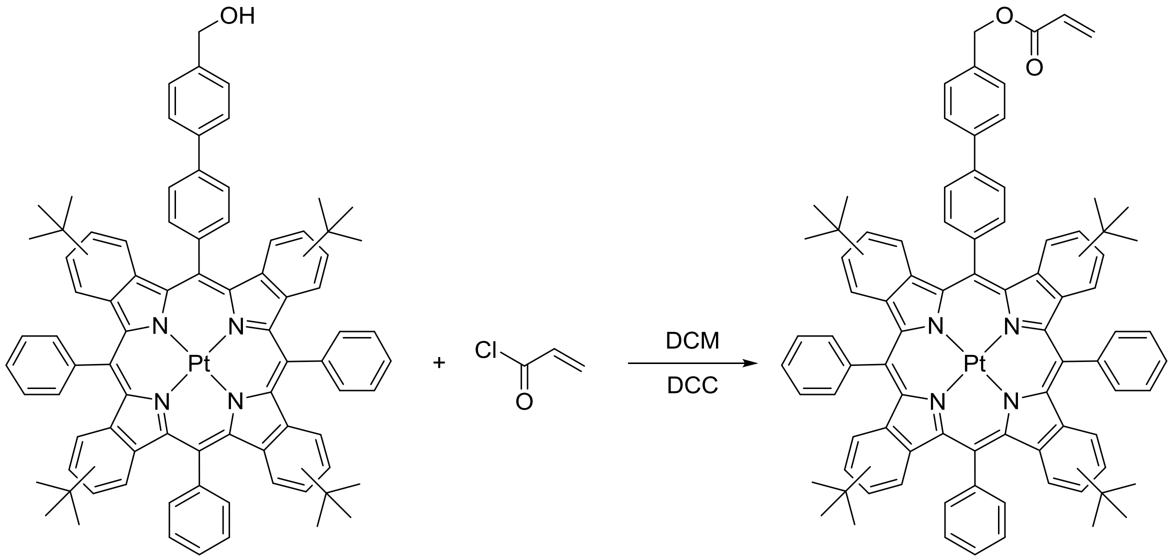
Yield: 0.106 g (86%)

R_f = 0.44 (CH/EE 5:1)

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 8.48 – 6.95 (m, 38H, $\mathbf{H}_{\text{Porphyrin}}$, $\mathbf{H}_{\text{Ar}}$), 6.30 – 6.24 (m, 1H, C**H**=CH), 6.06 – 5.87 (s, 1H, C**H**=CH), 5.23 (s, 4H, O-C$\mathbf{H_2}$), 3.33 (bs, 2H, C**H**-CH_2-CH), 3.15 – 3.00 (m, 2H, CO-C**H**), 2.96 (bs, 2H, C**H**-CH_2-CH), 2.8 – 1.90 (m, 4H, C$\mathbf{H_2}$-CH), 1.79 – 1.10 (m, 40H).

MS (MALDI-TOF) *m/z*: 1683.7147 (calcd for $C_{106}H_{96}N_4O_4Pt$, $[M]^+$ 1683.7086)

3.4.8 Pt(II)-5-(biphenyl -4-metyl-acrylate)-10,15,20-tri(phenyl)-tetrabenzo-*tert*-butyl-porphyrin



19

23

(endgroupPtTPTB*tbut*P)

A mixture of **19** (0.015 g, 0.0112 mmol), acrylic acid (3.1 µL, 0.0452 mmol) and DMAP (catalytic amount, spatula tip) were dissolved in dry, ice-cooled DCM (10 mL). DCC (0.011 g, 0.0533 mmol) was added and after 5 minutes the reaction mixture was allowed to warm to room temperature and the mixture was stirred for 2 hours. The precipitate was filtered off and the solvent was removed under reduced pressure. The product was purified by column chromatography (SiO_2, CH/EE 10:1) and dried *in vacuo*.

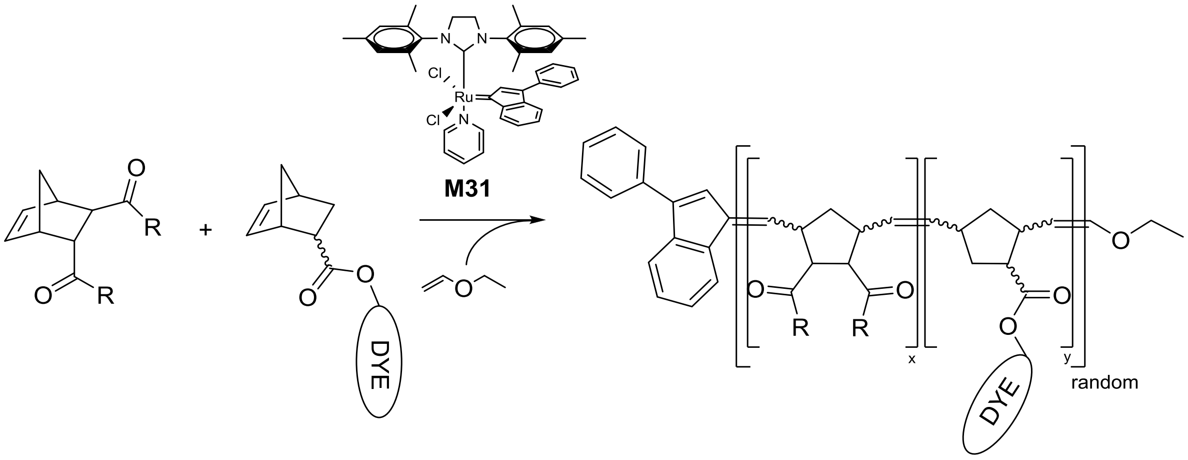
Yield: 0.007 g (45%)

R_f = 0.68 (CH/EE 5:1)

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 8.45 – 6.89 (m, 35H, $\mathbf{H}_{Porphyrin}$, $\mathbf{H}_{Ar}$), 6.60 – 6.42 (m, 1H, CH=C**H**H), 6.33 – 6.12 (m, 1H, C**H**=CH_2), 5.97 – 5.83 (m, 1H, CH=CH**H**), 5.25 (s, 1H, O-C$\mathbf{H_2}$).

MS (MALDI-TOF) *m/z*: 1391.6140 (calcd for $C_{90}H_{82}N_4O_2Pt$, $[M]^+$ 1391.5623)

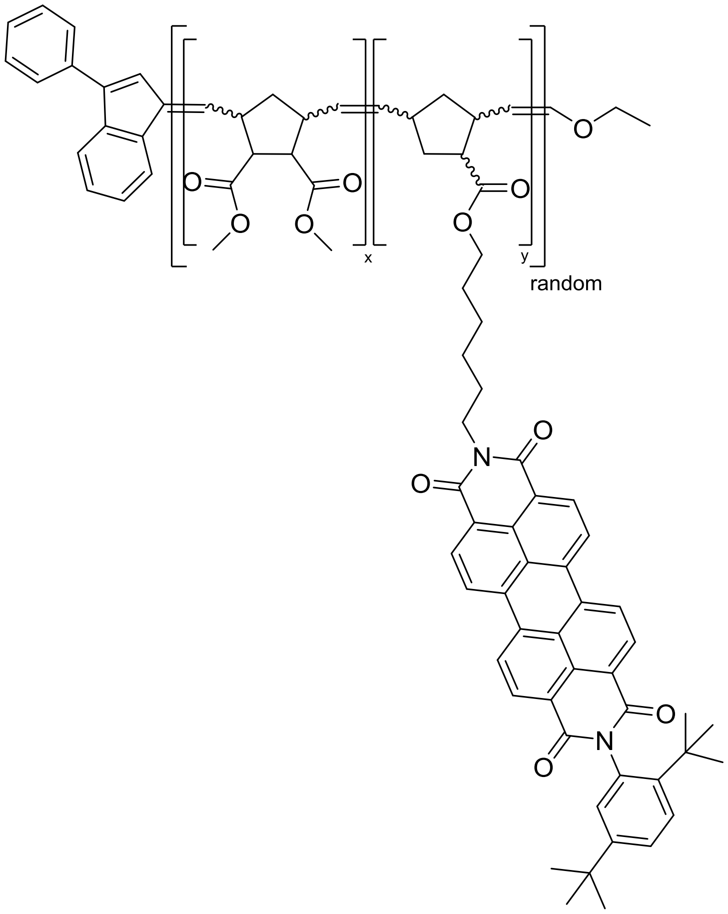
3.5 Polymerization



3.5.1 General procedure

The polymerization was carried in inert atmosphere. Stock solutions of the matrix monomer, the monomer-functionalized dye and the catalyst (**M31**) in dry DCM were prepared to overcome the limitation of weighing small masses. The corresponding volume of matrix monomer and norbornene-functionalized dye were put into a Schlenk tube. Dry DCM was added so that the total volume was about 5 mL. Finally the corresponding volume of catalyst was added. The reaction mixture was stirred at room temperature until the monomers could not be monitored *via* thin layer chromatography. The polymerization was terminated with an excess of ethyl-vinyl ether or **23** and was stirred for additional 30 minutes. The reaction mixture was concentrated to half the volume under N_2 flow. The polymer was precipitated in cold methanol three times. The solvent was decanted off and the product was dried *in vacuo*.

3.5.2 poly13-*tbutyl*AP-1wt% to poly13-tbutylAP-40wt%



poly13-tbutylAP-*X*wt%

Figure 30. The composition is given in table 2. The theoretical chain length was 1000 monomer units.

Seven polymers with a dye content of 1 wt%, 2 wt%, 4 wt%, 10 wt%, 20 wt%, 30 wt% and 40 wt%, respectively 0.26 mol%, 0.52 mol% , 1.04 mol%, 2.56 mol% 5.00 mol%, 7.32 mol% and 9.52 mol% were prepared analogously to the general procedure. To **13** (200 mg, 0.951 mmol) the corresponding amount of **4** and **M31** was added and the polymerization was terminated with an excess of ethyl-vinyl ether. The theoretical chain length was 1000 monomer units.

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 8.80 – 8.21 (m, 4 · mol% H, $\mathbf{H}_{\text{Perylene}}$), 7.60 (d, *J* = 8.4 Hz, 1 · mol% H, C**H**-CH-$C(CH_3)_3$), 7.47 (d, *J* = 8.1 Hz, 1 · mol% H, C**H**-CH-$C(CH_3)_3$), 5.62 – 5.04 (m, 2H, C**H**=C**H**), 4.30 – 3.82 (m, 4 · mol% H, O-C$\mathbf{H_2}$, N-C$\mathbf{H_2}$), 3.75 – 3.53 (m, 6H, O-CH_3), 3.42 – 2.59 (m, 4H,cp$^{1\text{-}4}$), 1.98 (bs, 1H, CH-C**H**H-CH), 1.80 – 1.15 (m, 1 + 8 · mol% + 18 · mol % H, CH-C**H**H-CH, N-CH_2-(C$\mathbf{H_2}$)$_4$, (C$\mathbf{H_3}$)$_3$).

Table 2. Characterization of the polymers poly13-*tbutyl*AP-*X*wt%.

	poly13-*tbutyl*AP-1wt%	**poly13-*tbutyl*A-2wt%**	**poly13-*tbutyl*AP-4wt%**	**poly13-*tbutyl*AP-10wt%**	**poly13-*tbutyl*AP-20wt%**	**poly13-*tbutyl*AP-30wt%**	**poly13-*tbutyl*AP-40wt%**
c(***tbutyl*AP**)	1 wt%	2 wt%	4 wt%	10 wt%	20 wt%	30 wt%	40 wt%
c(***tbutyl*AP**)	0.26 mol%	0.52 mol%	1.04 mol%	2.56 mol%	5.00 mol%	7.32 mol%	9.52 mol%
matrix:dye	997:3	995:5	990:10	974:26	950:50	929:71	909:91
	380:1	190:1	95:1	38:1	19:1	13:1	10:1
M_n	$6.21 \cdot 10^5$	$6.03 \cdot 10^5$	$6.35 \cdot 10^5$	$7.33 \cdot 10^5$	$2.25 \cdot 10^5$	$3.25 \cdot 10^5$	$2.56 \cdot 10^5$
PDI	1.05	1.23	1.19	1.24	3.50	5.86	9.05
T_G [°C]	92.76	93.91	96.16	101.13	108.63	118.15	122.00

3.5.3 poly13-*tbutyl*AP-*X*wt%_PtTPTB*tbut*PBr -*Y*wt%

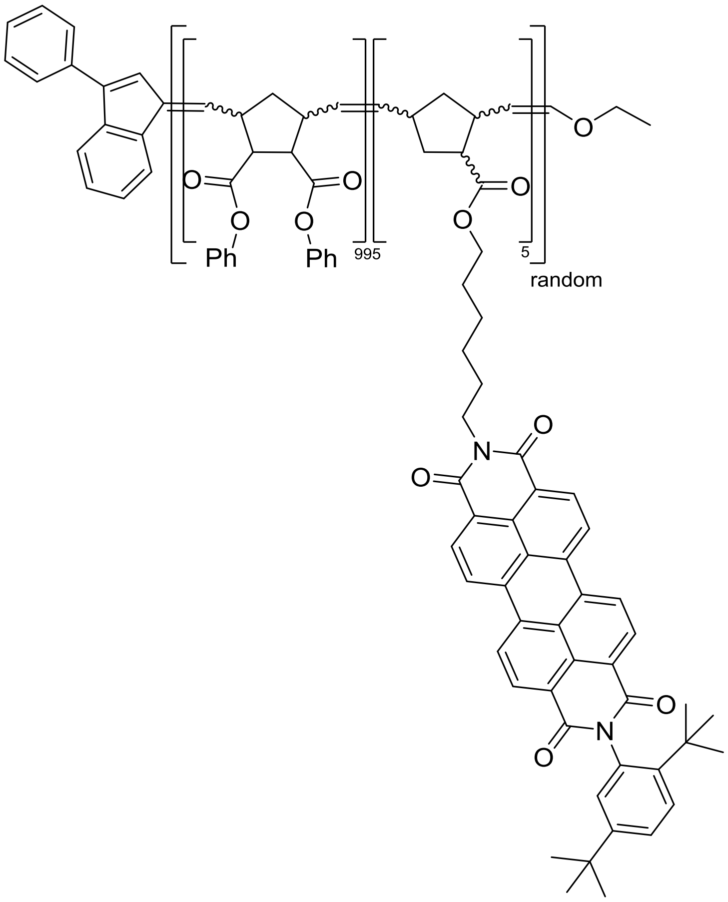
A concentration series with four sensitizer concentration was made. The copolymers were blended with 0.005 wt%, 0.05 wt%, 0.5 wt% and 5 wt% **18** (revered to the copolymers). 10 mg to 15 mg of each polymer dissolved in DCM (1 mL) in a 4 mL vial and the corresponding volume of a parent solution of **18** was added. For probes with 0.005 wt% and 0.05 wt% **18** the concentration of the parent solution was 1.33 mol/L and for probes with 0.5 wt% and 5 wt% the concentration was 0.0133 mol/L. The mixture was stirred for half an hour and subsequently the solvent was evaporated under nitrogen flow and dyed *in vacuo*. All weights, concentrations and the ratios between emitter and sensitizer are given in Table 3.

Table 3. Characterization of the polymers poly13-*tbutyl*AP-*X*wt%_PtTPTB*tbut*PBr-*Y*wt%.

	c(Emitter) [wt%]	c(Sensitizer) [wt%]	Emitter [mol]	Sensitize [mol]	Emitter:Sensitizer
poly13-*tbutyl*AP-1wt%_PtTPTB*tbut*PBr-0.005wt%	1 wt%	0.005 wt%	$1.17\cdot 10^{-7}$	$3.55 \cdot 10^{-7}$	328:1
poly13-*tbutyl*AP-1wt%_PtTPTB*tbut*PBr-0.05wt%	1 wt%	0.05 wt%	$1.35 \cdot 10^{-7}$	$4.11 \cdot 10^{-9}$	33:1
poly13-*tbutyl*AP-1wt%_PtTPTB*tbut*PBr-0.5wt%	1 wt%	0.5 wt%	$1.35 \cdot 10^{-7}$	$4.11 \cdot 10^{-8}$	3:1
poly13-*tbutyl*AP-1wt%_PtTPTB*tbut*PBr-5wt%	1 wt%	5 wt%	$1.90 \cdot 10^{-7}$	$5.80 \cdot 10^{-7}$	0.3:1
poly13-*tbutyl*AP-2wt%_PtTPTB*tbut*PBr-0.005wt%	2 wt%	0.005 wt%	$3.76 \cdot 10^{-7}$	$5.73 \cdot 10^{-10}$	657:1
poly13-*tbutyl*AP-2wt%_PtTPTB*t-but*PB -0.05wt%	2 wt%	0.05 wt%	$3.16 \cdot 10^{-7}$	$4.82 \cdot 10^{-9}$	66:1
poly13-*tbutyl*AP-2wt%_PtTPTB*tbut*PBr-0.5wt%	2 wt%	0.5 wt%	$2.29 \cdot 10^{-7}$	$3.49 \cdot 10^{-8}$	7:1
poly13-*tbutyl*AP-2wt%_PtTPTB*tbut*PBr-5wt%	2 wt%	5 wt%	$2.54 \cdot 10^{-7}$	$3.86 \cdot 10^{-7}$	0.7:1
poly13-*tbutyl*AP-4wt%_PtTPTB*tbut*PBr-0.005wt%	4 wt%	0.005 wt%	$5.16 \cdot 10^{-7}$	$3.93 \cdot 10^{-10}$	1313:1
poly13-*tbutyl*AP-4wt%_PtTPTB*tbut*PBr-0.05wt%	4 wt%	0.05 wt%	$6.22 \cdot 10^{-7}$	$4.74 \cdot 10^{-9}$	131:1
poly13-*tbutyl*AP-4wt%_PtTPTB*tbut*PBr-0.5wt%	4 wt%	0.5 wt%	$5.04 \cdot 10^{-7}$	$3.84 \cdot 10^{-8}$	13:1
poly13-*tbutyl*AP-4wt%_PtTPTB*tbut*PBr-5wt%	4 wt%	5 wt%	$5.04 \cdot 10^{-7}$	$3.84 \cdot 10^{-7}$	1.3:1
poly13-*tbutyl*AP-10wt%_PtTPTB*tbut*PBr-0.005wt%	10 wt%	0.005 wt%	$1.35 \cdot 10^{-7}$	$4.11 \cdot 10^{-10}$	3283:1
poly13-*tbutyl*AP-10wt%_PtTPTB*tbut*PBr-0.05wt%	10 wt%	0.05 wt%	$1.52 \cdot 10^{-6}$	$4.63 \cdot 10^{-9}$	328:1
poly13-*tbutyl*AP-10wt%_PtTPTB*tbut*PBr-0.5wt%	10 wt%	0.5 wt%	$2.11 \cdot 10^{-6}$	6.43E-08	33:1
poly13-*tbutyl*AP-	10 wt%	5 wt%	$1.70 \cdot 10^{-6}$	$5.19 \cdot 10^{-7}$	3:1

10wt%_PtTPTB*tbut*PBr-5wt%					
poly13-*tbutyl*AP-20wt%_PtTPTB*tbut*PBr-0.005wt%	20 wt%	0.005 wt%	$2.99 \cdot 10^{-6}$	$4.55 \cdot 10^{-10}$	6565:1
poly13-*tbutyl*AP-20wt%_PtTPTB*tbut*PBr-0.05wt%	20 wt%	0.05 wt%	$2.98 \cdot 10^{-6}$	$4.54 \cdot 10^{-9}$	657:1
poly13-*tbutyl*AP-20wt%_PtTPTB*tbut*PBr-0.5wt%	20 wt%	0.5 wt%	$2.40 \cdot 10^{-6}$	$3.65 \cdot 10^{-8}$	66:1
poly13-*tbutyl*AP-20wt%_PtTPTB*tbut*PBr-5wt%	20 wt%	5 wt%	$2.72 \cdot 10^{-6}$	$4.14 \cdot 10^{-7}$	7:1
poly13-*tbutyl*AP-30wt%_PtTPTB*tbut*PBr-0.005wt%	30 wt%	0.005 wt%	$4.09 \cdot 10^{-6}$	$4.16 \cdot 10^{-10}$	9848:1
poly13-*tbutyl*AP-30wt%_PtTPTB*tbut*PBr-0.05wt%	30 wt%	0.05 wt%	$4.69 \cdot 10^{-6}$	$4.76 \cdot 10^{-9}$	985:1
poly13-*tbutyl*AP-30wt%_PtTPTB*tbut*PBr-0.5wt%	30 wt%	0.5 wt%	$4.44 \cdot 10^{-6}$	$4.51 \cdot 10^{-8}$	98:1
poly13-*tbutyl*AP-30wt%_PtTPTB*tbut*PBr-5wt%	30 wt%	5 wt%	$3.81 \cdot 10^{-6}$	$3.87 \cdot 10^{-7}$	10:1
poly13-*tbutyl*AP-40wt%_PtTPTB*tbut*PBr-0.005wt%	40 wt%	0.005 wt%	$6.41 \cdot 10^{-6}$	$4.88 \cdot 10^{-10}$	13131:1
poly13-*tbutyl*AP-40wt%_PtTPTB*tbut*PBr-0.05wt%	40 wt%	0.05 wt%	$7.05 \cdot 10^{-6}$	$5.37 \cdot 10^{-9}$	1313:1
poly13-*tbutyl*AP-40wt%_PtTPTB*tbut*PBr-0.5wt%	40 wt%	0.5 wt%	$4.74 \cdot 10^{-6}$	$3.61 \cdot 10^{-8}$	131:1
poly13-*tbutyl*AP-40wt%_PtTPTB*tbut*PBr-5wt%	40 wt%	5 wt%	$7.05 \cdot 10^{-6}$	$5.37 \cdot 10^{-7}$	13:1

3.5.4 poly14-*tbutyl*AP-0.65wt%



poly14-*tbutyl*AP-0,65wt%

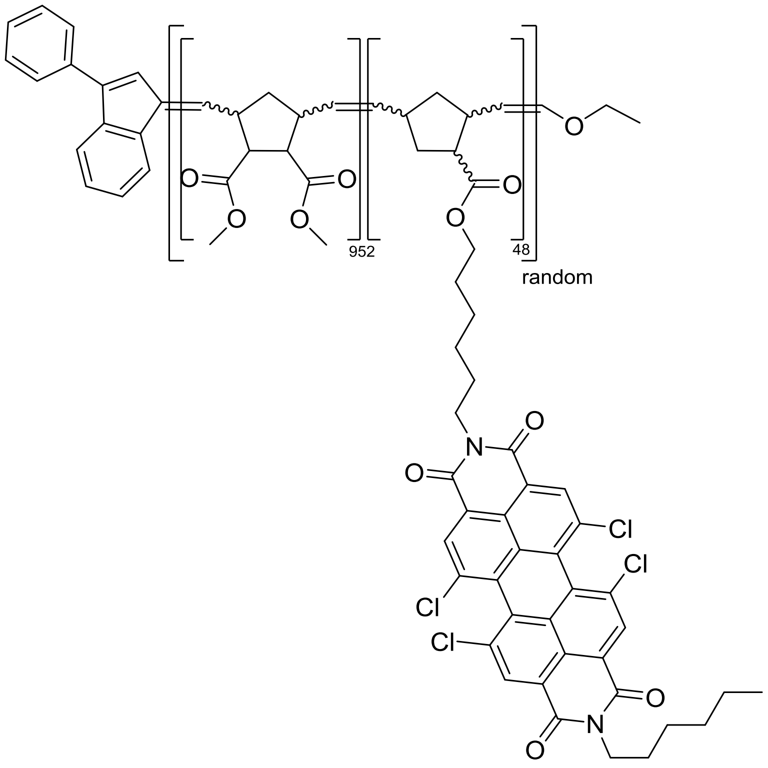
poly14-*tbutyl*AP-0.65wt%, with a dye content of 0.65 wt%, respectively 0.5 mol% was prepared analogously to the general procedure. To **14** (100 mg, 0.331 mmol) the corresponding amount of **11** (1.3 mg, 0.0016 mmol) and **M31** (0.24 mg, 0.00033 mmol) was added and the polymerization was terminated with an excess of ethyl-vinyl ether. The theoretical chain length was 1000 monomer units.

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 7.83 – 6.66 (m, 10H, $\mathbf{H}_{Ar}$), 5.57 – 4.56 (m, 2H, C**H**=C**H**), 4.32 – 2.39 (m, 4H, cp$^{1-4}$), 2.23 – 0.90 (m, 2H, CH-C$\mathbf{H_2}$-CH).

PDI: 1.19

T_G: 147.8 °C

3.5.5 poly13-ClPc6-20wt%



poly13-ClPc6-20wt%

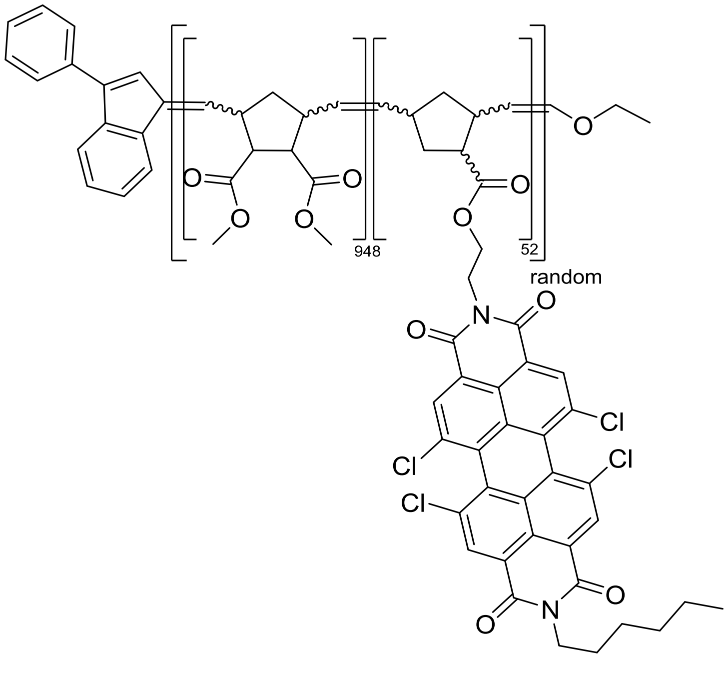
poly13-ClPc6-20wt%, with a dye content of 20 wt%, respectively 4.81 mol% was prepared analogously to the general procedure. To **13** (200 mg, 0.951 mmol) the corresponding amount of **11** (40 mg, 0.048mmol) and **M31** (0.73 mg, 0.00097 mmol) was added and the polymerization was terminated with an excess of ethyl-vinyl ether. The theoretical chain length was 1000 monomer units.

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 8.68 (s, 0.2H, $\mathbf{H}_{\text{Perylene}}$), 5.58 – 5.08 (m, 2H, C**H**=C**H**), 4.31 – 3.95 (m, 0.3H, N-C$\mathbf{H_2}$, O-C$\mathbf{H_2}$), 3.76 – 3.54 (m, 6H, O-CH_3), 3.43 – 2.62 (m, 4H, cp$^{1-4}$), 1.97 (s, 1H, CH-C**H**H-CH), 1.80 – 1.22 (m, 1.8H, CH-C**H**H-CH, N-CH_2-(C$\mathbf{H_2}$)$_4$-CH_3, N-CH_2-(C$\mathbf{H_2}$)$_4$-CH_2-O), 0.90 (m, 0.2H, C$\mathbf{H_3}$).

PDI: 3.73

Tg: 81.91 °C

3.5.6 poly13-ClPc2-20wt%



poly13-ClPc2-20wt%

poly13-ClPc2-20wt%, with a dye content of 20 wt%, respectively 5.14 mol% was prepared analogously to the general procedure. To **13** (100 mg, 0.476 mmol) the corresponding amount of **9** (20 mg, 0.0257 mmol) and **M31** (0.36 mg, 0.000487 mmol) was added and the polymerization was terminated with an excess of ethyl-vinyl ether. The theoretical chain length was 1000 monomer units.

^{1}H-NMR (δ, 20°C, $CDCl_3$, 300 MHz): 8.69 (s, 0.2H, **H**$_{\text{Perylene}}$), 5.58 – 5.01 (m, 2H,C**H**=C**H**), 4.56 – 4.41 (m, 0.1H, O-C**H₂**), 4.30 – 4.13 (m, 0.2H, N-C**H₂**-CH₂-O, N-C**H₂**), 3.76 – 3.54 (m, 6H, O-C**H₃**), 3.43 – 2.59 (m, 4H, cp$^{1\text{-}4}$), 1.97 (s, 1H, CH-C**H**H-CH), 1.80 – 1.29 (m, 1.4H, CH-C**H**H-CH, N-CH₂-(C**H₂**)₄-CH₃), 0.95 – 0.85 (m, 0.2, C**H₃**).

PDI: 4.21

Tg: 81.94 °C

3.5.7 poly13-PtTPT*tbut*BP-0.005wt% to poly13-PtTPTB*tbut*P-5wt%

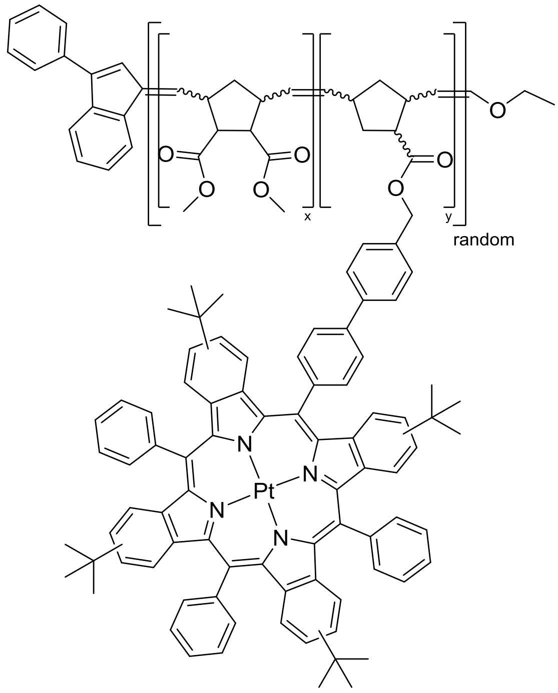


Figure 31. The composition is given in table 4. The theoretical chain length was 1000 monomer units.

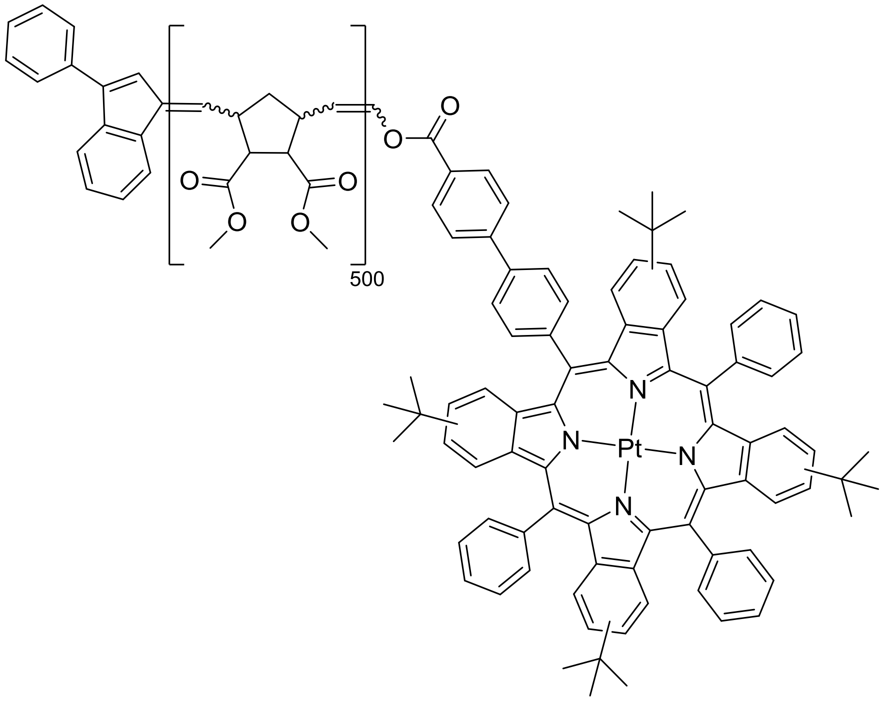
Four polymers with a dye content of 0.005 wt%, 0.05 wt%, 0.5 wt% and 5 wt%, respectively 0.000764 mol%, 0.00721 mol% , 0.0721 mol% and 0.7160 mol% were prepared analogously to the general procedure. To **13** (200 mg, 0.951 mmol) the corresponding amount of **21** and **M31** was added and the polymerization was terminated with an excess of ethyl-vinyl ether, expect **poly13-PtTPTB*tbut*P-5wt%** in this batch was halved.

^{1}H-NMR (δ, 20°C, CDCl$_3$, 300 MHz): 5.60 – 5.08 (m, 2H, C**H**=C**H**), 3.74 – 3.55 (m, 6H, O-CH$_3$), 3.45 – 2.58 (m, 4H,cp$^{1-4}$), 1.97 (bs, 1H, CH-C**H**H-CH), 1.45 (bs, 1H, CH-C**H**H-CH)

Table 4. Characterization of the polymers poly13-PtTPT*tbut*P-*X*wt%.

	poly13-PtTPTB*tbut*P-0.005wt%	**poly13-PtTPTB*tbut*P-0.05wt%**	**poly13-PtTPTB*tbut*P-0.5wt%**	**poly13-PtTPTB*tbut*P-5wt%**
c(**PtTPTB*tbut*P**)	0.005 wt%	0.05 wt%	0.5 wt%	5 wt%
c(**PtTPTB*tbut*P**)	0.000764 mol%	0.00721 mol%	0.0721 mol%	0.7160 mol%
matrix:dye	130819:1	13867:1	1387:1	138:1
M_n	$4.73 \cdot 10^4$	$5.21 \cdot 10^5$	$2.06 \cdot 10^6$	$1.05 \cdot 10^4$
PDI	1.01	1.03	1.95	1.47
T_G [°C]	93.39	94.46	91.54	96.31

3.5.8 poly13-endgroupPtTPTB*tbut*P



poly13-endgroupPtTPTB*tbut*P

poly13-endgroupPtTPTB*tbut*P was prepared analogously to the general procedure. To **13** (200 mg, 0.951 mmol) the corresponding amount of **M31** was added and the polymerization was terminated with an excess of **23.** The theoretical chain length was 500 monomer units.

M_n: $3.21 \cdot 10^5$

PDI: 1.03

T_G: 91.0°C

4 Conclusion and Outlook

Three different perylene diimide derivatives with norbornene ester side groups were synthesized on purpose to be covalently bound emitters in polymeric TTA-UC (Figure 32). This was the first time perylene diimide was used in this contest. **ClPc2** and **ClPc6** differed only in the length of the spacer and had in contrast to ***tbutyl*AP** a twisted structure. ***tbutyl*AP** was the most promising chromophore due the high luminescence quantum yield and TTA-UC was proven in the literature[27–30] before and so the focus was set on this dye.

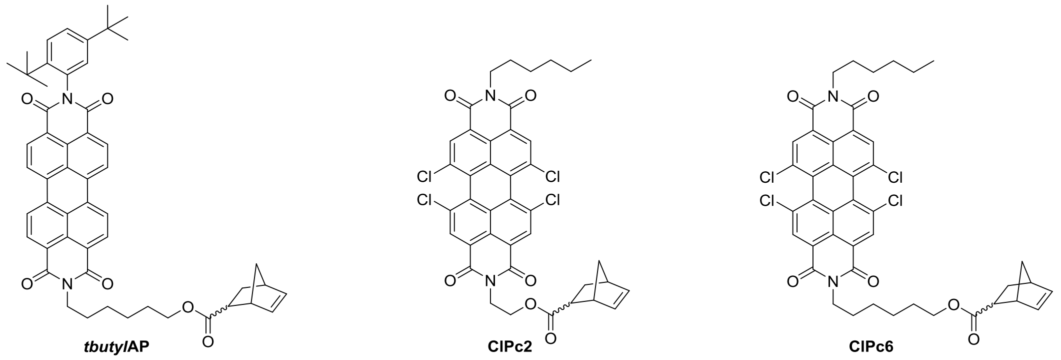


Figure 32. Overview on the norbornene-functionalized perylene diimide derivatives.

Random copolymers with a ***tbutyl*AP** content of 1 wt%, 2 wt%, 4 wt%, 10 wt%, 20 wt%, 30 wt% and 40 wt% were prepared by ROMP (Figure 33). Aggregation of the chromophores was observed with ^{1}H-NMR spectroscopy at higher dye contents (> 4 wt%) in $CDCl_3$ solution. In contrast to that the UV-Vis spectra were not shifted in DCM solutions. The fluorescence quantum yield was visibly reduced due to self quenching. For the TTA-UC measurement a concentration series of the statistic copolymers and moleculary dissolved the sensitizer was made in order to cover a wide range of inter-chromophore distances and concentrations and to optimize the TTA-UC. The photophysical characterization was performed in cooperation with the Joanneum Research Weiz but TTA-UC emission has not been measured yet, because of problems with the measurement setup.

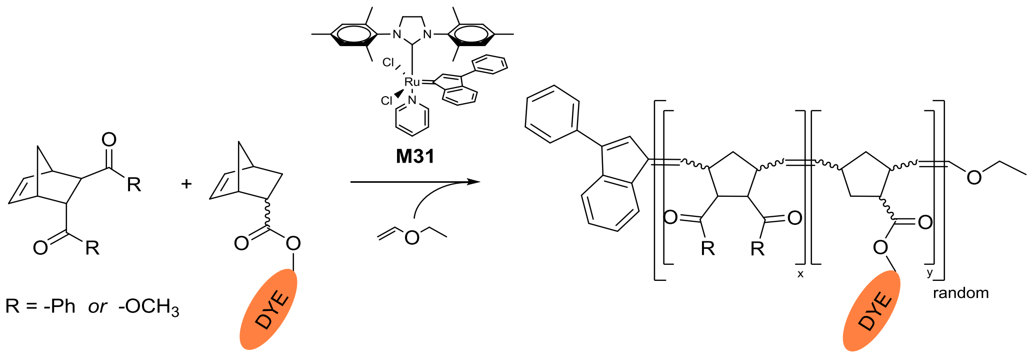
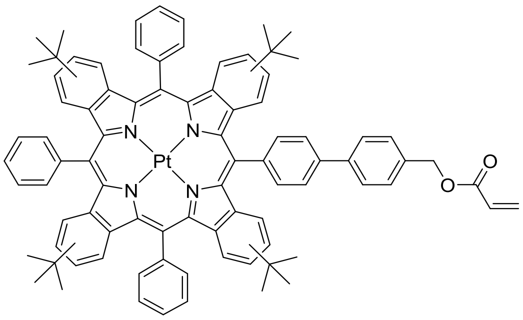


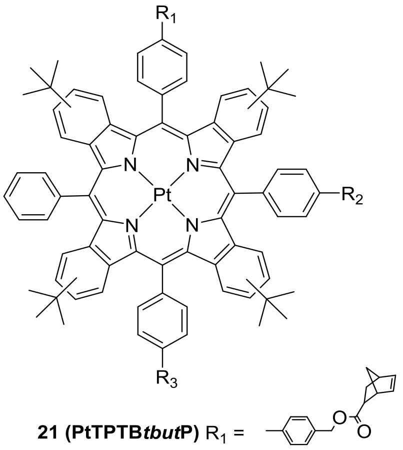
Figure 33. Polynorbornenes with pendant dye moieties.

Pt-Tetraphenyltetrabenzo-*tert*-butly-porphyrin with norbornene ester side groups (**PtTPTB*tbut*P**) was synthesized for the first time (Figure 34). Random copolymers with a **PtTPTB*tbut*P** content of 0.005 wt%, 0.05 wt%, 0.5 wt% and 5 wt% were prepared by ROMP. Beside the norbornene-functionalized derivatives also acrylate bearing **endgroupPtTPTB*tbut*P** was synthesized to terminate the ROM-polymerization and to obtain polymers with a single sensitizer chromophore at the chain end. The principle was proven in preliminary tests.



23

(endgroupPtTPTB*tbut*P)



21 (PtTPTB*tbut*P) R$_1$ =

R$_2$ = R$_3$ = H

22a R$_1$ = R$_2$, R$_3$ = H

or

22b R$_1$ = R$_3$, R$_2$ = H

Figure 34. Acrylate- and norbornene-functionalized Pt-Tetraphenyltetrabenzo-*tert*-butly-porphyrin.

To our knowledge TTA-UC with 1,6,7,12-tetrachloroperylene-3:9,10-bis(dicarboximide) as a chromophore has not been published yet. The effect of the spacer length on the mobility and the TTA-UC efficiency will be part of further studies. Another interest of future research is connected to substitution of the perylene: It was shown with related chemical structures that substitution with chlorine or bromine could increase the lifetime of the excited triplet state.[62]

On the one hand this can give new metal-free sensitizers and on the other hand the TTA-UC efficiency may also increases. Substitution in the bay leads to twisted structure and the effect on forming of the encounter complex during the TTA process is another interesting research topic.

5 Literature

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