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Post-functionalization of macroporous pDCPD with tetrazines - the impact on mechanical properties

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Abstract

Porous polymers and their post-polymerisation functionalization gained significant attention in recent years. One particular class of (macro)porous polymers is high internal phase emulsion templated polymers. Ring-Opening Metathesis Polymerisation (ROMP) of dicyclopentadiene (DCPD) is one of the most promising ways to prepare inherently reactive macroporous emulsion templated foams with good mechanical characteristics (Yield point 1.9 MPa, elongation @ break 20-30%). Herein the post-polymerisation functionalization of the double bonds of macroporous DCPD-foams via the inverse electron Diels-Alder (iEDDA) reaction with 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine is studied. Emphasis is laid on the influence of the functionalization on the mechanical properties of the foams. In a further step, such modified foams were used to load transition metals onto the scaffold and the impact of this step on the mechanical properties of the foams was assessed. Finally, dichlorobis(p-cymene)ruthenium(II) was loaded on the modified support with the aim to establish a heterogenized version of a ruthenium-based transfer hydrogenation catalyst. However, based on the testing of the activity of a homogenous analogue in the transfer hydrogenation of several acetophenone derivatives with 2-propanol, it could be shown that such types of complexes are not able to catalyse the intended transformation.

Kurzfassung

Poröse Polymere und deren Funktionalisierung nach der Polymerisation erzielten erhebliche Aufmerksamkeit in den letzten Jahren. Eine besondere Klasse von makroporösen Polymeren sind polyHIPEs (High Internal Phase Emulsion = Emulsion mit hohem Anteil an interner Phase) die über "emulsion templating" (Formgebung durch Emulsions-Strukturierung) hergestellt werden. Die Ring-öffnende-Metathese-Polymerisation (ROMP) von Dicyclopentadien (DCPD) ist einer der vielversprechendsten Möglichkeiten, inhärent reaktiv makroporösem Schäume mit guten mechanischen Eigenschaften herzustellen (Streckgrenze 1,9 MPa, Bruchdehnung 20-30%). Anschließend wurde die Doppelbindungen der makroporösen DCPD-Schäume über die Diels-Alder Reaktion mit inversen Elektronen bedarf (iEDDA) mit 3,6-di(pyridin-2-yl)-1,2,4,5-Tetrazin modifiziert und untersucht. Der Schwerpunkt liegt auf dem Einfluss auf die mechanischen Eigenschaften der Schaumstoffe nach der Funktionalisierung. In einem weiteren Schritt wurde dieses modifizierte Polymer verwendet, um Übergangsmetalle auf der Oberfläche zu koordinieren und die Auswirkungen dieser Maßnahme auf die mechanischen Eigenschaften der Schaumstoffe zu untersuchen. Schließlich wurde Dichloro(p-cymol)-Ruthenium(II) auf dem modifizierten Träger koordiniert mit dem Ziel, eine heterogene Version eines Ruthenium basierten Transfer-Hydrierkatalysator herzustellen. Jedoch, bezogen auf die Aktivität eines homogenen Äquivalents dieses Komplexes in der Transfer-Hydrierung von mehreren Acetophenon-Derivate mit 2-Propanol, konnte gezeigt werden, dass diese Arten von Komplexen nicht in der Lage sind, die gewünschte Reaktionen zu katalysieren.

List of Abbrevations

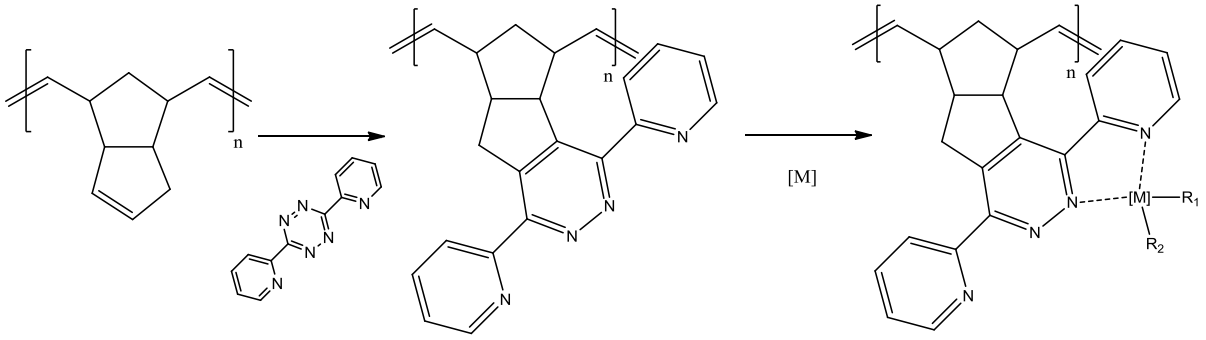
ADMET	Acyclic Diene Metathesis Polymerization
bipy-Pz	3,6-di(pyridin-2-yl)pyridazine
bipy-Tz	3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine
CM	Cross Metathesis
DCM	Dichloromethane
DCPD	Dicyclopentadiene
Et_3N	triethylamine
HIPE	High Internal Phase Emulsion
iEDDA	inverse electron demand Diels-Alder
iPrOH	2-propanol
KOH	potassium hydroxide
KOtBu	potassium-*tert*-butanolate
MeOH	methanol
NMR	Nuclear Magnetic Resonance
O/W	emulsion oil-in-water emulsion
polyDCPD	poly(dicyclopentadiene)
polyHIPE	Polymerized High Internal Phase Emulsion
Py	pyridine
RCM	Ring Closing Metathesis
ROM	Ring Opening Metathesis
ROMP	Ring Opening Metathesis Polymerization
RT	room temperature
SEM	Scanning Electron Microscopy
THF	Tetrahydrofurane
W/O	emulsion water-in-oil emulsion

Table of content

1. Introduction

The preparation and modification of porous polymers is a fast increasing field of expertise. Porous materials were introduced in the late 1950s and until now many different areas of applications are investigated (e.g. as supports for heterogeneous catalysis, chromatography, ion exchange and tissue engineering). In 1982 polyHIPEs (poly high internal phase emulsion) were introduced for the first time which can be prepared via emulsion templating.[1,2,3] A monomer which can be used for the preparation of polyHIPEs is dicyclopentadiene (DCPD). The resulting poly(dicyclopentadiene) (pDCPD) is easy to modify because of the high degree of unsaturation. Knall et al. showed that it is possible to modify these macroporous pDCPD foams with 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine via the inverse electron Diels-Alder reaction (iEDDA) and the resulting pyridazines were used as ligands for transition metals.[4]

The scope of inverse electron demand Diels-Alder reactions with tetrazines for the post polymerization functionalization of macroporous poly(dicyclopentadiene) prepared by emulsion templating was investigated. For this study different tetrazines has been synthesised and reacted with the double bonds of the polyHIPE. To investigate the mechanical properties tensile tests were performed and compared to unmodified samples. Furthermore, the modified polyHIPEs were then used as ligands for transition metals.



Scheme 1: Reaction pathway of polyHIPE modification

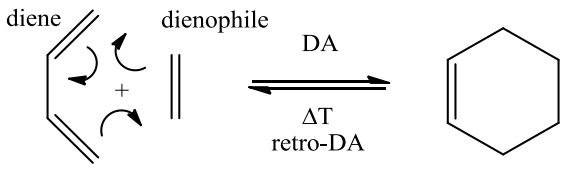
Eu(III) was found to coordinate with two ligands[4] what might improve the mechanical properties, whereas analogous Ru(II) compounds[5] were found to be catalytically active in transfer hydrogenation reactions. Therefore, the pyridazine ligands were used to coordinate europium(III)nitrate pentahydrate and dichlorobis(p-cymene)ruthenium(II).

[1] D. Barby, Z. Haq, *Eur. Pat.*, 1982, **60**, 138
[2] H. Zhang,A A.I. Cooper, *Soft Matter*, 2005, **1**, 107-113
[3] N.R Cameron, *Polymer*, 2005, **46**, 1439-1449
[4] A. C. Knall, S. Kovacic, M. Hollauf, D. Reishofer, R. Saf, C. Slugovc, *Chem. Commun.*, 2013, **49**, 7325-7327
[5] Rueping, A. Antonchick, T. Theissmann, *Angewandte Chemie* (International ed. in English), 2006, **45** (22), 3683–3686

2. General Aspects

2.1. Diels-Alder reaction/iEDDA

The Diels-Alder reaction is a reaction between a conjugated diene and an alkene. Specifically, this reaction is a 4+2 cycloaddition between a diene and a dienophile.[6] Otto Diels and Kurt Alder were the first who described this reaction in 1928.



Scheme 2: Diels-Alder and retro Diels-Alder reaction

This reaction is the most used of the pericyclic reactions[7] and it has five subclasses (normal, neutral, retro, hetero and inverse electron demand).[8] As shown in Scheme 2 the Diels-Alder reaction is a reversible reaction (retro-Diels–Alder reaction). Upon heating or acid/base mediation the starting materials are formed again (diene, dienophile).[9]

A special feature for all Diels-Alder reactions is that always a new bond is formed between the diene and the dienophile in a strict [$\pi 4_s + \pi 2_s$] form. For that reason this reaction has a high degree of stereocontrol (*endo* rule) and level of calculability.[10] It is also a thermal reaction (initiation by heat) and it forms new six-membered rings.[11]

To determine the character of the reaction (neutral, normal or inverse electron demand) the HOMO and LUMO of the cycloaddends have to be compared. Figure 1 shows the energy levels of neutral, normal or inverse electron demand. Electron donating groups increase the energy level of the HOMO of the diene, while electron withdrawing groups decrease the LUMO energy level of the dienophile. The kinetics of the reaction depends on the energy difference between the LUMO and the HOMO of the two cycloaddends. The smaller the difference of the gap, the faster the reaction is.[12]

[6] O. Diels, K. Alder, *"Synthesen in der hydroaromatischen Reihe". Justus Liebig's Annalen der Chemie*, 1928, **460**, 98-122
[7] V. Gold, A. D. McNaught, A. Wilkinson, *Compendium of Chemical Terminology*, 2nd Edition, 1997
[8] R. A. A. Foster, M. C. Willis, *Chem. Soc. Rev.*, 2013, **42**, 63
[9] B. Rickborn, *Org. React*, 1998, **52**, 1
[10] J. Poulin, C. M. Grise-Bard, L. Barriault, *Chem. Soc. Rev.*, 2009, **38**, 3092
[11] J. G. Smith, *"The Diels-Alder Reaction." Organic Chemistry. 3rd ed. New York*, 2011. 588–89
[12] I. Fleming, *Frontier Orbitals and Organic Chemical Reactions, John Wiley & Sons, Ltd, West Sussex*, 1976

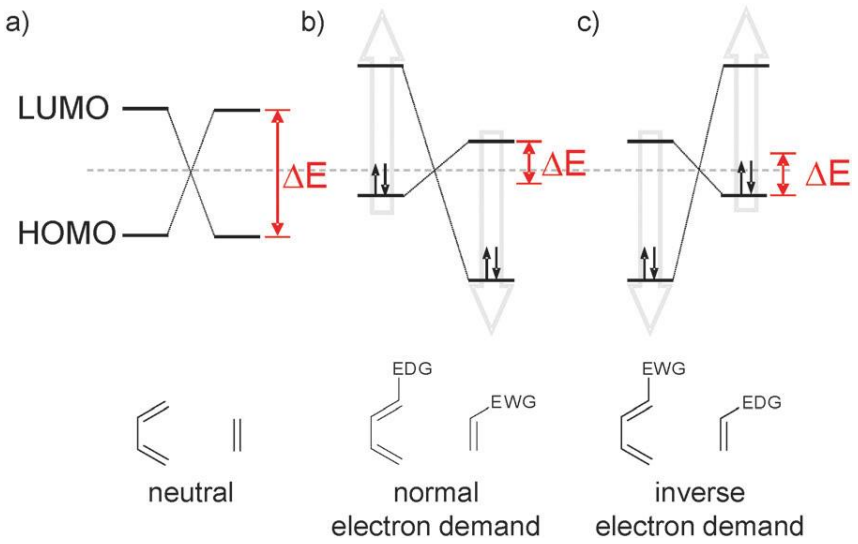


Figure 1: Frontier orbital model of (a) neutral, (b) normal electron demand and (c) inverse electron demand Diels–Alder additions (EDG = electron-donating group, EWG = electron-withdrawing group)[8]

Because of the big energy gap in "neutral" Diels-Alder reaction (1,3-butadiene + ethene), the equilibrium is far from the product side. The difference between the neutral and the normal electron demand is that the diene of the normal electron demand has electron donating groups and the dienophilic alkene electron withdrawing groups (Figure 1).

As described before the Inverse electron demand Diels-Alder reaction (iEDDA) is a subclass of the Diels-Alder reaction. In this case, the diene has electron withdrawing groups and the dienophile electron donating groups. The first significant advances in exploring this reaction were explained by Sauer et al.[13] Sauer monitored the characteristic absorbance (530nm) of the tetrazine to determine the reaction rates. Sauer showed also that with a higher electron density (e.g. dihydrofuran reacts 6 times faster than cyclopenten) and higher ring strain (e.g. cyclobutene reacts 14 times faster than cyclopenten) the reaction rate increase. The stereochemistry has also an influence. As an example the reaction rate of *trans* cyclooctene is 376000 times higher than of *cis* cyclooctene.[14]

In the following, the iEDDA reaction with tetrazines is described more closely, as it was employed throughout this work.

[13] J. Sauer, D. K. Heldmann, J. Hetzenegger, J. Krauthan, H. Sichert and J. Schuster, *Eur. J. Org. Chem.,* 1998, 2885

[14] F. Thalhammer, U. Wallfahrer, J. Sauer, *Tetrahedron Letters*, 1990, **31**, 6851-6854

2.2. Tetrazine/Pyridazine

The tetrazine molecule consists of a six-membered aromatic ring containing four nitrogen atoms. There are three isomers: (a) 1,2,3,4-tetrazines, (b) 1,2,3,5-tetrazines and (c) 1,2,4,5-tetrazines.

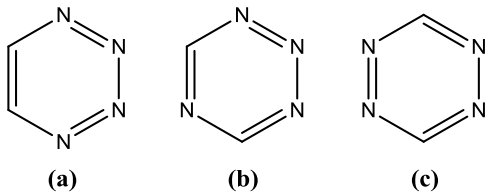


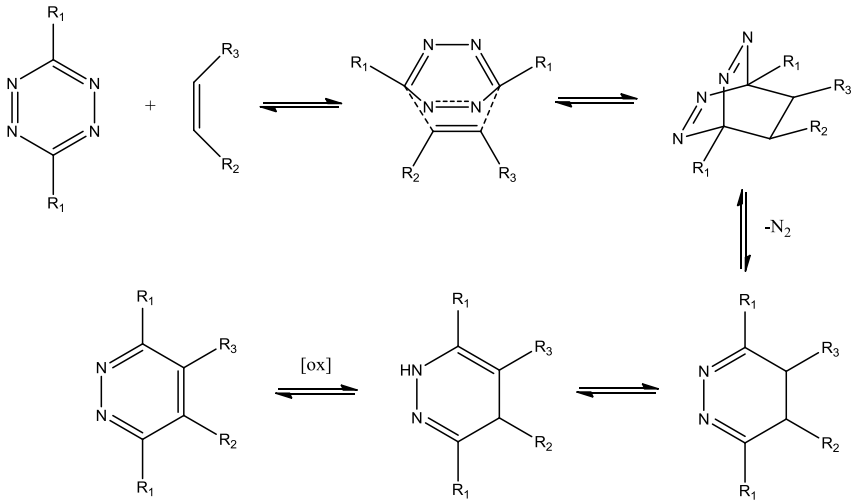
Figure 2: isomers of tetrazine

The most investigated isomer is the 1,2,4,5-tetrazine which can be used in the iEDDA click chemistry. There are different methods reported in the literature to synthesis tetrazines. One of the best known syntheses uses hydrazine hydrate.[15] Tetrazines can be used to synthesise functionalised pyridazine derivatives with the before explained iEDDA addition[16] as an alternative to heteroaryl-coupling reaction[17] (typically Stille- or Suzuki-coupling).

The iEDDA addition between 1,2,4,5-tetrazines and olefins is also known as Carboni-Lindsey[18] reaction. The reaction scheme (Scheme 3) of the iEDDA reaction between these two compounds was introduced simultaneously by two groups in 2008. The Fox group showed that proteins could be modified. This report was significant because it demonstrated that the reaction works under physiological conditions.[19] Devaraj, Weissleder and Hilderbrand used the cycloaddition in live cell imaging.[20]

In the first step of the reaction the dihydro-pyridazine is formed which will further oxidise to the corresponding pyridazine.

[15] W. A. Butte *,* F. H. Case *, J. Org. Chem.* 1961 *,* ***26*** *,* 4690 –4692
[16] R.N. Warrener, P. A. Harrison , *Molecules*, 2001, **6**, 353-369
[17] (a) L. A. Cuccia, J.-M. Lehn, J.-C. Homo, M. Schmutz, Angew, *Chem., Int. Ed.*, 2000, **39**, 233; (b) L. A. Cuccia, E. Ruiz, J.-M. Lehn, J.-C. Homo, M. Schmutz, *Chem.–Eur. J.*, 2002, **8**, 3448; (c) R. Dorta, L. Konstantinovski, L. J. W. Shimon, Y. Ben-David, D. Milstein, *Eur. J. Inorg. Chem.*, 2003, **70**
[18] R. A. Carboni, R. V. Lindsey, *J. Am. Chem. Soc.*, 1959, **81**, 4342
[19] M. L. Blackman, M. Royzen, J. M. Fox, *J. Am. Chem. Soc.*, 2008, **130**, 13518
[20] N. K. Devaraj, R. Weissleder, S. A. Hilderbrand, *Bioconjugate Chem.*, 2008, **19**, 2297



Scheme 3: iEDDA reaction scheme

The oxidation of the dihydropyridazine can be done with DDQ (2,3-dichloro-5,6dicyanobenzoquinone).[21] The reason why tetrazine are used and not triazines is the higher reactivity of the leaving group (Figure 3).

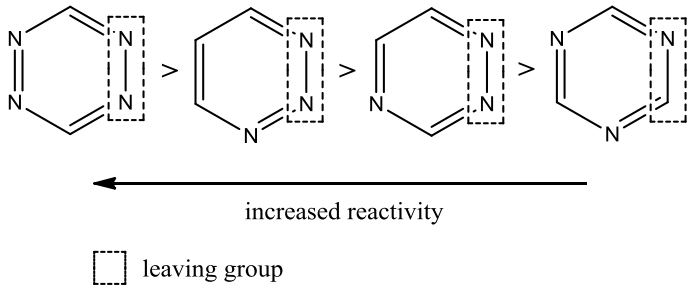


Figure 3: reactivity trends of tetra- and triazines[8]

Besides the usage of this reaction as metal-free click chemistry and fields of bioorthogonality,[22] the obtained pyridazines are also very interesting ligands for metal-complexing. These complexes have well-defined supramolecular architectures with many interesting features.[23] It is reported in the literature that derivatives of 3,6-di(pyridin-2-yl)pyridazine (Figure 4Figure 4) can coordinate to copper,[24] silver,[25] nickel,[26] iridium,[27]

[21] A. C. Knall, C. Slugovc, *Chem Soc Rev*, 2013, **42**, 5131-5142
[22] J. C. Jewett, C. R. Bertozzi, Chem. *Soc. Rev.*, 2010, **39**, 1272
[23] U. S. Schubert, C. Eschbaumer, *Angew. Chem.*, 2002, **114**, 2016-3050
[24] M.-T. Youinou, N. Rahmouni, J. Fischer, J. A. Osborn, *Angew. Chem.*, 1992, **104**, 771-773; *Angew. Chem. Int. Ed. Engl.*, 1992, **31**, 775-778
[25] P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel, D. Fenske, *Angew. Chem.*, 1997, **109**, 2067-2070; *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 1978-1981
[26] N.-D. Sung, K.-S. Yun, T.-Y. Kim, K.-Y. Choi, M. Suh, J.-G. Kim, I.-H. Suh, J. Chin, *Inorg. Chem. Commun.*, 2001, 377-380
[27] (a) A. M. M. Lanfredi, A. Tiripicchio and F. Ugozzoli, *J. Chem. Soc. Dalton Trans.*, 1988, 651-656; (b) N. Tsukada, T. Sato, H. Mori, S. Sugawara, C. Kabuto, S.Miyano, Y. Inoue, *J. Organomet. Chem.*, 2001, **627**, 121-126

palladium,[27] ruthenium[28] and europium.[4] These complexes can be used as magnetic arrays[29], porous hosts,[30] information storage devices[31] and as catalyst in chemical reactions.

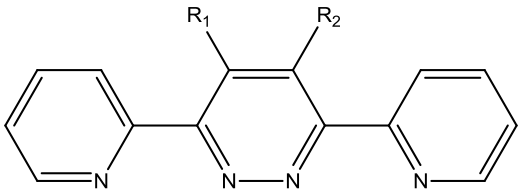


Figure 4: structure of 3,6-di(pyridin-2-yl)pyridazine derivate

2.3. PolyHIPEs

PolyHIPEs are porous polymers which use high internal phase emulsions (HIPE) as templates for the polymerisation. This material had their first introduction in 1982.[1] For an emulsion it is important that the two or more liquid components are immiscible. One of these liquids (the internal phase) is dispersed in the others-external or continuous phase. It can be distinguished between two types of emulsion, water-in-oil (W/O) (hydrophobic polymers) and oil-in-water (O/W) (hydrophilic polymers). These emulsions can be extended to a water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O) systems. For the polymerisation of HIPE polymers usually free radical polymerisation is used. With these emulsions many types of materials can be synthesised including biodegradable materials, copolymers, organic-inorganic hybrids and nanocomposites. These materials can then be used as low dielectric constant substrates, supports for heterogeneous catalysis, chromatography, separation (also as separators in lithium-ion batteries[32]), ion exchange and tissue engineering to name but a few.[2,3]

During the polymerisation the internal phase can evaporate and cavities from former emulsion droplets (so-called voids) get interconnected via windows which accrue during the evaporation. The result of this process is a well-defined, interconnected macroporous polymer. There is often a significant difference between the structure of a HIPE and the resulting polyHIPE.[33] A typical polyHIPE structure is shown in Figure 5.[34] The SEM micrograph shows the voids and the interconnection of them via windows.

[28] A.Golka, P.J. Keyte, M.N. Paddon-Row, *Tetrahydron*, 1992, **48**, 7663-7678
[29] (a) N. E. Chakov, S. C. Lee, A. G. Harter, P. L. Kuhns, A. P. Reyes, S. O. Hill, N. S. Dalal, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.*, 2006, **128**, 6975; (b) R. T. W. Scott, C. J. Milios, A. Vinslava, D. Lifford, S. Parsons, W. Wernsdorfer, G. Christou, E. K. Brechin, *Dalton Trans.*, 2006, 3161
[30] M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.*, 2005, **38**, 369
[31] M. Ruben, E. Breuning, J. P. Gisselbrecht, J. M. Lehn, *Angew. Chem., Int. Ed.*, 2000, **39**, 4139
[32] S. Kovacic, H. Kren, P. Krajnc, S. Koller, C. Slugovc, *Macromol. Rapid Commun.*, 2013, **34**, 581
[33] J. F. Brown, P. Krajnc, N.R. Cameron, *Ind. Eng. Chem. Res.*, 2005, **44**, 8565-8572
[34] A. C. Knall, S. Kovacic, C. Slugovc, Covalent modification of unsaturated polymers using iEDDA click chemistry (3.4.2013)

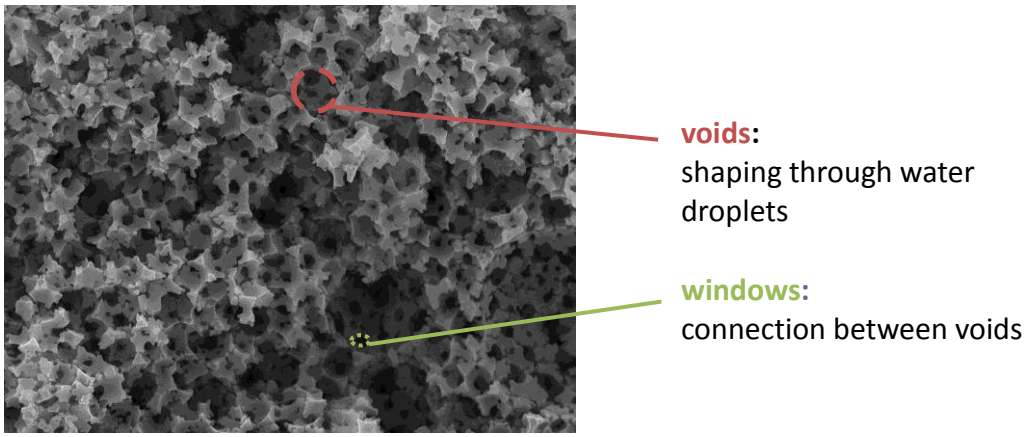


Figure 5: SEM micrograph of poly HIPE[34]

Lissant was the first who defined that HIPEs have an internal phase content higher than 70%[35] but in the last years HIPEs were defined with an internal phase content of 74%[36] (representing the densest packing of uniform, non-deformable spheres) or higher. For internal phase contents higher than 74%, the monodispersed droplets get deformed to polyhedral shapes.

The stability of the HIPE emulsion can be influenced by different factors, including the temperature, molecular structures of the phases and the surfactant, the ratio of surfactant and dispersed phase and the presence of stabilizing salts.[37] Also the rate and time of stirring has a significant effect on the structure of the HIPE.[38]

There are four different types of instability in emulsions towards a total breakup resulting in separation of two phases. These types are flocculation, creaming, Ostwald ripening and finally coalescence. Flocculation occurs when the attractive force between the droplets is stronger than the repulsive force. The result is that droplets attract each other and sink to the bottom.[39] If dispersed droplets migrate to the top the effect is called creaming (influenced by buoyancy or centripetal force). Ostwald ripening is a thermodynamically driven spontaneous process. The driving force of this effect is that larger droplets are more energetically favoured than smaller.[40] Coalescence occurs if two or more droplets get combined to form a larger droplet. The driving force of this effect is the decreasing of the surface between both phases. This is the final process and is not reversible.[41] As shown in Equation 1 the differential Gibbs free energy (dG) rises linear with the increase of surface (dA).[42]

[35] K. J. Lissant, *Emulsions and Emulsion Technology*, Part 1, Chapter 1, Macel Dekker, New York, 1974
[36] N. R. Cameron, D. C. Sherrington, *Adv. Polym. Sci.*, 126, 163-214
[37] R. Ponds, C. Solans, M. J. Stebe, P. Erra, J. C. Ravey, *Prog Colloid Polym Sci*, 1992, **89**, 110-113
[38] R. J. Mannheimer, *J Colloid Interf Sci*, 1972, **40**, 370-382
[39] A. T. Hubbard, Encyclopedia of Surface and Colloid Science, *CRC Press.*, 2004 , 4230
[40] L. Ratke, P. W. Voorhees, Growth and Coarsening: Ostwald Ripening in Material Processing, *Springer*, 2002, 117-118
[41] Y. De Smet, L. Deriemaeker, R. Finsy, *Langmuir,* 1999, **15**, 6745-6754
[42] D.F. Evans, H. Wennerstrom, *The colloidal domain*, 1994, 44

Equation 1: Differential Gibbs free energy

$$dG = \gamma * dA$$

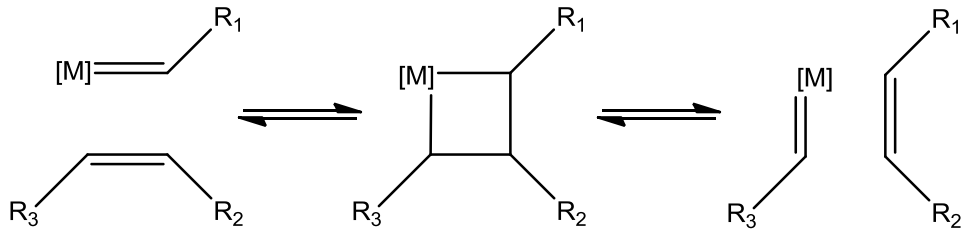
γ = interfacial tension

The best way to stabilize an emulsion is to add a surfactant. The purpose of the surfactant is to lower the differential Gibbs free energy via the reduction of interfacial tension. A typical surfactant is an amphiphilic molecule. That means that the molecule has a polar head, and a hydrophilic tail. The types of surfactants are differentiated by their head group (anionic, cationic, zwitter-ionic or non-ionic).[43]

In the last years an upcoming monomer for polyHIPE was dicyclopentadiene (DCPD). Via Ring-Opening Metathesis Polymerisation (ROMP), poly-(dicyclopentadiene) (pDCPD) is obtained. This polymer is highly cross-linked and achieved the best mechanical properties reported for HIPE materials.[44] Moreover, the polymer is highly unsaturated, so it is easy to functionalise it. Perring and co-workers used MCPBA (metachloroperoxybenzoic acid) for epoxidation.[45] They also showed that it is possible to brominate[46] the double bonds of the polyHIPE. Knall et al. showed that it is possible to use the double bonds for iEDDA reaction with tetrazines and to coordinate transitions metals via the thus grafted di(pyridyl) pyridazine ligands.[4]

2.4. Ring-Opening Metathesis Polymerisation (ROMP)

As described above, a DCPD emulsion can be polymerised by the Ring-Opening Metathesis Polymerisation (ROMP). Olefin metathesis was first reported in 1960 by Robinson et al. and the first reaction mechanism was suggested 1971 by Herisson and Chauvin.[47] Since then a lot of different catalysts have been evolved to catalyse the reaction (e.g. by transition metals like tungsten or ruthenium).[48]



Scheme 4: Reaction mechanism of the metathesis reaction[49]

[43] L. L. Schramm, *Emulsions, Foams and Suspensions*, 2005, 76-81
[44] S. Kovacic, K. Jerabek, P. Krajnc, C. Slugovc, *Polym. Chem.*, 2012, **3**, 325
[45] M. Perring, T. R. Long, N. B. Bowden, *J. Mater. Chem.*, 2010, **20**, 8679
[46] M. Perring, N. B. Bowden, *Langmuir*, 2008, **24**, 10480
[47] J.-L. Herisson, Y. Chauvin, *Makromol. Chem.*, 1971, **141**, 161-167
[48] W. L. Truett, D. R. Johnson, I. M. Robinson, B. A.Montague, *J. Am. Chem. Soc*., 1960, **82**, 2337

In the last years well defined, water and air stable ruthenium catalysts were developed which are easy to use under different conditions.[49] The metathesis reaction is a powerful carbon-carbon double bond forming reaction and besides ROMP there are also other variations like the ring closing metathesis (RCM), cross metathesis (CM), ring opening metathesis (ROM) and acyclic diene metathesis polymerization (ADMET).[50]

The driving force for ROMP is the release of ring strain of cyclic olefins. DCPD has two rings with a different degree of ring strain. The norbornene ring has a ring strain of 27.2 kcal/mol and the cyclopentene of approx. 6.2 kcal/mol.[51] For that reason the norbornene double bond reacts first. Because of the high functional group tolerance of ruthenium catalyst (reactivity of Ru-catalysts against different functional groups: olefins > acids > alcohol/water > aldehydes > ketones > esters/amides) the metathesis works with a lot of different norbornene derivate.[49]

For this work the catalyst M2 from Umicore GmbH was used for the polymerisation of the DCPD emulsion. M2 is modified Grubbs 2nd generation catalyst.

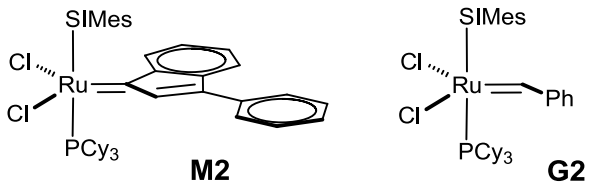


Figure 6: left: M2; right Grubbs 2nd Generation catalyst (G2)

[49] T.M. Trnka, R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18-29
[50] C. Slugovc, Macromol. Rapid Commun. 2004, 25, 1283
[51] M. F. Z. Lerum, W. Chen, *Langmuir*, 2011, **27**, 5403-5409

3. Results and Discussion

3.1. Shoulder bar preparation

The preparation of polyHIPEs via ring opening metathesis polymerization was first described in 2002 by Deleuze et al.[52] In this synthesis ''Grubbs'' first generation catalyst (G1) was used to polymerise tetracyclo[6,2,13,6,02,7]dodeca-4,9-diene. In 2010 a new approach to synthesize polyHIPEs has been described by Kovačič et al.[53] Dicyclopentadiene (DCPD) was stabilized with Pluronic® L121 (poly(ethylene glycol)-block-poly(propylene glycol)- block-poly(ethylene glycol)) and polymerized with Umicore's M2 catalyst. All synthesised polyHIPE samples in this work were done by following this procedure.

3.1.1. Emulsion preparation

To calculate the amount of internal phase (H_2O dest.) amount Equation 2 was used.

Equation 2: calculation of H_2O amount

$$m_{H_2O} = \frac{\emptyset * m_{DCPD} + \emptyset * m_{Toluene}}{1 - \emptyset}$$

M_{H2O} = mass of H_2O [g]
m_{DCPD} = mass of DCPD [g]
$m_{Toluene}$ = mass of Toluene [g]
$\emptyset$ = porosity

The emulsion was prepared by adding 37.12 mL of water to 9 mL DCPD (thereby, a porosity of 80% is achieved), 60 µL toluene per mL DCPD, the initiator M2 (1:10000 eq respect to DCPD) and 5wt% of the surfactant Pluronic® L121 with respect to DCPD. The amount of surfactant was chosen because the literature[54] showed that with this formulation a polyHIPE with a high Young's modulus (97 MPa) and average pore size of 6.7 µm could be obtained.

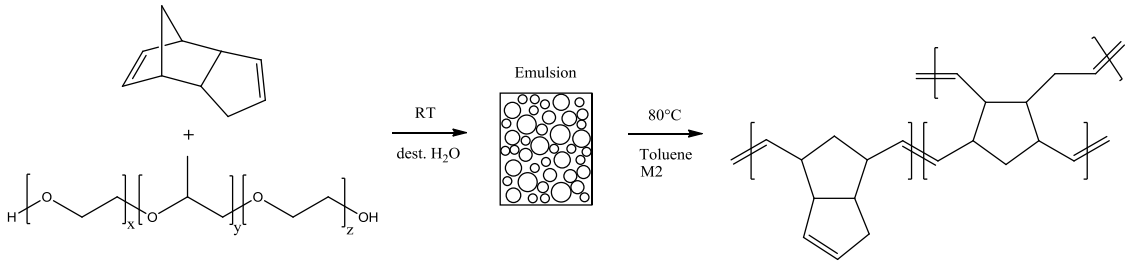
Table 1: pDCPD weighed portions

DCPD	H_2O	M2		Surfactant	
[g]	[mL]	[mg]	[M2:DCPD]	[mg]	[w%]
8.811	37.12	6.33	1:10000	441	5

The emulsions were prepared in a 3-neck flask equipped with an overhead stirrer. DCPD and the surfactant were combined in the flask and the internal phase (H_2O) was added dropwise (one drop each 4 sec). After the first droplets the reaction solution turned milky, which

[52] H. Deleuze, R. Faivre, V. Herroguez, *Chem. Commun.*, 2002, 2822-2823
[53] S. Kovacic, P. Krajnc, C. Slugovc, *Chem. Commun.*, 2010, **46**, 7504-7506
[54] S. Kovacic, N. B. Matsko, K. Jerabek, P. Krajnc, C. Slugovc, *J. Mater. Chem. A*, 2013, **1**, 487

indicates emulsion formation. For every 10 mL water, the stirring speed was increased for 100 rpm. After addition is completed, the emulsion was stirred for another hour to make sure that the emulsion is homogenous. Then, the catalyst, dissolved in toluene, was added and the emulsion was filled into the defined preheated sample mold. This step has to be done really fast, otherwise the emulsion will polymerise in the flask. It was important that there are no holes or other artefacts in the shoulder bars, which could act as predetermined breaking points.



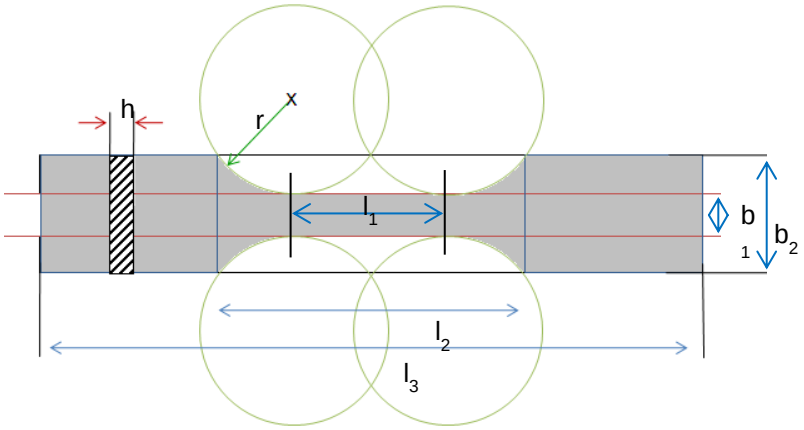
Scheme 5: Preparation of polyHIPEs

The emulsions were cured for 4h at 80°C in the oven. During this process the water evaporates from the emulsion leaving holes and windows behind. The colour of the shoulder bars turned from brown-red (colour of M2) to white. After the curing the shoulder test bars were purified by immersion in acetone for 24h. In the final step the polymer was dried in vacuo.

Figure 7: polyHIPE filled in mould

The shoulder bars were used for tensile tests to determine the mechanical properties of materials (Chapter 3.4.). Figure 12A (page23) shows a SEM micrograph of the polyHIPE with 5wt% surfactant.

Figure 8 shows the dimensions of the prepared shoulder test bar.[55]



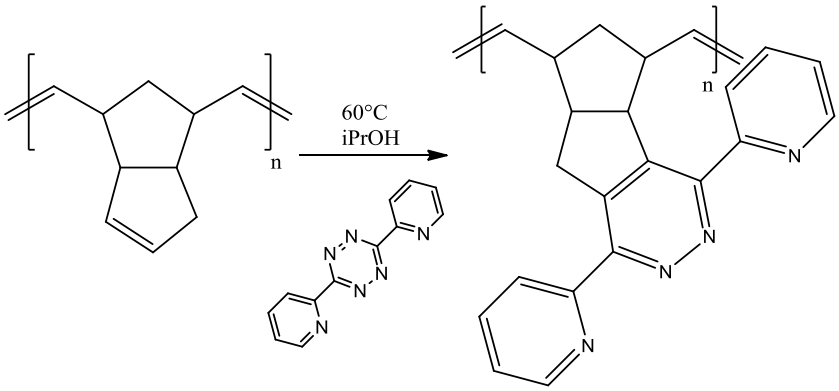
l_1 =	30 mm
l_2 =	65 mm
l_3 =	140 mm
b_1 =	9 mm
b_2 =	25 mm
r =	20 mm
h =	5 mm

Figure 8: Dimensions of large shoulder test bar

[55] A. Leitgeb, PhD thesis "Contributions to the Advancement of Ruthenium Based Initiators for Olefin Metathesis", Graz 2012.

3.2. Shoulder bar modification with bipy-Tz

For the later modification with transition metals it was important to modify the shoulder test bars first with 0.2eq bipy-Tz (DCPD as a repeating unit). Bipy-Tz was chosen for the click chemistry modification reaction with the polyHIPE due to the good solubility in iPrOH (Chapter 3.5.1.1.). For this modification the bipy-Tz was dissolved in iPrOH and heated up to 60°C. The solution with the shoulder test bar was then stirred for 48h-144h (Figure 9).



Scheme 6: modification of pDCPD with bipy-Tz

With longer reaction time more double bonds got functionalised. The conversion was obvious because of the increased weight and the changed colour. After the reaction the shoulder test bar was yellow (Figure 13B, page 23). The colour correlated also to other bipy-Tz alkene reactions. After the modification the shoulder test bars were purified with acetone to remove free bipy-Tz, otherwise the determination of the increased weight is inaccurate. In the final step the polymer was dried in vacuo.

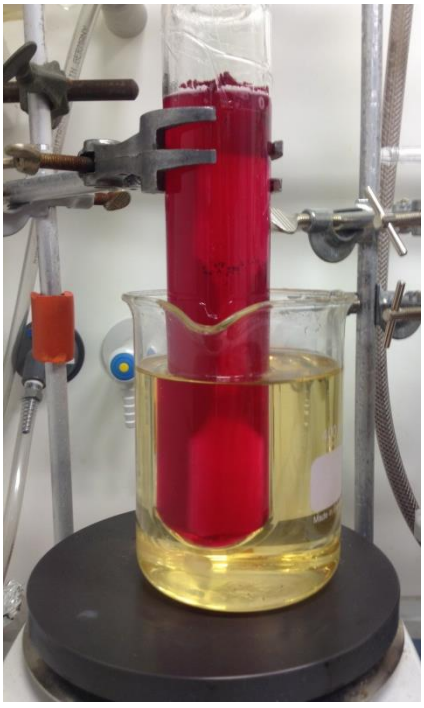


Figure 9: shoulder bar in iPrOH/bipy-Tz solution

With THF as solvent the modification degree was higher than with iPrOH because the polymer swelled better.[4] But after the modification in THF the shoulder bar was deformed in a way that made measuring the mechanical properties of these samples useless. A combination of both solvents was tested. If the THF amount was too low there was no difference to iPrOH shoulder bars and if the THF amount was too high the shoulder bars were deformed.

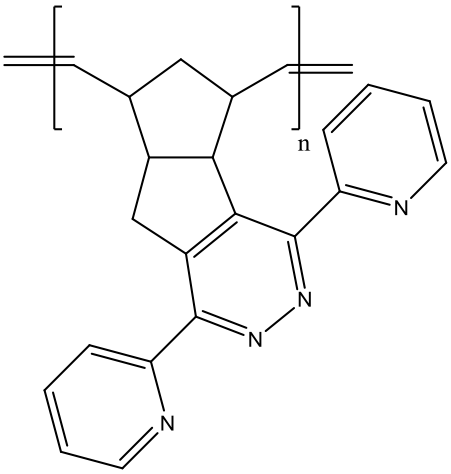


Figure 10: bipy-Tz modified pDCPD

The modified shoulder bars were also used for tensile tests and compared with the unmodified material (Chapter 3.4.). Figure 12B (page23) shows a SEM micrograph of the bipy-Tz modified polyHIPE.

3.3. Shoulder bar modification with transition metals

The bipy-Tz shoulder test bars were modified with two different transition metals. First, europium(III)nitrate pentahydrate was applied to prove that the coordination of transition metals is possible and to perform tensile test (investigate a potential crosslinking by coordinating). The second one was dichlorobis(p-cymene)ruthenium(II) which should lead to a catalyst for transfer hydrogenation.

3.3.1. europium(III)nitrate pentahydrate

For the europium(III)nitrate pentahydrate modification 0.05eq of the complex (calculated to DCPD as repeating unit) was dissolved in acetonitrile and the shoulder bar was put in the solution for 24h. With this amount 25% of the pyridazine units would be modified. After a few seconds the polyHIPE changed the colour in the solution to shining yellow. In the final step the polymer was dried in vacuo and the colour changed to yellow-gold (Figure 13C, page 23). The coordination of Eu(III) readily visible, because the grafted Eu(III) complexes showed red fluorescence at 365nm (Figure 11B, page 23).

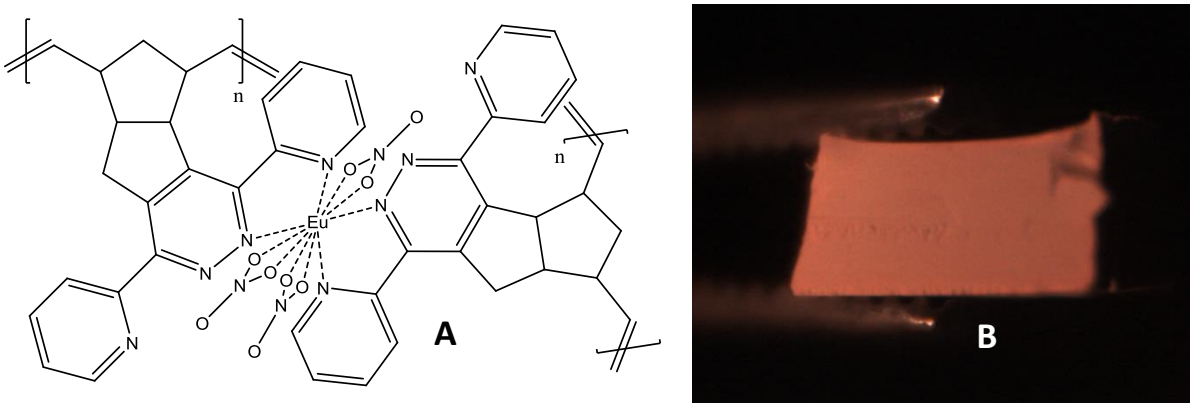


Figure 11: A) Eu(III) complex on polyHIPE; B) fluorescence at 365nm

These transition metal modified shoulder bars were also used for tensile tests and compared with the other materials (Chapter 3.4.) Figure 12C shows a SEM micrograph of the $Eu(NO_3)_3$ impregnated polyHIPE.

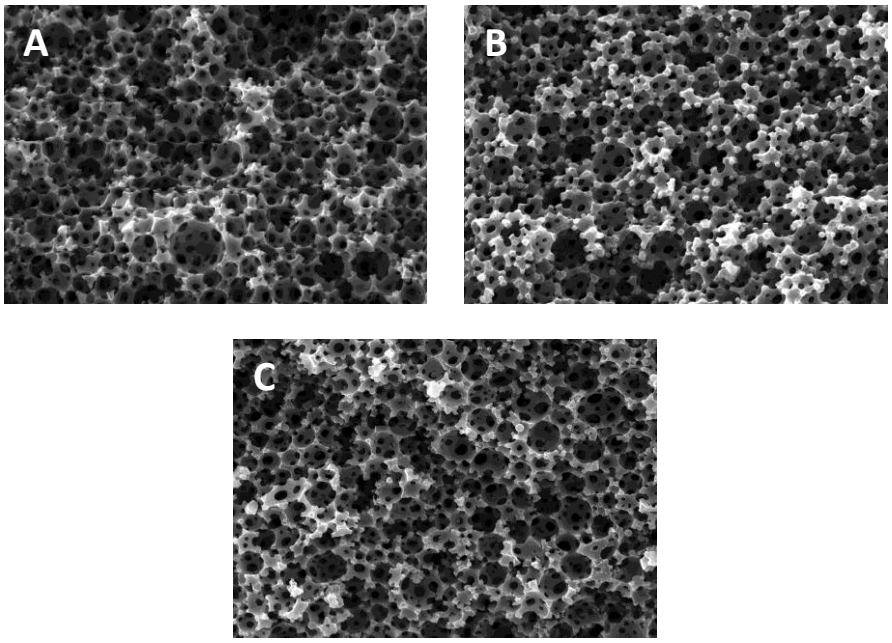


Figure 12: SEM micrographs of A) pDCPD foam, B) after modification with 0.2 equiv. of bipy-Tz and C) after impregnation with $Eu(NO_3)_3$

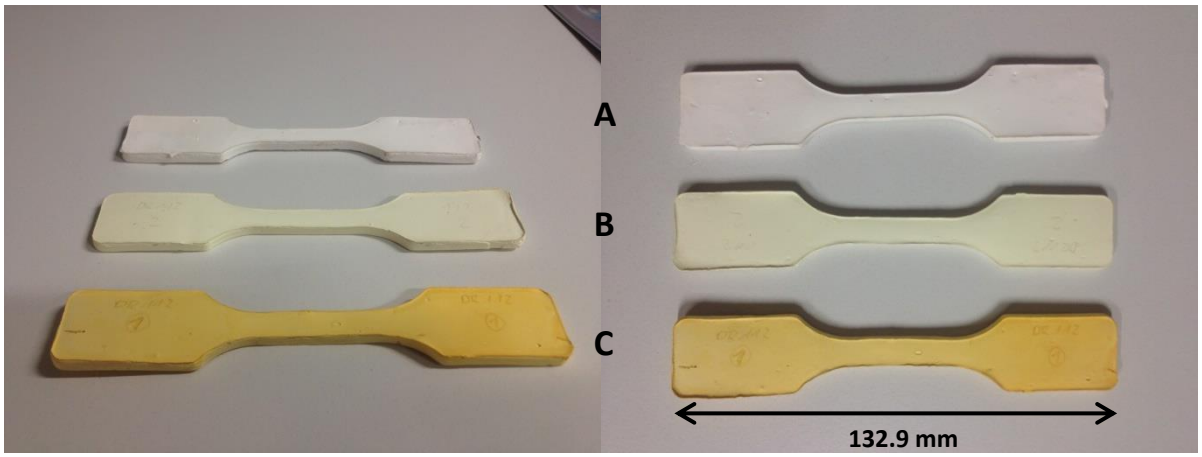


Figure 13: A) polyHIPE; B) bipy-Tz modified; C) Eu(III) modified

3.3.2. dichlorobis(p-cymene)ruthenium(II)

For the dichlorobis(p-cymene)ruthenium(II) modification only a piece of the shoulder bar was modified. The complex (0.05eq calculated to DCPD as a repeating unit) was dissolved in DCM and the monolith was put into the solution for 24h, again aiming for a modification degree of 25%. After a few seconds the polyHIPE changed the colour in the solution to dark brown. In the final step the monolith was dried in vacuo.

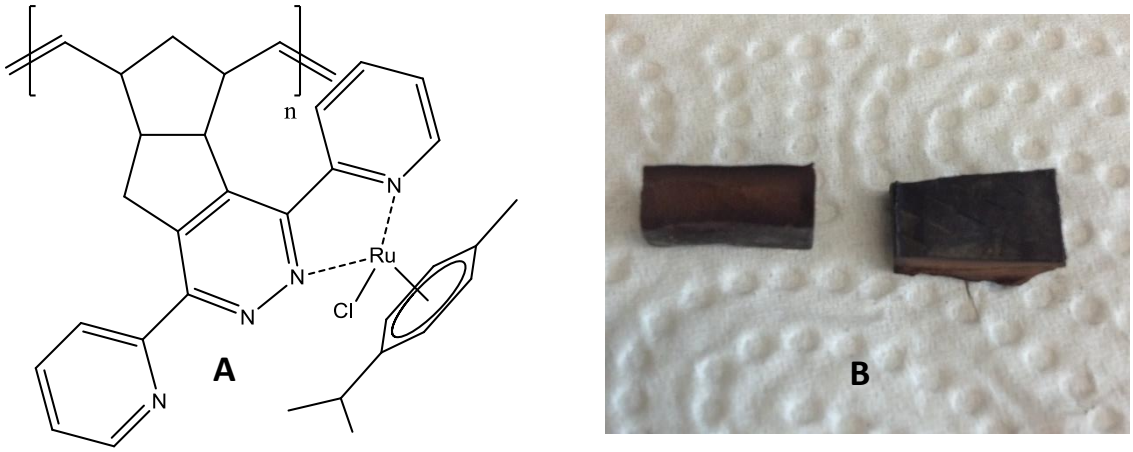


Figure 14: A) Ru(II) complex on polyHIPE; B) Sample after modification

Figure 14, B shows that the catalyst is coordinated through the whole sample and not only on the outer surface. The modified monolith was then used for transfer hydrogenation (Chapter 3.6.).

3.4. Tensile test

The prepared materials were tested for tensile strength to determine the Young's moduli, maximum strength and maximum elongation at yield. All three types of prepared and modified shoulder bars were tested (Figure 13, page 23).

Possible shrinkage of the test bars during modification has to be considered. For that reason it is important to measure all dimensions of the shoulder test bar after the curing and every modification because they could differ to the sample mold. All calculations were done with measured dimensions and not with the dimensions of the sample mold. For the measurement the shoulder bar was fixed like shown in. The starting length L_0 between both clamps was 80 mm. The tensile test was performed with a speed of 1 mm/min^{-1}.

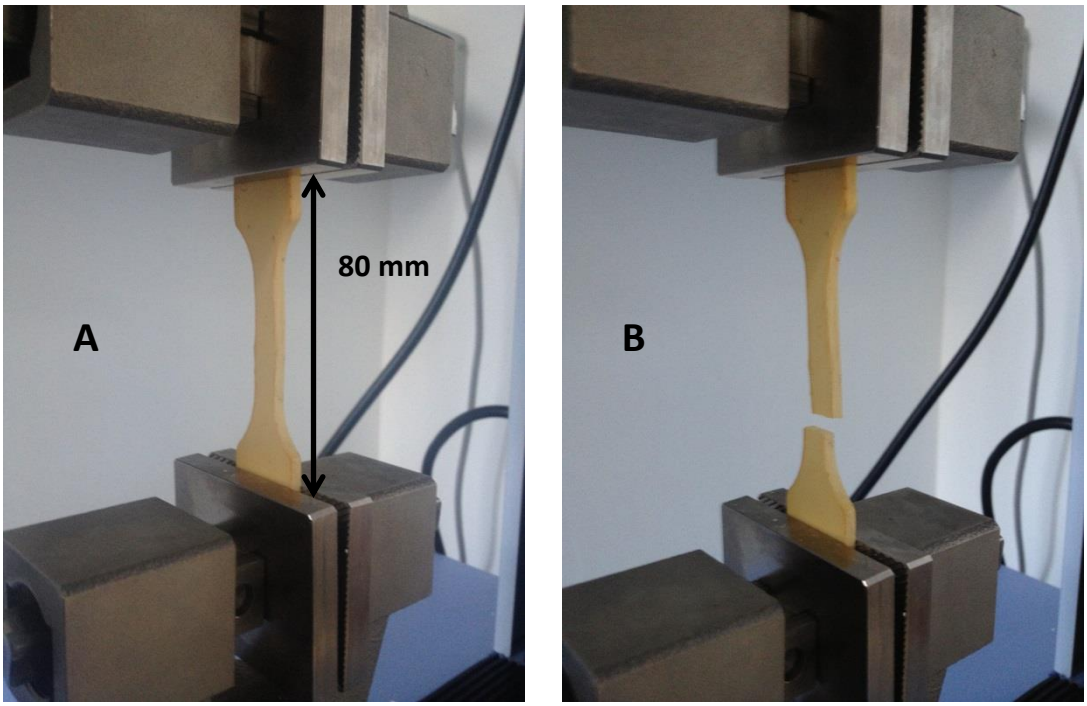


Figure 15: tensile test; A) before; B) after

The maximum strength and maximum elongation at yield were determined according to the graph. With Equation 3 the Young's modulus was calculated from the linear part of the stress-strain curves.

Equation 3: Young's modulus calculation

$$E = \frac{F * A_0}{\Delta L * L_0} * 0.1 = \frac{\sigma}{\varepsilon} * 0.1$$

E = Young's modulus [GPa]
σ = tensile stress [MPa]
ε = tensile strain [%]
F = tensile strength [N]
L_0 = start clamp distance [mm]
ΔL = elongation [mm]
A_0 = cross section area [mm²]

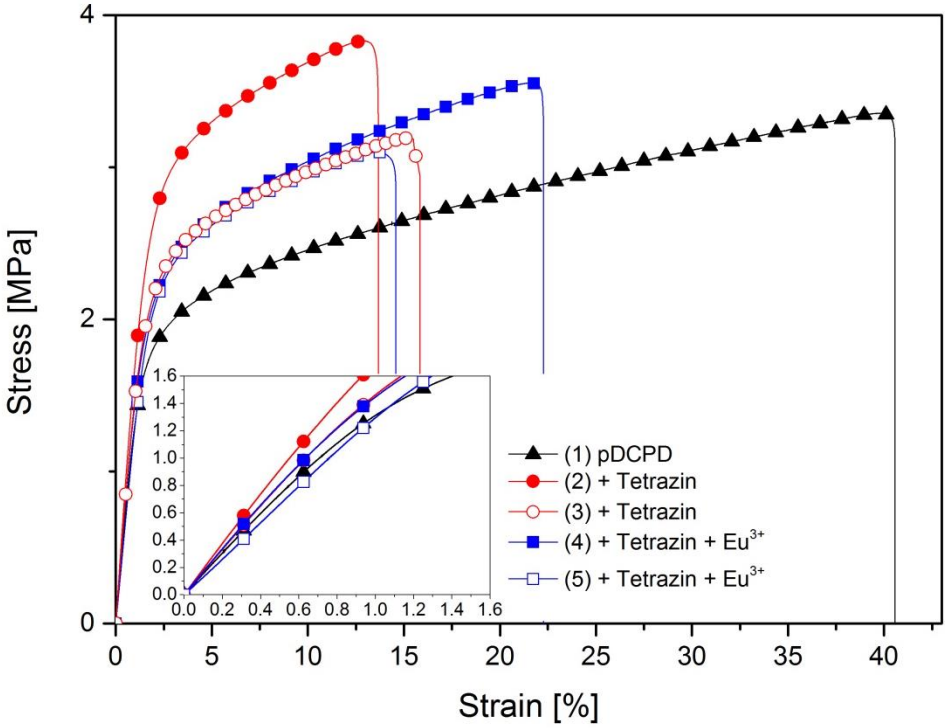


Figure 16: stress-strain diagram from mechanical testing of pDCPD

Table 2: Characterisation of pDCPD foams

sample	bipy-Tz on pDCPD	bipy-Tz	time	Eu(III)	Youngs's modulus	yield point	elongation at break
	[mg]	[%]	[h]		[MPa]	[MPa]	[%]
(1)	-	-	-	-	150	3.34	40.6
(2)	350	17.9	144	-	190	3.81	13.7
(3)	139	7.8	48	-	174	3.19	15.8
(4)	232	12.6	48	X	179	3.55	22.3
(5)	183	10.0	48	X	135	3.09	14.5

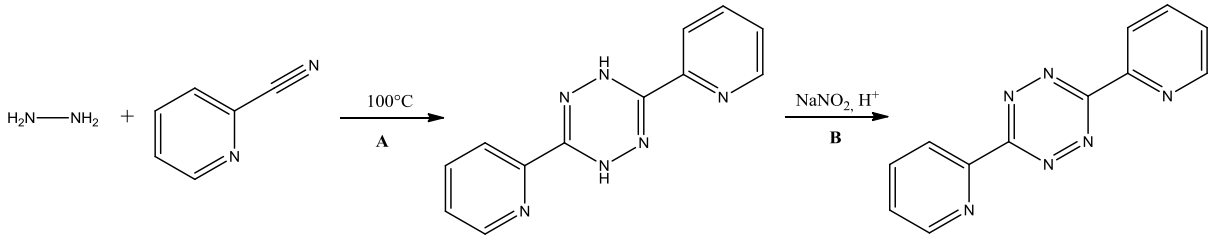
The tensile tests showed that the Young's modulus increased after the modification with bipy-Tz and that there is no discernible influence on the maximum strength. Further, increasing bipy-Tz concentration on the polyHIPE led to increased Young's modulus. The possibility of a transition metal coordinating to more than one bipy-Py was investigated. This would give extra cross-linking and might have a favourable influence on the mechanical properties. If that is the case, a broken coordination bond could recoordinate again. Unfortunately, the Eu(III) modified material showed no additional improvement to bipy-Tz modified material. In the literature,[54] polyHIPE's with 80% porosity and 5w% surfactant were reported with a Young's modulus of approximately 100 MPa, a yield point of 1.9 MPa and elongation at break between 20 - 30%. These values disagree with the obtained data for the pure pDCPD for several reasons. Firstly, in the literature less catalyst amount was used (1:7000) for the polymerisation. Secondly, it is not observable how high the purity of the DCPD was in literature and how old it was when it was used. If there were more stabilizer or epoxides in the DCPD they will destroy the catalyst. In consequence of this less cross-linked pDCPD would be obtained and the Young's Modulus decrease.

3.5. Synthesis

3.5.1. Tetrazine synthesis

3.5.1.1. 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine (bipy-Tz)[18]

3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine (bipy-Tz) was prepared with the hydrazine hydrate method. In the first step of the synthesis hydrazine hydrate and 2-cyanopyridine were combined and heated for 4.5h at 100°C (Scheme 7, A) to obtain the orange solid dihydro-bipy-Tz (Figure 17A). The precipitate is filtrated as long as it is warm for maximal yield.



Scheme 7: Synthesis of bipy-Tz

In the second step the dihydro product was oxidised to bipy-Tz (Scheme 7, B). For this synthesis dihydro-bipy-Tz was dissolved in glacial acetic acid and a $NaNO_2/H_2O$ solution was added dropwise. After adding the oxidant the colour of the product changed from orange to violet (Figure 17B) and nitrous gases were formed (NO_2^- decomposed to NO_x). Conversion was detected by TLC analysis. After 2h the product was purified by recrystallization from EtOH, filtered and then dried in vacuo. The overall yield of bipy-Tz was 40 - 50 %. A characteristic ^{1}H-NMR spectrum for both products (**1**, **2**) is depicted in Figure 18.

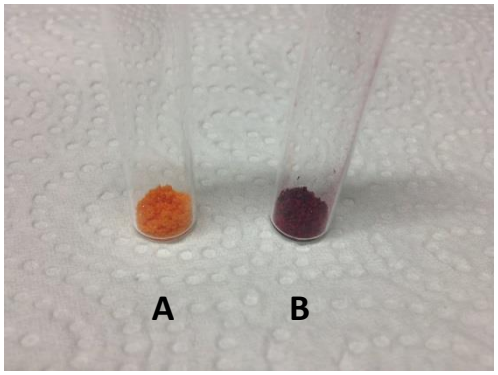


Figure 17: A) dihydro-bipy-Tz; B) bipy-Tz

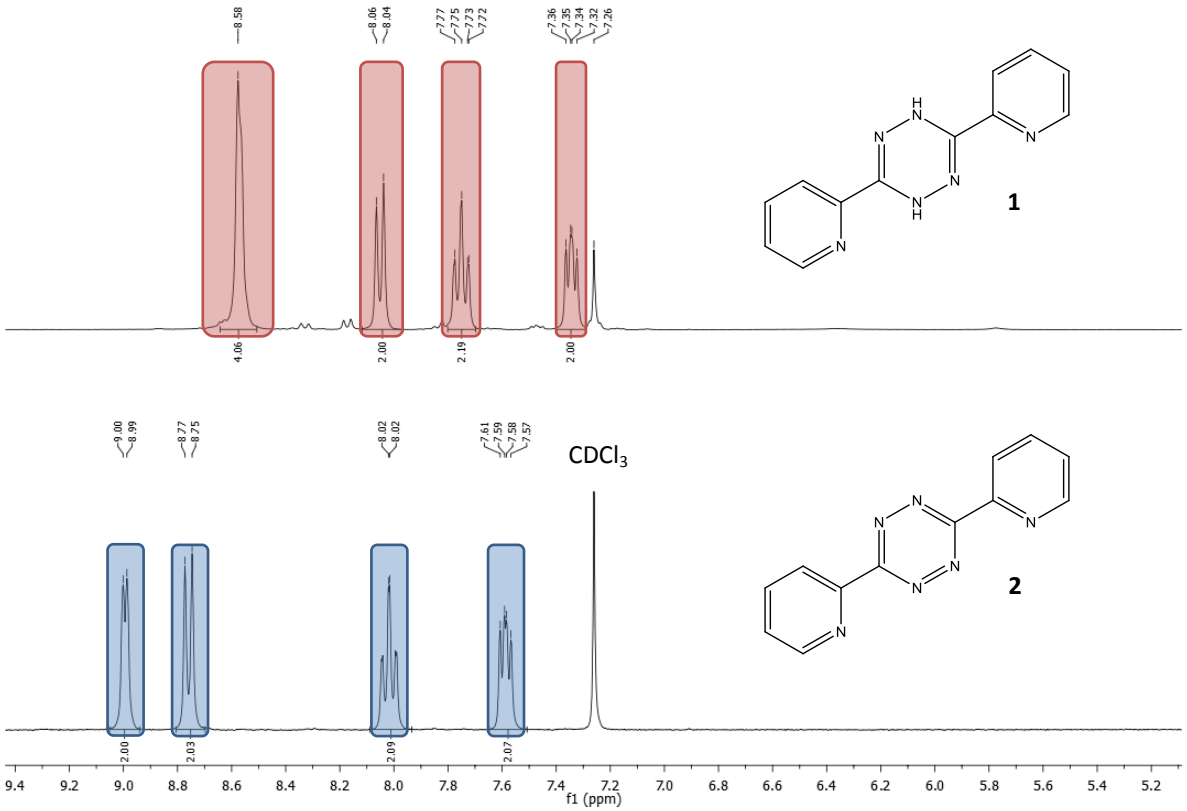


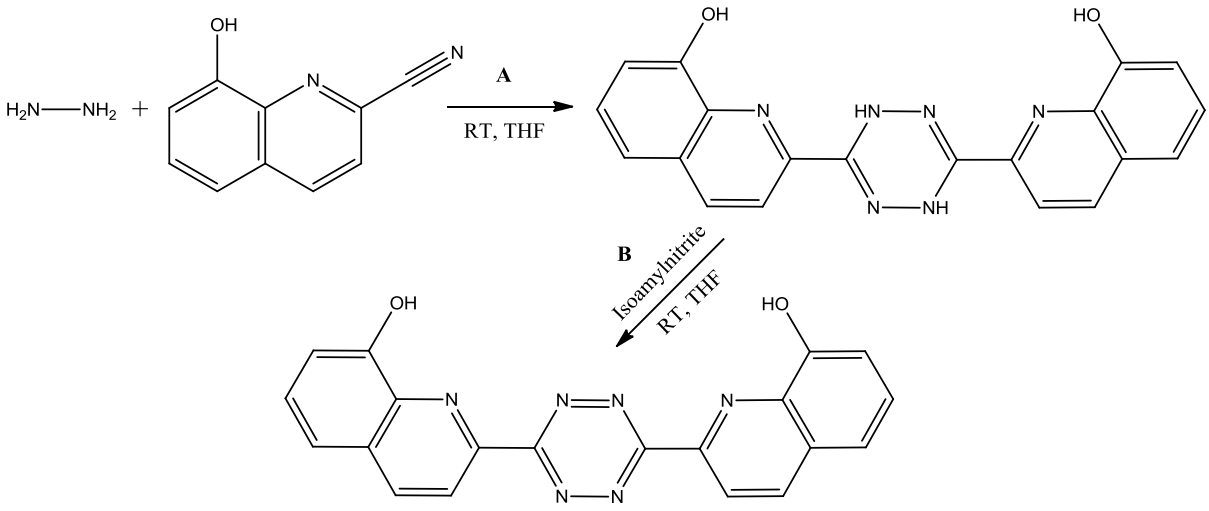
Figure 18: ^{1}H NMR spectrum of dihydro-bipy-Tz (**1**) and bipy-Tz (**2**) (300 MHz, $CDCl_3$)

For the dihydro-bipy-Tz **1** all ten protons are formed in the aromatic area (9.00-7.58 ppm). The peak at 8.58 ppm is assigned to four protons, two from the pyridine and the NH groups of the dihydro tetrazine. After the oxidation step, only four signals corresponding to the four protons of the pyridine rings were formed. Both products are totally symmetric. All shifts and splitting patterns correspond to those published literature.[56] A complete list of all signals can be found in the experimental part (Chapter 5.2.1.2.).

[56] R. Hoogenboom, G. Kickelbick, U. S. Schubert, *Eur. J. Org. Chem.*, 2003, 4887-4896

3.5.1.2. 2,2'-(1,2,4,5-tetrazine-3,6-diyl)bis(quinolin-8-ol)

2,2'-(1,2,4,5-tetrazine-3,6-diyl)bis(quinolin-8-ol) was also prepared with the hydrazine hydrate method. In the first step 8-hydroxyquinoline-2-carbonitrile was dissolved in hydrazine hydrate (Scheme 8, A). THF was added for a better solubility of the educt. The reaction was stirred at room temperature for 6h. During that time, an orange precipitate formed in the THF phase. Deionised water was added to the reaction. The THF was removed by evaporation and the reaction was cooled in the fridge for 30 min. The formed precipitate was removed by filtration, washed with cold ethanol and dried in vacuo. The yield of the purified dihydro product was 85%.



Scheme 8: Synthesis of 2,2'-(1,2,4,5-tetrazine-3,6-diyl)bis(quinolin-8-ol)

In the second step the dihydro product was oxidised to 2,2'-(1,2,4,5-tetrazine-3,6-diyl)bis(quinolin-8-ol) (Scheme 8, B). First, the oxidation was tried under the same conditions like for the oxidation of the dihydro-bipy-Tz with sodium nitrite and glacial acid at 0°C. According to the data obtained in ^{1}H-NMR spectroscopy this oxidation did not work. For this reason an oxidation of the dihydro product with isoamylnitrite was tested. The dihydro product was dissolved in THF and isoamylnitrite was added. The mixture was stirred overnight at room temperature a. The obtained violet precipitate was filtered and dried in vacuo. Yield of the purified product was 41%.

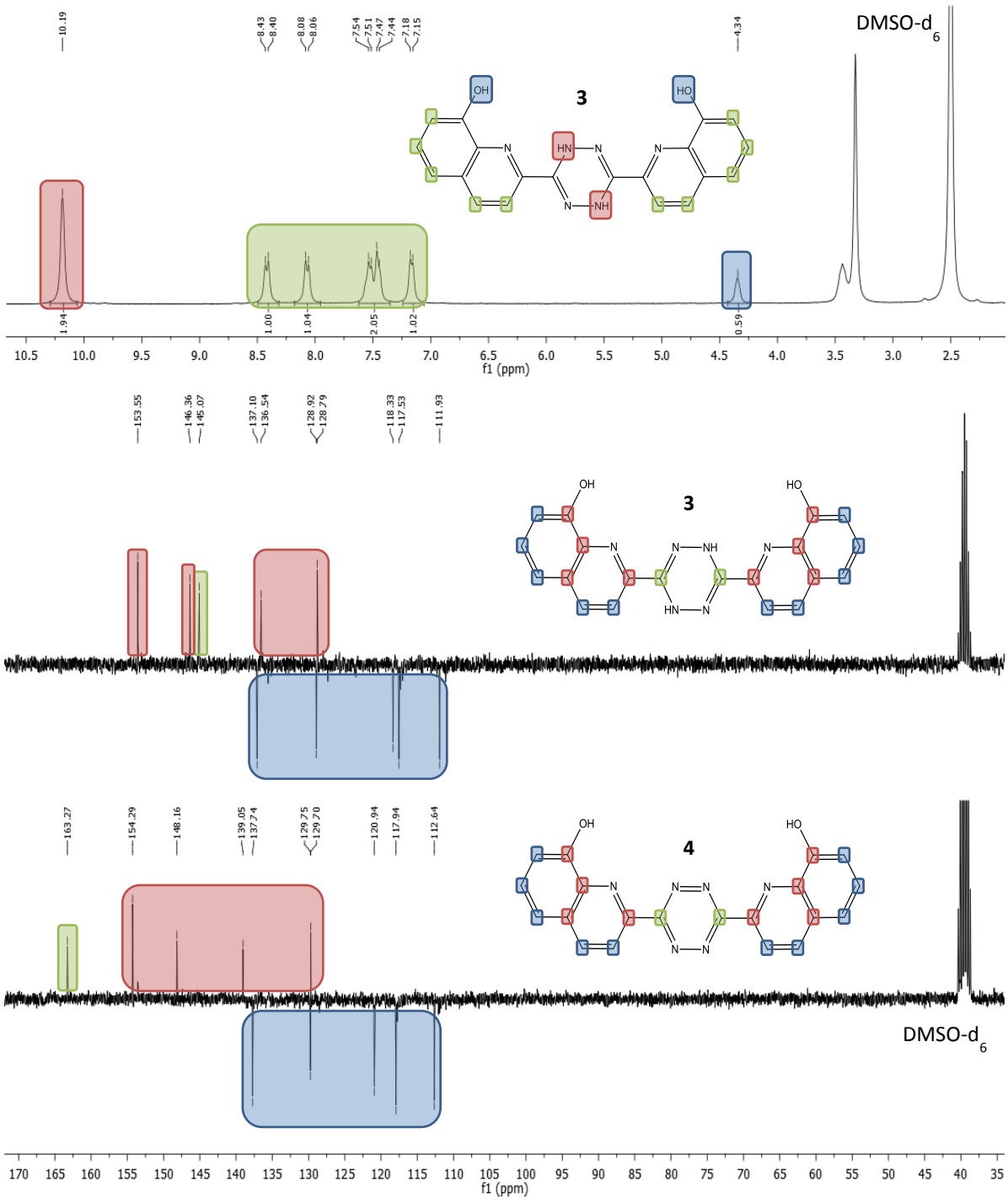


Figure 19: ^{1}H NMR spectrum of **3** and APT spectrums of **3** and **4** (^{1}H: 300 MHz; APT: 75.53 MHz, DMSO-d_6)

After the full conversion the peak of the quaternary carbon in the tetrazine ring shifted from 146.4 ppm to 163.3 ppm. This shift was already observed in the literature for other tetrazine oxidations.[56] The rest of the peaks are almost at the same place because there is no influence of the oxidation. Because of the symmetry of the molecules every peak is representing two carbons. A complete list of all signals can be found in the experimental part (Chapter 5.2.1.4.).

3.5.1.2.1. EI mass spectroscopy

For 2,2'-(1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl)bis(quinolin-8-ol) and 2,2'-(1,2,4,5-tetrazine-3,6-diyl)bis(quinolin-8-ol) EI mass spectroscopy was performed to determine the exact mass.

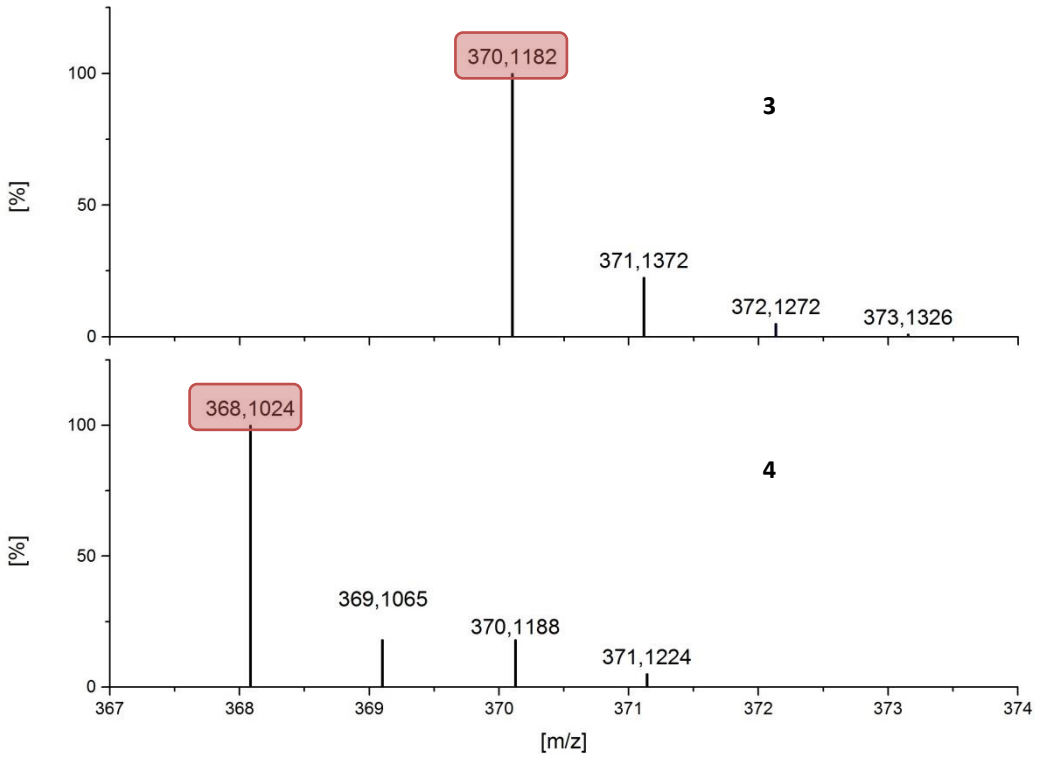
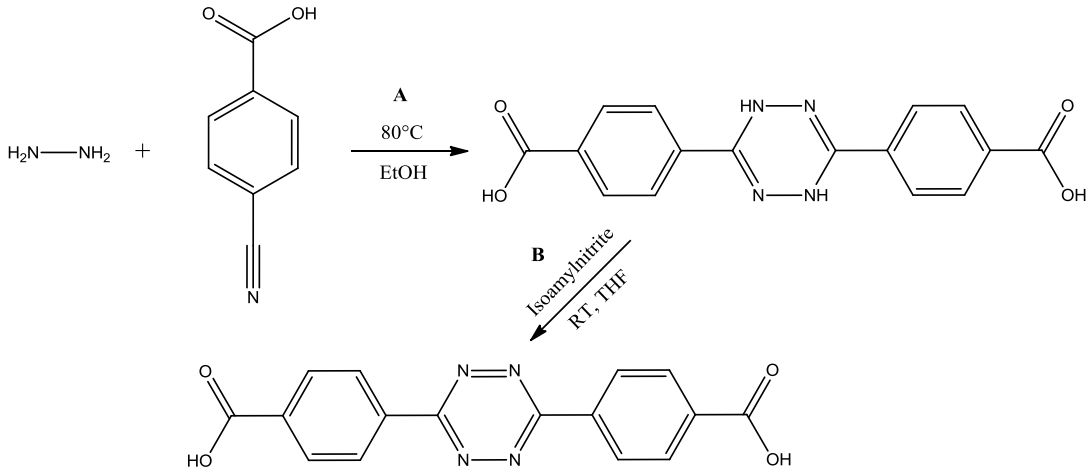


Figure 20: EI data of product **3** (top) and **4** (bottom)

The obtained data correlated with the results of NMR. In both cases the experimental determined mass matched the calculated ones (Figure 20). Product **4** lost two N-H protons in the EI. For that reason the exact mass decreased from 370.1182 m/z to 368.1024 m/z.

3.5.1.3. 4,4'-(1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid

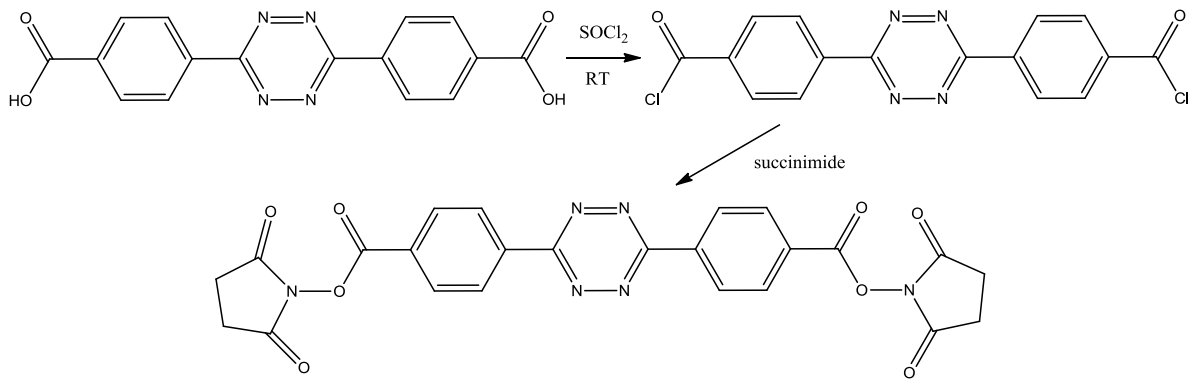
4,4'-(1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid was also prepared with the hydrazine hydrate method. Because of the poor solubility of 4-cyanobenzoic acid the method was modified. Firstly, 4-cyanobenzoic acid was dissolved in dry EtOH and stirred at 80°C. Then, hydrazine hydrate was added to the white suspension and the reaction mixture stirred for 6h. During that time, a yellow precipitate formed which was collected by filtration, washed with cold ethanol and dried in vacuo. Yield of the product was 64%.



Scheme 9: Synthesis of 4,4'-(1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid

The oxidation of the dihydro product was done like the oxidation of quinolone because the oxidation with sodium nitrite and glacial acid at 0°C did not work (according to ^{1}H-NMR). 4,4'-(1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid was suspended in THF. After the addition of isoamylnitrite and acetic acid the reaction changed its colour from yellow to pink. The mixture was stirred overnight at room temperature. Then, THF was removed by evaporation and the pink precipitate dried in vacuo. Yield of the product was 88%.

4,4'-(1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid wasn't sufficiently soluble for NMR spectroscopy. The identity of the product was confirmed upon further chemical reactions. The product was transformed to its acid chloride and then further to an active ester (succinimide) (done by Astrid Knall, Scheme 10, page 34)



Scheme 10: Synthesis of bis(2,5-dioxopyrrolidin-1-yl) 4,4'-(1,2,4,5-tetrazine-3,6-diyl)dibenzoate (done by Astrid Knall)

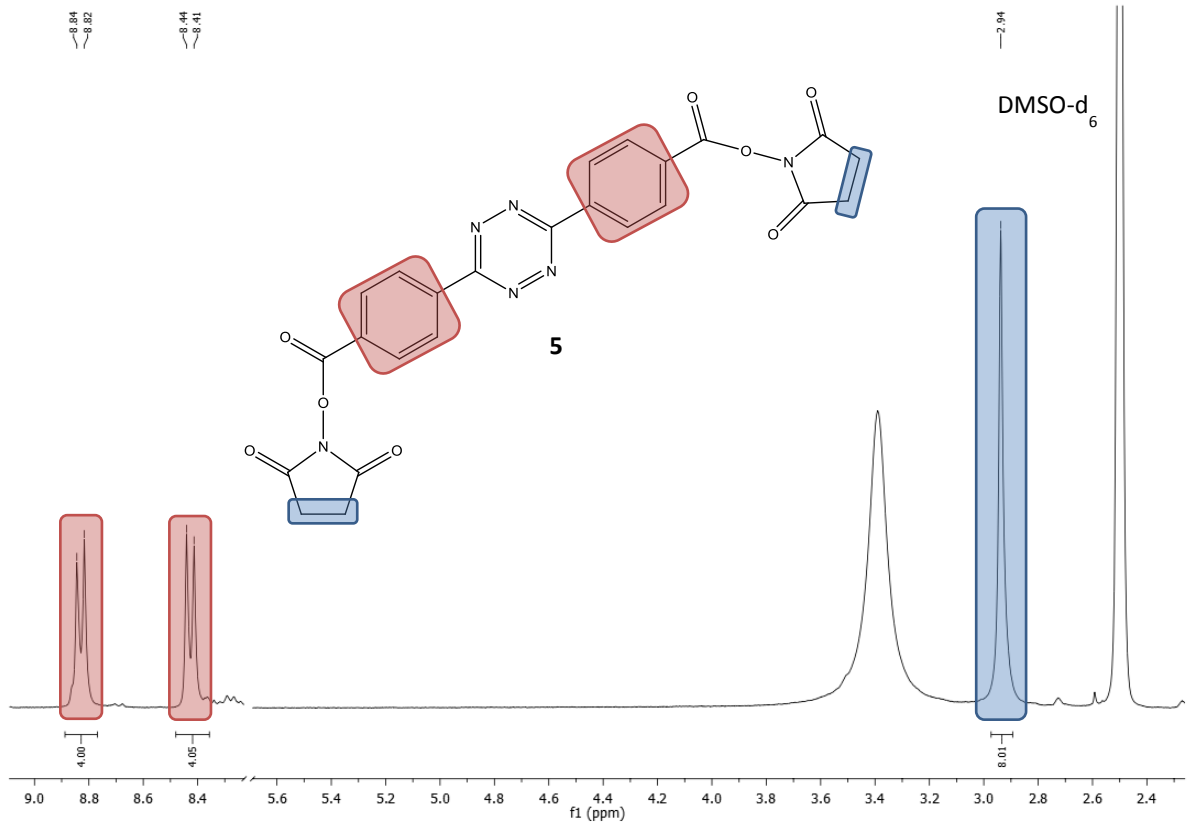


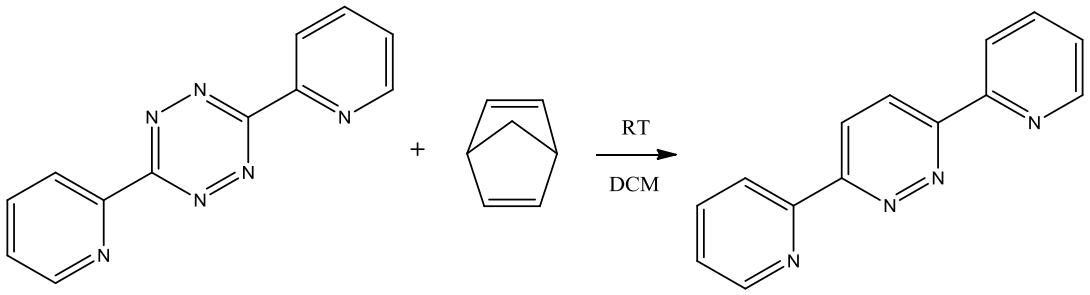
Figure 21: ^{1}H NMR spectrum of 1,1'-(4,4'-(1,2,4,5-tetrazine-3,6-diyl)bis(benzoyl))bis(pyrrolidine-2,5-dione) **5** (300 MHz, DMSO-d_6)

The ^{1}H-NMR shows aromatic phenyl peaks at 8.83 ppm and 8.42 ppm. The CH groups of the succinimide peak shown up at 2.94 ppm.

3.5.2. Pyridazine synthesis

3.5.2.1. 3,6-di(pyridin-2-yl)pyridazine (bipy-Pz)

Bipy-Pz was synthesised as ligand for the ruthenium (II) complex to obtain a reference substance for the polyHIPE-ruthenium system (Scheme 11).



Scheme 11: Synthesis of bipy-Py

A protocol of Warrener et al. was followed for the synthesis.[16] Bipy-Tz was dissolved in DCM and norbornadiene was added. After stirring overnight a brown precipitate formed. The brown solid was purified by recrystallization from EtOH. The solution was filtered and dried in vacuo. Brown needle-shaped crystals were obtained. Yield of the product was 55%.

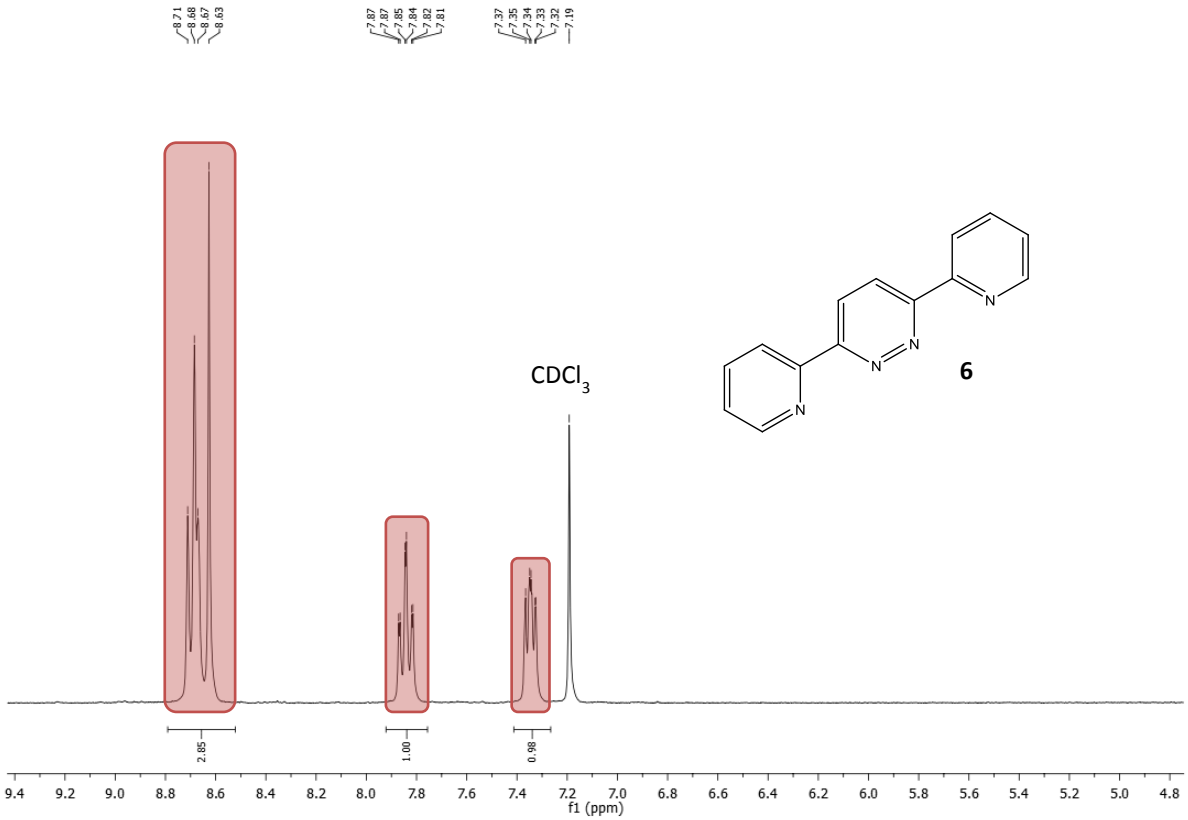
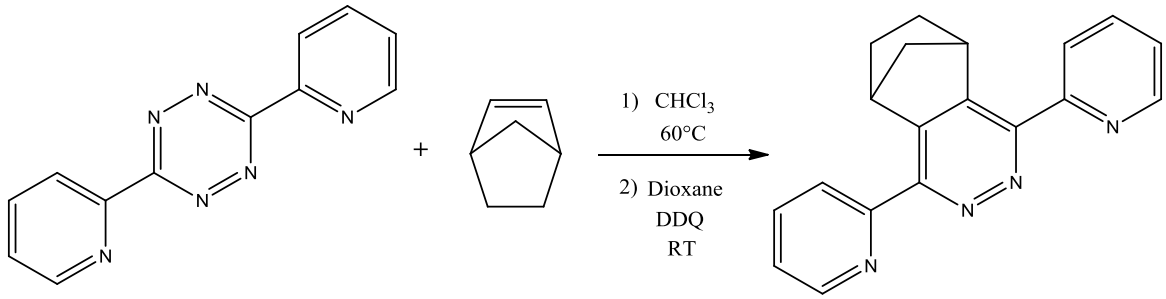


Figure 22: ^{1}H NMR spectrum of bipy-Py **6** (300 MHz, $CDCl_3$)

The peaks between 8.71-8.63 ppm represent the proton of the pyridazine and two protons of pyrimidine. All peaks correspond to the literature.[16] A complete list of all signals can be found in the experimental part (Chapter 5.2.2.1.).

3.5.2.2. 1,4-di(pyridin-2-yl)-5,6,7,8-tetrahydro-5,8-methanophthalazine

The synthesis of 1,4-di(pyridin-2-yl)-5,6,7,8-tetrahydro-5,8-methanophthalazine was done to obtain a reference substance for possible by-products during the shoulder bar modification. A protocol from Golka et al.[28] was followed. In the first step the bipy-Tz was dissolved in $CHCl_3$ and norbornene was added. The mixture was stirred for 5h at 60°C (Scheme 12, 1).



Scheme 12: Synthesis of 1,4-di(pyridin-2-yl)-5,6,7,8-tetrahydro-5,8-methanophthalazine

The ^{1}H-NMR (Figure 23, **7**) after 5h showed the dihydro **7** product but also the oxidised 1,4-di(pyridin-2-yl)-5,6,7,8-tetrahydro-5,8-methanophthalazine product. The signal at 9.18 ppm is characteristic for a dihydro product (N-H peak). The integrals at the norbornene area are not exact because of contamination.

In the second step the $CHCl_3$ was evaporated and the solid redissolved in dioxane for the oxidation with DDQ (Scheme 12, 2). After working up, the ^{1}H-NMR (Figure 23, **8**)[16] was measured and showed a full conversion.

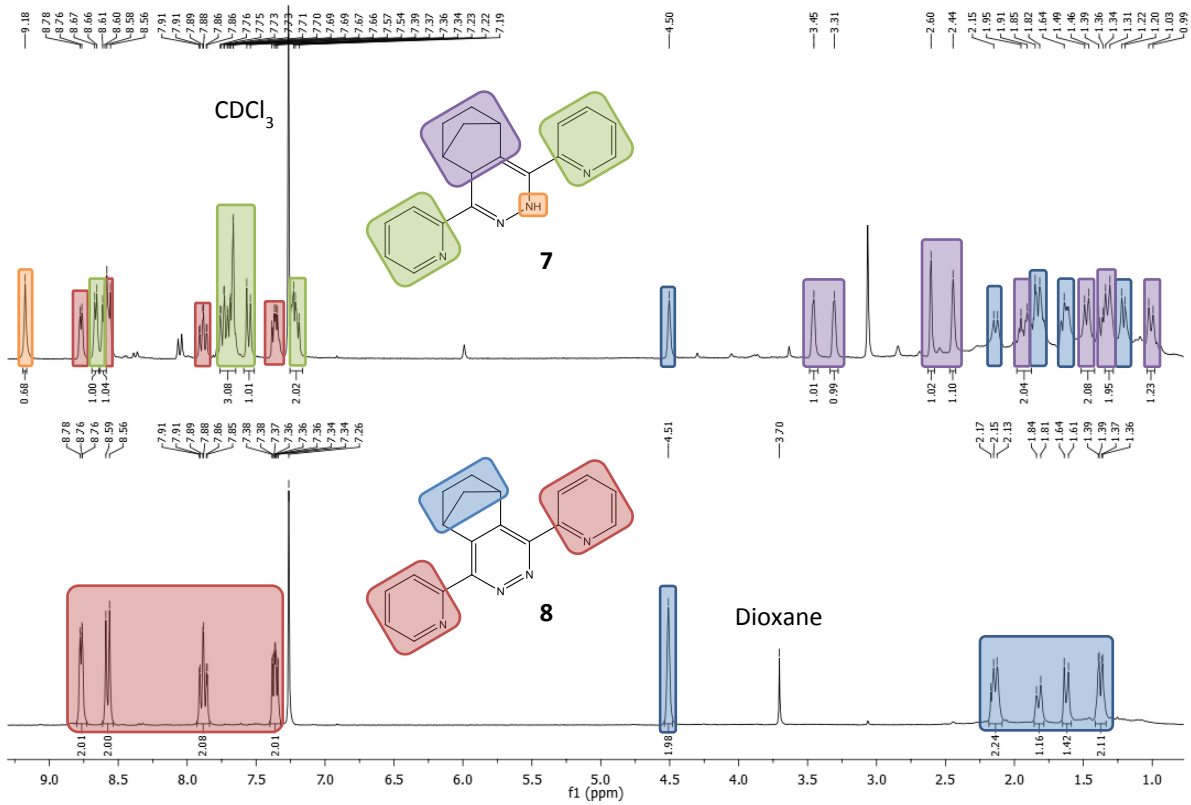


Figure 23: ^{1}H NMR spectrum of 1,4-di(pyridin-2-yl)-2,4a,5,6,7,8-hexahydro-5,8-methanophthalazine **7** and 1,4-di(pyridin-2-yl)-5,6,7,8-tetrahydro-5,8-methanophthalazine **8** (300 MHz, $CDCl_3$)

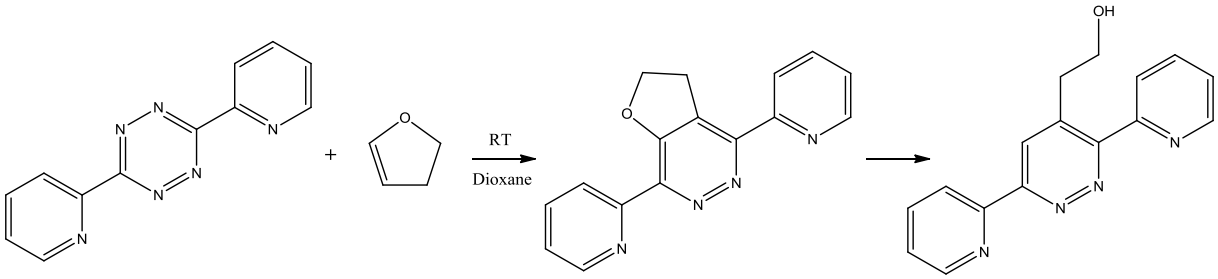
The first step leads to a mixture of two products (*endo*-**7** and *exo*-**7**), but after oxidation both stereoisomers are converted to **8**. All characteristic peaks for the pyridine (8.77, 8.57, 7.88, 7.34 ppm) and norbornene part (4.51, 2.14, 1.83, 1.63, 1.38 ppm) are found. The same applied to peaks of the APT-NMR (Chapter 5.2.2.1.).

3.5.2.3. 2-(3,6-di(pyridin-2-yl)pyridazin-4-yl)ethanol

The synthesis of 2-(3,6-di(pyridin-2-yl)pyridazin-4-yl)ethanol was also done to obtain a reference substance for possible by-products during the shoulder bars modification. The problem was, that the THF solvent, which was also tested, sometimes includes 2,3-dihydrofurane which can react with the bipy-Tz before it clicks with the pDCPD double bounds of the polyHIPE.[14]

In the literature[56] the synthesis of 2-(3,6-di(pyridin-2-yl)pyridazin-4-yl)ethanol is only described with 3-Butyn-1-ol as starting material.[13]

For the first synthesis method bipy-Tz was dissolved in dioxane and 2,3-dihydrofuran was added. The reaction was stirred overnight at room temperature (Scheme 13).



Scheme 13: Synthesis of 2-(3,6-di(pyridin-2-yl)pyridazin-4-yl)ethanol

The synthesis was also done using the same conditions like the shoulder bar modification in iPrOH and 60°C to see if the results are correlating. Under both reaction conditions the same product was obtained (Figure 24).

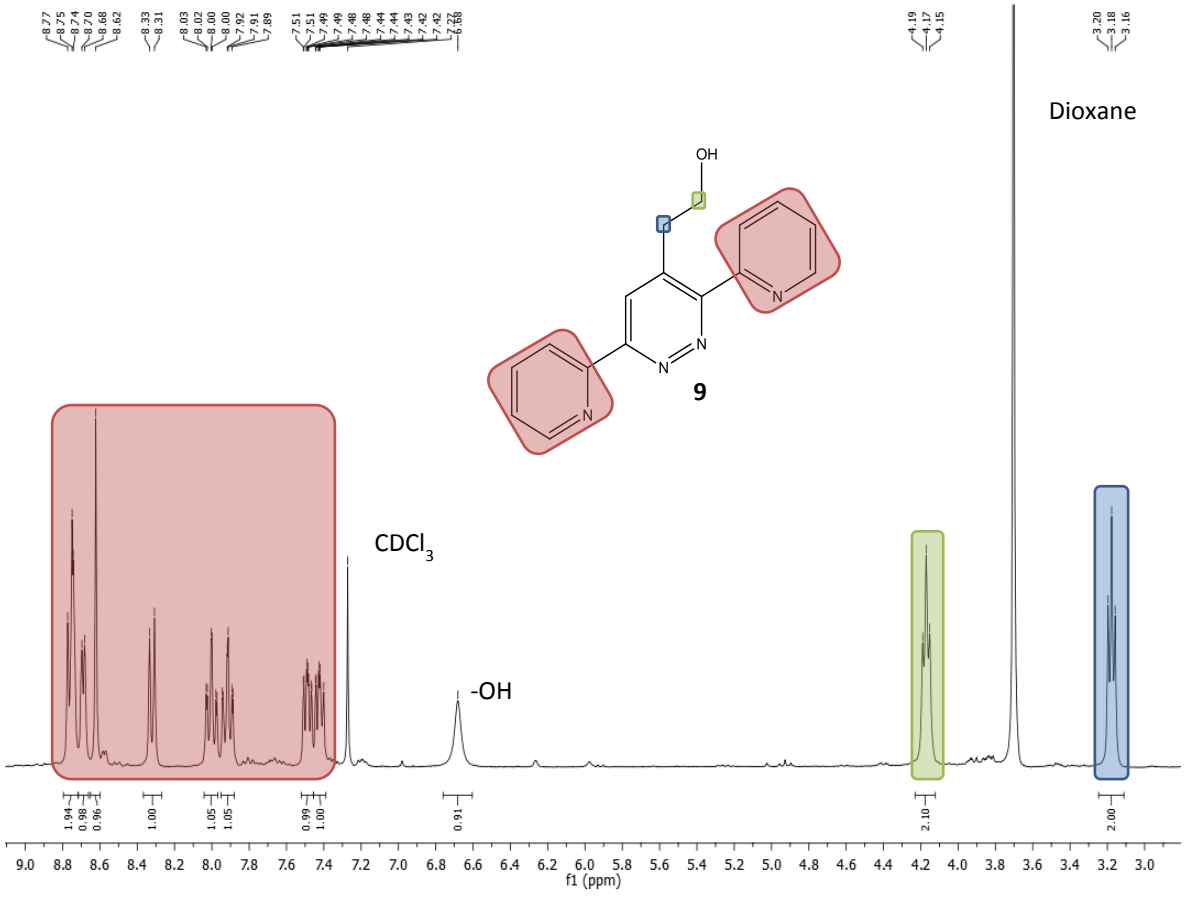


Figure 24: ^{1}H NMR spectrum of 2-(3,6-di(pyridin-2-yl)pyridazin-4-yl)ethanol **9** (300 MHz, $CDCl_3$)

The ^{1}H-NMR showed all significant peaks and also the proton integrals correlated to the literature[56]. The same applied to peaks of the APT-NMR (Chapter 5.2.2.4.)

3.5.2.4. Modification of polyisoprene (Lithene) with bipy-Tz

Lithene was modified with bipy-Tz to figure out if terminal (vinyl) double bonds would react better than internal (*cis*, *trans*) double bonds. Literature describes that more substituted molecules have a lower reaction speed.[16]

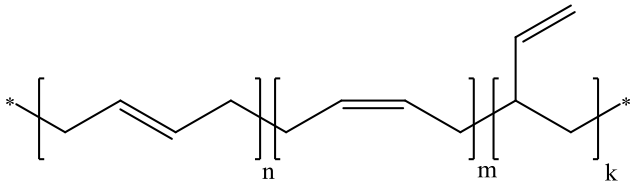


Figure 25: Repeating units Lithene

Different Lithene samples (AH, AL, N4-9000, P4-25P) were analysed with ^{1}H-NMR. Lithene AH was used because the ^{1}H-NMR showed that the amount of 1,2-vinyl double bonds was with 50-55% the highest and toluene concentration was low. These results correlated to technical data sheets of the Lithene samples[57].

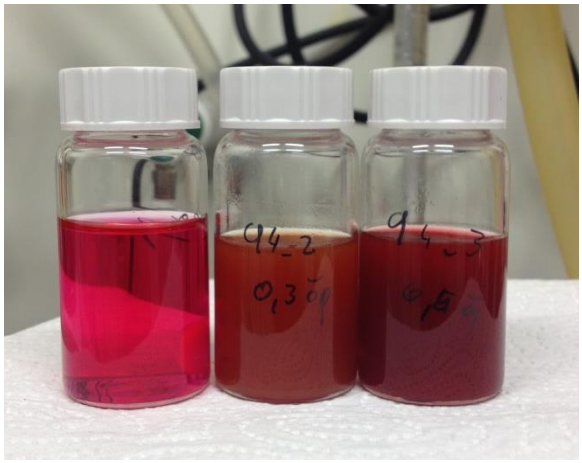


Figure 26: Lithene/bipy-Tz reactions

The reactions were performed in glass vials with bipy-Tz concentrations of 0.1-0.5eq (Table 3) (calculated to vinyl double bonds as a repeating unit) and DCM as solvent.

Table 3: weighed portions of Lithene and bipy-Tz

Lithene AH	bipy-Tz		reaction time
[mg]	[eq]	[mg]	[days]
200	0.1	87	5
200	0.3	262	7
200	0.5	436	10

[57] http://www.synthomer.com/markets-products/productfinder/products-a-z/?no_cache=1 (19.10.2013)

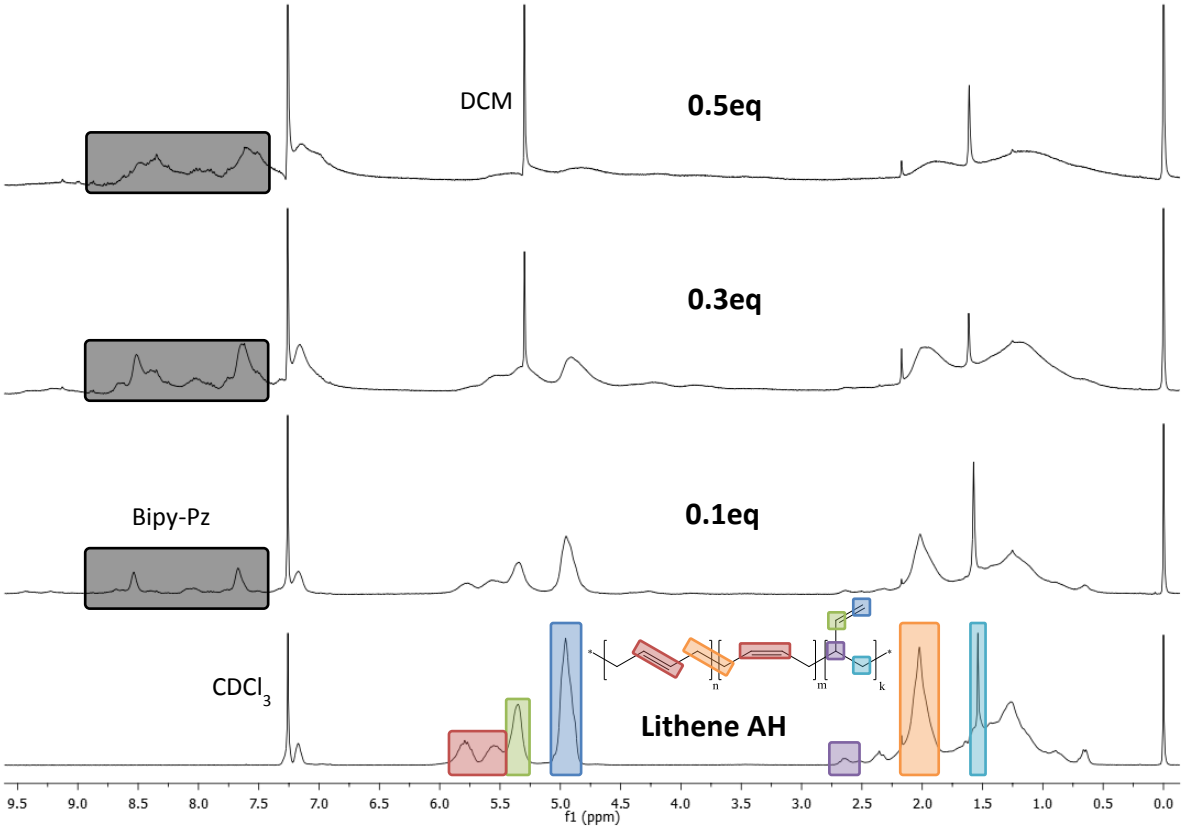


Figure 27: ^{1}H NMR spectrum of Lithene AH, 0.1eq., 0.3eq. and 0.5eq. (300 MHz, $CDCl_3$)

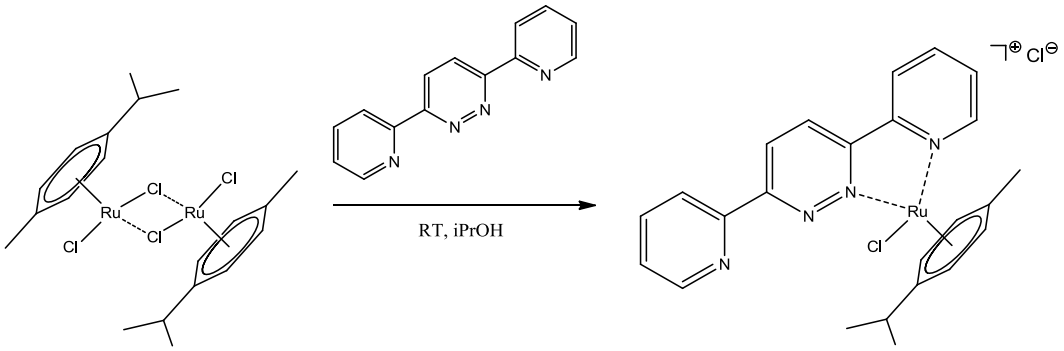
The ^{1}H-NMR showed that bipy-Tz has been entirely consumed in all three cases. The ratio between the *cis,trans*- and vinyl integrals indicated no preference of bipy-Tz to any type of double bonds, similar to what we observed for pDCPD previously[16]. It was also shown that with higher bipy-Tz concentration the specific peaks for the Lithene double bonds between 4.75-6.00 ppm disappeared and the aromatic peaks (bipy-Pz) got stronger.

3.5.3. Complex synthesis

3.5.3.1. Bipy-pyridazin complex (**com1**)

Because of bad reproducibility of the polyHIPE/catalyst to educt ratio, a reference complex **com1** was prepared. The analysis of the complex was also done with the reference complex **com1**.

To obtain the final reference substance for the ruthenium-derivatised pDCPD foams, 3,6-di(pyridin-2-yl)pyridazine ligand and dichlorobis(p-cymene)ruthenium(II)-dimer were combined (Scheme 14). Bipyridine-pyridazine molecules were been already described as ligands.[28,58]



Scheme 14: Synthesis of 3,6-di(pyridin-2-yl)pyridazinechlorobis(p-cymene)ruthenium(II)

Bipy-Py was dissolved in DCM and dichlorobis(p-cymene)ruthenium(II) was added. The mixture was stirred for 40h at room temperature under nitrogen atmosphere because there shouldn't be any O_2 in the reaction. During that time, a dark yellow precipitate formed. The precipitate was dissolved in DCM and reprecipitated with Et_2O. The solution was filtered and the precipitate dried in vacuo. The complex was stored under N_2 because it was not air-stable.

[58] G. Cooke, G. M. O Maille, R. Quesada, L. Wang, S. Varughese, S. M. Draper, *Dalton Trans.*, 2011, **40**, 8206

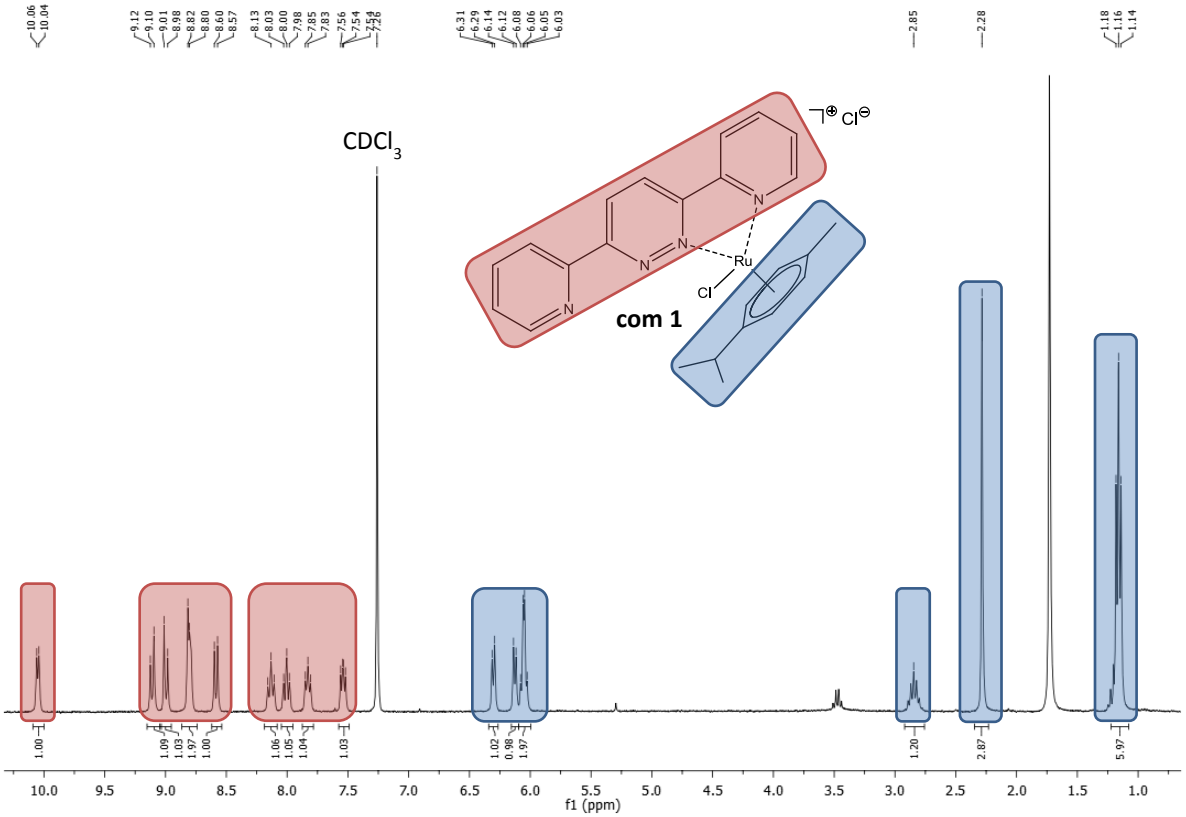


Figure 28: ^{1}H NMR spectrum of 3,6-di(pyridin-2-yl)pyridazinechlorobis(p-cymene)ruthenium(II) **com 1** (300 MHz, $CDCl_3$)

The ^{1}H-NMR shows that the Ru(II) coordinates to the bipy-Py. Because of the coordination the bipy-Tz lost its symmetry and all protons had separate peaks. That also correlated to the hypothesis and literature[28,58] that only one Ru(II) could coordinate to the bipy-Tz, otherwise the complex would be symmetric again. A complete list of all signals can be found in the experimental part (Chapter 5.2.3.1.).

3.5.3.1.1. X-ray structure

For stereochemical analysis, crystals were grown by slowly reprecipitating from a complex/DCM solution with Et_2O and measured by single crystal X-ray diffraction. Then, the molecular structure of **com1** was obtained (Figure 29).

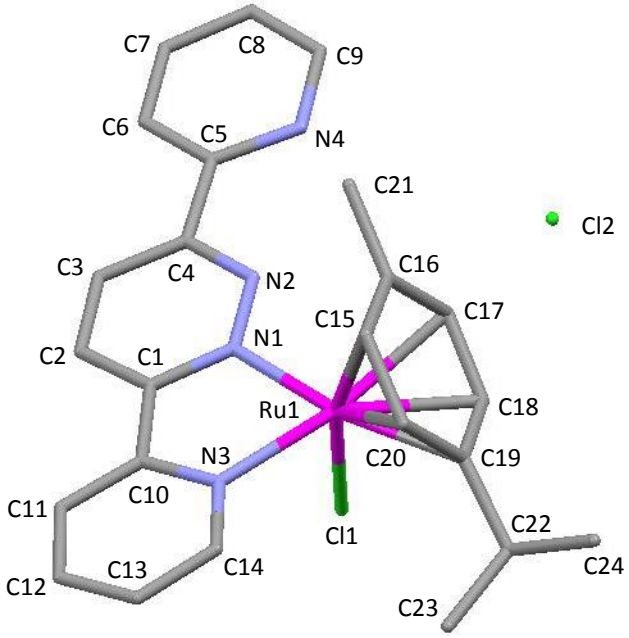


Figure 29: X-ray structure of the pyridazine complex **com1**

The stereochemical analysis showed that the assumed structure from the ^{1}H-NMR was correct. It seems that it is impossible that two Ru(II) complexes coordinate to only one bipy-Pz.

Table 4: Selected bond lengths of pyridazine complexes and ref complex1[59] (Å)

pyridazine complex	Interatomic distance	ref complex1	Interatomic distance
	Å		Å
Ru(1)-Cl(1)	2.3988 (5)	Ru(1)-Cl(1)	2.4132(5)
Ru(1)-N(1)	2.0604 (18)	Ru(1)-N(1)	2.0943(14)
Ru(1)-N(3)	2.1014 (17)	Ru(1)-N(2)	2.0988(13)
Ru(1)-C(15)	2.188 (2)	Ru(1)-C(1)	2.1843(16)
Ru(1)-C(16)	2.223 (2)	Ru(1)-C(2)	2.2105(18)
Ru(1)-C(17)	2.207 (2)	Ru(1)-C(3)	2.1873(16)
Ru(1)-C(18)	2.185 (2)	Ru(1)-C(4)	2.1864(19)
Ru(1)-C(19)	2.231 (2)	Ru(1)-C(5)	2.1758(17)
Ru(1)-C(20)	2.196 (2)	Ru(1)-C(6)	2.2024(16)
N(1)-N(2)	1.329 (2)		
N(3)-C(14)	1.346 (3)		
C(2)-C(3)	1.372 (3)		

The Ru-C and Ru-Cl bond lengths are in both complexes nearly the same. There is only a difference between the Ru-N bond lengths, because N1 binds to another nitrogen (N2) which is stronger electron withdrawing than the carbon (C14) beside N3. The ligand of ref complex1 is symmetric, so both Ru-N bond lengths are similar.

[59] J. Canivet, L. Karmazin-Brelot, G. Süss-Fink, *Journal of Organometallic Chemistry.,* 2005, **690**, 3202-3211

Table 5: Selected angle lengths of pyridazine complexes and ref complex1[59] (°)

pyridazine complex	Bond angles	ref complex1	Bond angles
	[°]		[°]
N(1)-Ru(1)-N(3)	76.68 (7)	N(1)-Ru(1)-N(2)	77.64(5)
N(1)-Ru(1)-Cl(1)	83.30 (5)	N(1)-Ru(1)-Cl(1)	85.42(4)
N(3)-Ru(1)-Cl(1)	86.68 (5)	N(2)-Ru(1)-Cl(1)	85.80(4)

Because of the influence of the electron withdrawing nitrogen the angle between N(1)-Ru(1)-Cl(1) and N(3)-Ru(1)-Cl(1) are not similar to those in ref complex 1.

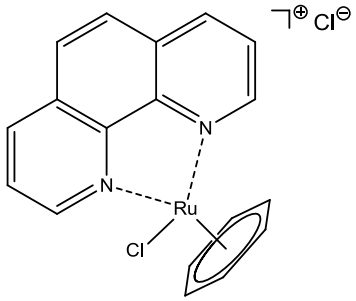


Figure 30: structure ref complex1

3.5.3.2. bipy complex (**com2**)

The bipy complex **com2** was prepared under the same conditions as **com1** but for a better solubility iPrOH was used instead of DCM.

The complex wasn't soluble in $CDCl_3$, therefore, D_2O was used instead. So there was no possibility to compare the complex with the bipy-Pz complex. In the presence of D_2O the chloride could be exchanged in the complex. This process depends on the D_2O concentration and the time. It was also documented that the complex could build a dimer under these conditions.[60]

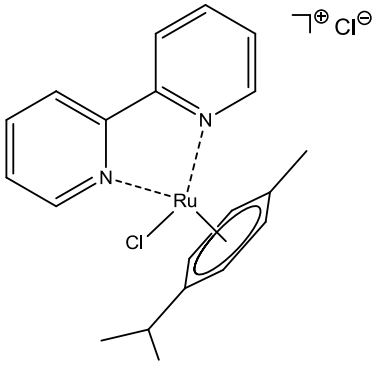


Figure 31: sturcture **com2**

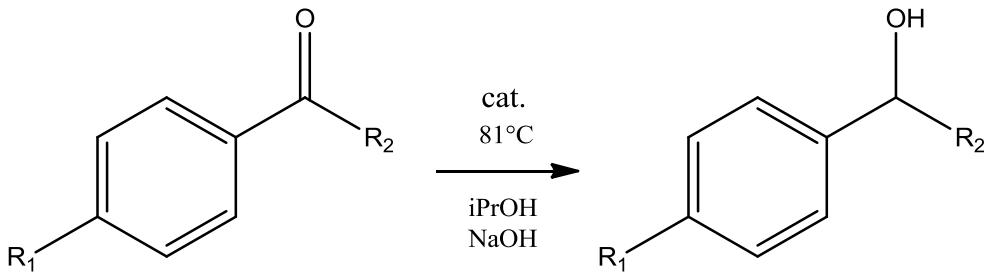
For that reason, a chloride and a D_2O complex were found in the ^{1}H-NMR. The ratio between these complexes is Cl/D_2O = 10/1. A complete list of all ^{1}H-NMR signals can be found in the experimental part (Chapter 5.2.3.2.).

[60] L. Biro, E. Farkas, P. Buglyo, *Dalton Trans.*, 2012, **41**, 285

3.6. Transfer hydrogenation

In the transfer hydrogenation the hydrogen is donated from another molecule, which is itself oxidized. Different heterogeneous or homogeneous catalysts[61] and different conditions (iPrOH/iPrONa[62], iPrOH/iPrOK[63], HCOOH/Et_3N[64]) are employed. The synthesised reference bipy-pyridazin complex was used as catalyst for the transfer hydrogenation in the system to find out if that the ruthenium-derivatised pDCPD is an active catalyst.

All synthesised transfer hydrogenation products were obtained with the same procedure. Substrate, catalyst, NaOH and iPrOH were put in a Schlenk flask and stirred for 24h at 81°C (Scheme 15). Depending on the amount of catalyst the reaction changed the colour to brown or black. The reactions were monitored by ^{1}H-NMR.



Scheme 15: General synthesis of transfer hydrogenation products

In this system iPrOH will be oxidised to acetone and the ketone will be reduced to the alcohol. Acetophenone was the first substrate which was tested. Five different catalytic loadings (0.01eq, 0.001eq, 0.0001eq, 0.00001eq and 0.000001eq) were tested to obtain the lowest loading which is useful. After 24h ^{1}H-NMR showed, a full conversion in all runs. However, acetophenone was too volatile and therefore evaporated during drying of the product mixtures, so that the conversion could not be exactly determined. For that reason substrates with higher molecule weights were used. 1-(4-nitrophenyl)ethanone and 1-(4-hydroxyphenyl)ethanone were tested but the reaction didn't work. ^{1}H-NMR showed that the 1-(4-nitrophenyl)ethanone polymerised under these reaction conditions.

The next substrate was 1-(4-chlorophenyl)ethanone **10** because there was no reactive group beside the ketone under these conditions. The first reaction with a catalytic loading of 0.01eq showed a conversion of 95% after 24h. For that reason a reaction series was done (Table 6) to determine the lowest possible loading.

[61] R. A. W. Johnstone, A. H. Wilby, I. D. Entwistle, *Chem. Rev.*, 1985, **85**, 129
[62] C. Standfest-Hauser, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, L. Xiao, W. Weissensteiner, J. Chem. Soc., Dalton Trans., 2001, 2989-2995
[63] A. E. Díaz-Álvarez, V. Cadierno, *Appl. Sci.*, 2013, **3**, 55-69
[64] X. Xu, R. Wang, J. Wan, X. Ma, J. Peng, *RSC Advances*, 2013, **3**, 6747

Table 6: weighed portions of transfer hydrogenation with 1-(4-chlorophenyl)ethanone

1-(4-chlorophenyl)ethanone		Complex 1	NaOH	iPrOH	comment
[mg]	[eq]	[eq]	[eq]	[ml]	
833	1	0.01	0.02	4	no reaction
833	1	0.01	0.12	4	conversion (95%)
833	1	0.001	0.12	4	conversion (91%)
833	1	0.0001	0.12	4	conversion (86%)
833	1	0.00001	0.12	4	conversion (88%)
833	1	0.000001	0.12	4	conversion (88%)
833	1	-	0.12	4	conversion (88%)

Table 6 displays that a catalytic loading of 0.000001eq to the ketone is sufficient to obtain a conversion with high yield after 24h. It displays also that a NaOH loading of 0.12eq is required for the reaction, probably to activate the catalyst.

To obtain the maximum conversion the reactions were monitored for 46h with ^{1}H-NMR (Figure 32).

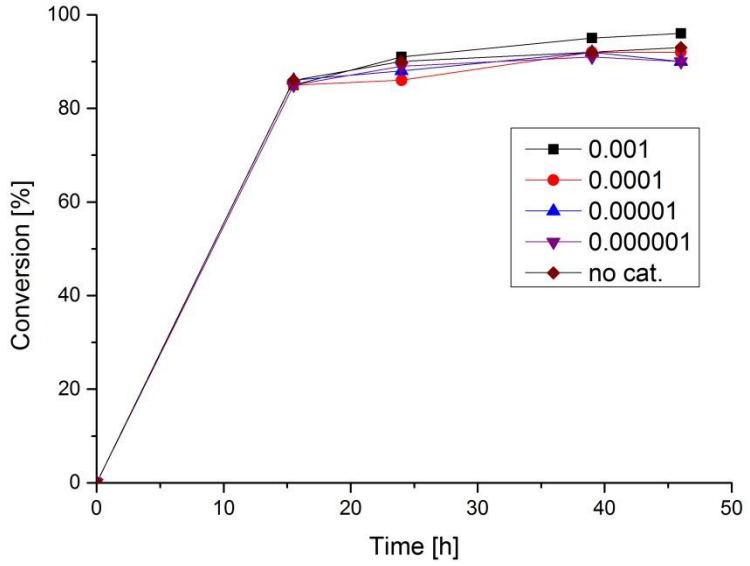


Figure 32: reaction conversion with 1-(4-chlorophenyl)ethanol

The curves show that a catalytic loading of 1ppm also gave a conversion up to 88%. As an example of all measured ^{1}H NMR, Figure 33 shows a spectrum after 16h with a loading of 0.01eq.

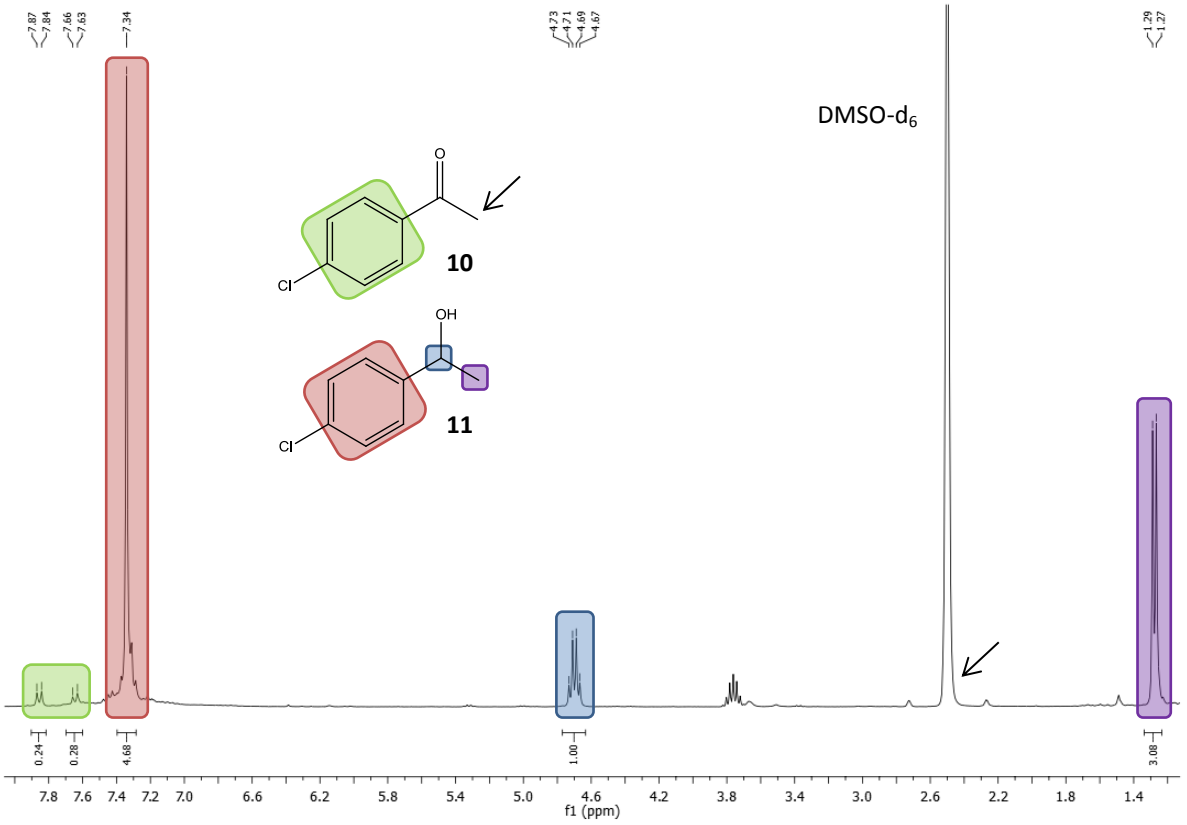


Figure 33: ^{1}H NMR reaction spectrum of 1-(4-chlorophenyl)ethanol **11** after 16h (0.01eq) (300 MHz, DMSO-d_6)

The characteristic peaks of the product of the reduction namely 1-(4-chlrorphenyl)ethanol **11** are located at 4.70 ppm (CH) and 1.28 ppm (CH_3). The conversion can be readily calculated taking the ratio of the integrals of the educt and product peaks into account.

To confirm these results 1,2-diphenylethanone **12** was tested as substrate for the transfer hydrogenation. The first reaction with a catalytic loading of 0.01eq and a NaOH loading of 0.12eq showed only a conversion of 33% after 24h. That is consistent because the chlorophenyl is stronger electron withdrawing groups than the phenyl. For that reason a reaction then with the same catalyst but higher NaOH loading (0.36eq) was done. This reaction had a conversion of 94% after 24h (Figure 34).

Table 7: weighed portions of transfer hydrogantion with 1,2-diphenylethanone

1-(4-chlorophenyl)ethanone		Complex 1	NaOH	iPrOH	comment
[mg]	[eq]	[eq]	[eq]	[ml]	
725	1	1:100	0.02	4	no reaction
725	1	1:100	0.12	4	conversion (33%)
725	1	1:100	0.36	4	conversion (94%)

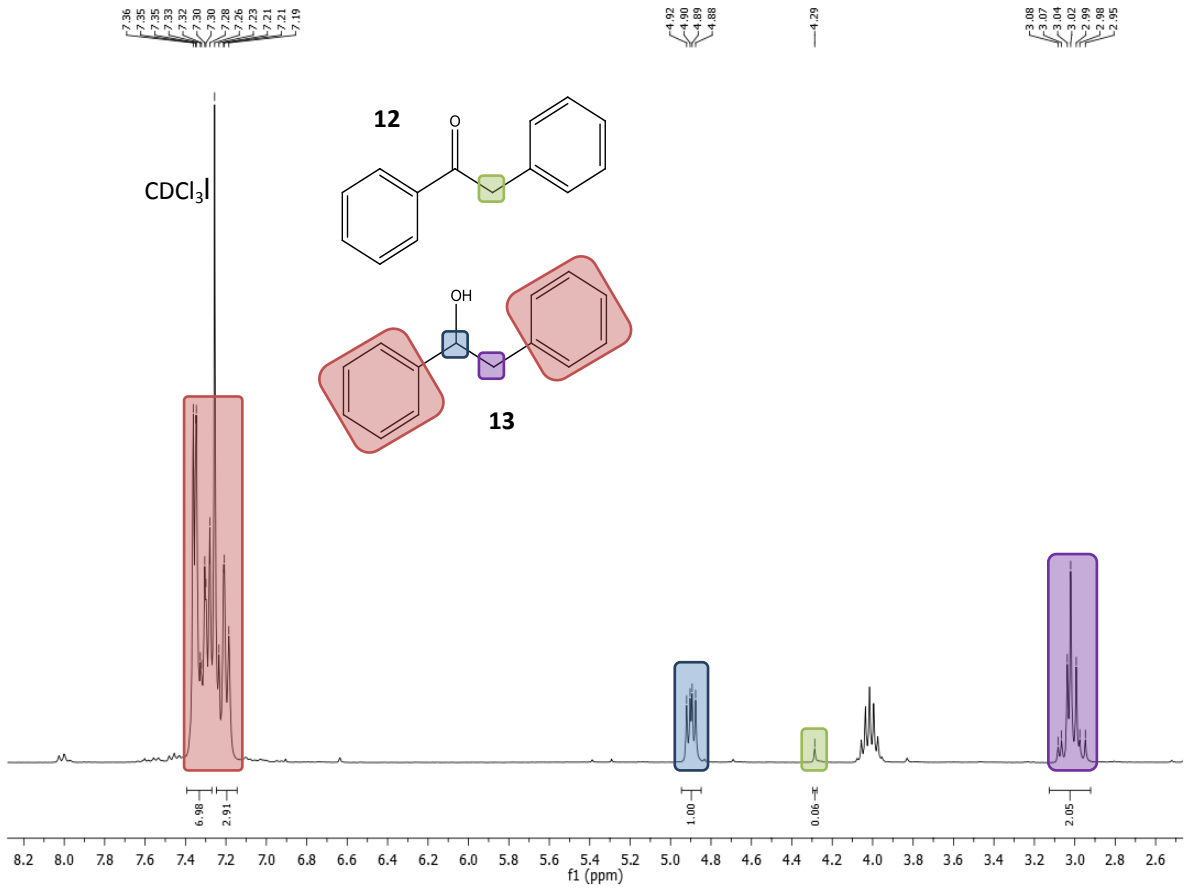


Figure 34: ^{1}H NMR reaction spectrum of 1,2-diphenylethanol **13** after 24h (0.01eq) (300 MHz, DMSO-d_6)

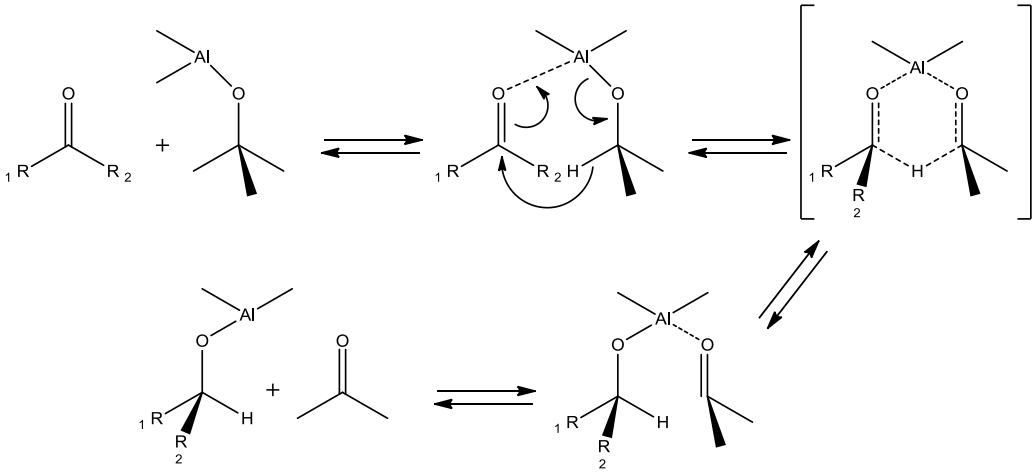
The characteristic peaks of the product of the reduction, namely 1,2-diphenylethanol (**13),** are located at 4.90 ppm (CH) and 3.02 ppm (CH_2). The reference educt peak is located at 4.29 ppm. The conversion can be readily calculated taking the ratio of the integrals of the educt and product peaks into account.

Because a high amount of NaOH was necessary to get any conversion, a blank reaction without any catalyst and a NaOH loading of 0.36eq was done. ^{1}H-NMR showed the same product peaks as in Figure 34. Because of these results a blank sample reaction was also done with **10**. The reaction worked without any catalyst. To exclude the possibility that the NaOH is contaminated the reactions were done with KOH. That gave the same results like before.

Based on these results, it seems likely that **com1** exhibits no catalytic activity in transfer hydrogenation.

A possibility why the reduction worked without the **com1** catalyst could be a Meerwein-Ponndorf-Verley type reduction. This reaction is a reversible reduction of ketones and

aldehydes to their corresponding alcohols utilizing aluminium[65] and alkali alcoholate[66]. The tested sodium and potassium transfer hydrogenation systems also included a little percentage (>0.001%) of aluminium. It is suspected that in combination with the iPrOH they react to the catalysts $Al(iPrO)_3$, Na(iPrO) and K(iPrO).



Scheme 16: Meerwein-Ponndorf-Verley reaction pathway[67]

Alkali metal alkoxides have a small coordination number (Li) or low charge density (Na, K). For this reason, they were described with high amounts[68] up to 200 mol% in the literature. However, bases were only used in catalytic amounts in the herein presented reaction. Accordingly, the originally intended use of immobilized Ru on pyridine modified polyHIPE is meaningless.

[65] W. Ponndorf , *Angewandte Chemie,* 1926*,* **39** (5), 138–143
[66] H. Meerwein, R. Schmidt, *Justus Liebigs Annalen der Chemie*, 1925, **444** (1), 221–238
[67] C. F. de Graauw, J. A. Peters, H. van Bekkum, J. Huskens, *Synthesis*, 1994, **10**, 1007-1017
[68] E. J. Campbell; H. Zhou; S. T. Nguyen, *Organic Letters*, 2001, **3**, 2391–2393

3.7. Base catalysed click reaction

The relatively unreactive 3,6-di(pyrrol-2-yl)pyridazine could be successfully converted using bases as catalyst.[69] Therefore, we were also interested whether the norbonene-tetrazine iEDDA reaction could be base-accelerated. The reaction row was done with KOtBu, NaOH, DBU, Et_3N and without any base.

Table 8: weighed portions of norbonene/bipy-Tz

bipy-Tz	norbonene	solvent	base		Tz:N:B	time
[g]	[mg]			[mg]	[mol]	[h]
0.02	7.96	THF	KOtBu	10.3	1:1:1	0.1
0.02	7.96	THF	NaOH	3.4	1:1:1	32
0.02	7.96	THF	DBU	12.9	1:1:1	48
0.02	7.96	THF	Et_3N	8.6	1:1:1	60
0.02	7.96	THF	-	-	1:1:1	60

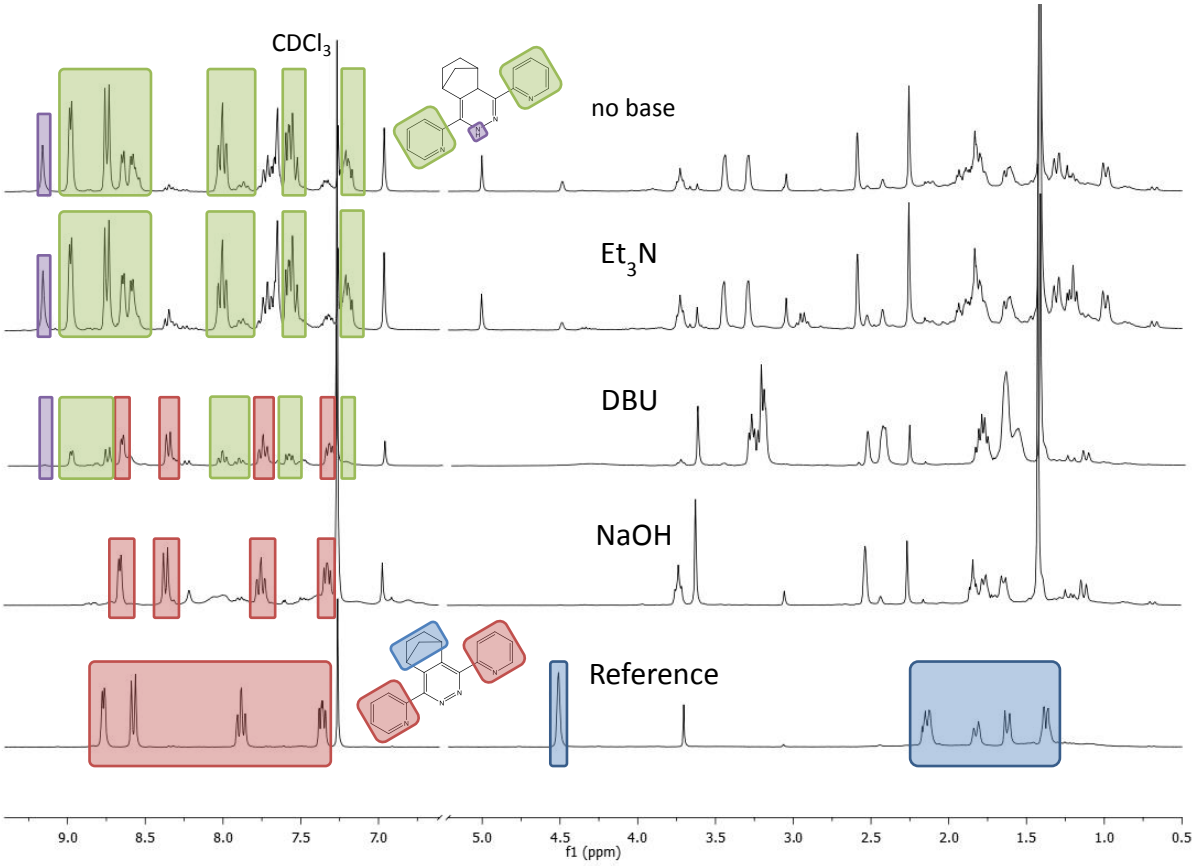


Figure 35: ^{1}H NMR spectrum of base catalysed click reactions (300 MHz, $CDCl_3$)

[69] B. A. Trofimov, T. E. Glotova, D. A. Shabalin, M. Yu. Dvorko, I. A. Ushakov, E. Yu. Schmidt, A. V. Kuzmin, A. I. Mikhalevaa, *Adv. Synth. Catal.*, 2013, **355**, 1535-1539

In the literature,[69] good results were shown with KOtBu as base but in the tested system there was only decomposition product produced. The reason is a solvent effect because instead of DMSO THF was used.

The ^{1}H-NMR shows that depending on base strength more of reduced or the oxidised product was formed. With NaOH primarily the oxidised product was synthesised however with DBU the oxidised and the reduced dihydro product were formed. The ^{1}H-NMR of the Et_3N reaction was similar to the reaction without any base. It seems that Et_3N as base is too weak. The NaOH prepared sample was analysed with EI-TOF mass spectroscopy and 80% of the sample was 1,4-di(pyridin-2-yl)-5,6,7,8-tetrahydro-5,8-methanophthalazine.

4. Conclusion and Outlook

The target of preparing polyHIPEs and the further modification with tetrazine and transition metals was successfully demonstrated within this work.
Different tetrazines were synthesised and because of the good solubility and reactivity 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine was used for the modification of the polyHIPEs. The results of tensile tests showed that the Young's modulus increased after the modification with bipy-Tz from 150 MPa to 174-190 MPa. Further, increasing bipy-Tz concentration on the polyHIPE led to higher the Young's moduli. The yield at break was with 3.4 MPa nearly the same like without any modification. The elongation at break decreased from 40.6% to 13.7-22.7%. All tested shoulder bars were modified in iPrOH. With THF as solvent, the shoulder bars had a higher degree of modification but they were deformed in a way which made the tensile tests inaccurate or even impossible. With the resulting dipyridine-pyridazine groups it was possible to coordinate Eu(III) and Ru(II) on the macroporous pDCPD foams. It could be shown that transition metals coordinate through the whole sample and not only on the surface. The mechanical properties of the Eu(III) modified shoulder bars showed no further improvement. Ru(II) complexes were formed utilizing the pyridyl pyridazine moieties on the support and the scope of such modified foams as heterogeneous catalysts for the transfer hydrogenation of ketones with 2-propanol was investigated. To facilitate this purpose a homogenous variant of the corresponding Ru complex was prepared and used as a model catalyst.

As ligand for the reference complex 3,6-di(pyridin-2-yl)pyridazine was used which was obtained from the iEDDA reaction from 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine and norbornadiene. This complex was then used in the transfer hydrogenation reaction and it was demonstrated that this particular compound is not suited as a catalyst for this reaction.

5. Experimental

5.1. Reagents and Instruments

5.1.1. Reagents

All chemicals were purchased from commercial sources (Sigma Aldrich, Fluka, ABCR, Orgentis Chemicals or Alfa Aesar) and used without further purification unless specified otherwise. M2 ([1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(3-phenyl-1H-inden-1-ylidene)(tricyclohexylphosphine)ruthenium(II)) for ring opening metathesis polymerisation (ROMP) and dichlorobis(p-cymene)ruthenium(II)-dimer were obtained from UMICORE AG & Co. KG. Unless specified otherwise, solvents and auxiliary materials were used as purchased.

For TLC silica gel 60 F254 on aluminium sheets (Merck) was used. Visualization was done by exposure with UV light and / or dipping into an aqueous solution of $KMnO_4$ (0.1 %) or sulphuric solution of cerium sulphate /ammonium molybdate.

Silica gel 60 (220-440 mesh ASTM) was used for column chromatography.

5.1.2. Instruments

NMR spectroscopy (^1H, APT, ^{13}C, COSY, HSQC) was done on a Bruker Avance 300 MHz spectrometer. Deuterated solvents (Chloroform-d, DMSO-d_6, D_2O) were obtained from Cambridge Isotope Laboratories Inc. and remaining peaks were referenced according to literature. Peak shapes are specified as follows: s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quadruplet), m (multiplet).

X-ray crystal structures were recorded on a Bruker Kappa APEX II diffractometer using Mo K_α radiation by Ana Torvisco, Institute for Inorganic Chemistry, Graz University of Technology.

Element analysis for C, H and N content were determined with a Universal-Elementaranalysator Vario El III. The oxygen content was calculated as the residual weight to 100% weight loss.

Tensile strength tests were done on a Shimadzu Autograph AGS-X. The force measuring range is between 10-10kN. Samples were measured with a speed of 1 mm/min and a clamping length of 80mm.

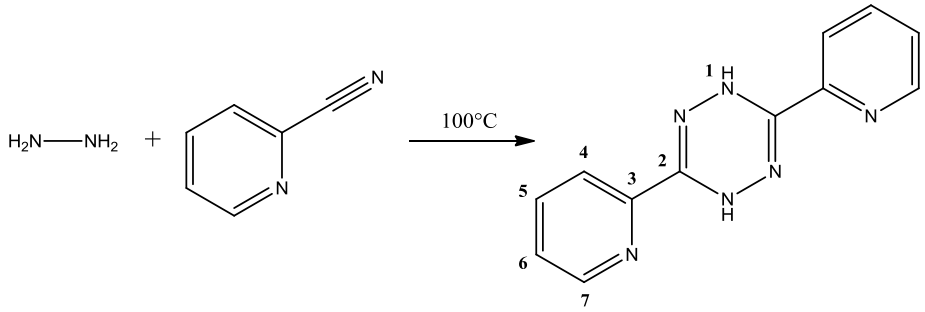
Scanning Electron Microscopy (SEM) was carried out on a Quanta200 3D microscope, using a tungsten cathode as electron source. High and low vacuum measurements were recorded with a large field gaseous secondary electron detector (LF-GSED). Magnifications ranging from 100X to 20.000X were achieved using a voltage between 3 - 20 kV.

Electron impact (EI, 70eV) mass spectra (EI-TOF-MS) were recorded on a Waters GCT Premier equipped with direct insertion (DI).

5.2. Synthesis

5.2.1. Tetrazine synthesis

5.2.1.1. 3,6-di(pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine[18]**Fehler! Textmarke nicht definiert.**



Scheme 17: Synthesis of 3,6-di(pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine

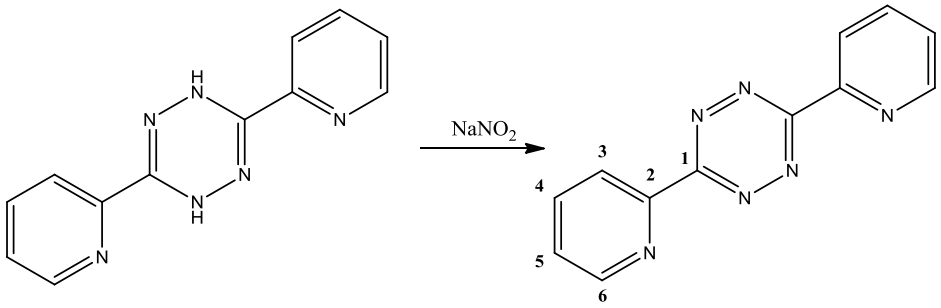
2-cyanopyridine (10 g, 96 mmol, 1eq) was dissolved in hydrazine hydrate (14.96 ml, 240 mmol, 2.5eq, 50% aq. soln.) and heated to 100°C for 4.5h. During that time, a dark yellow precipitate was formed which was collected by filtration and washed with cold ethanol. The orange solid was purified by recrystallization in EtOH. The solution was filtered and dried in vacuo. Yield: 10.54 g (92%).

TLC: R_f = 0.39 (DCM/MeOH, 20:1, (v:v))

^{1}H-NMR: (δ, 20°C, $CDCl_3$, 300.36 MHz): 8.58 (2H, tet^1; 2H, py^7), 8.05 (d, 2H, py^4), 7.75 (t, 2H, py^6), 7.34 (t, 2H, py^5).

APT: (δ, 20°C, $CDCl_3$, 75.53 MHz): 148.5 (2C, py^7), 147.6 (2C, py^3), 146.7 (2C, tet^2), 136.8 (2C, py^5), 125.0 (2C, py^6), 121.4 (2C, py^4).

5.2.1.2. 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine (bipy-Tz)[18]



Scheme 18: Synthesis of 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine (bipy-Tz)

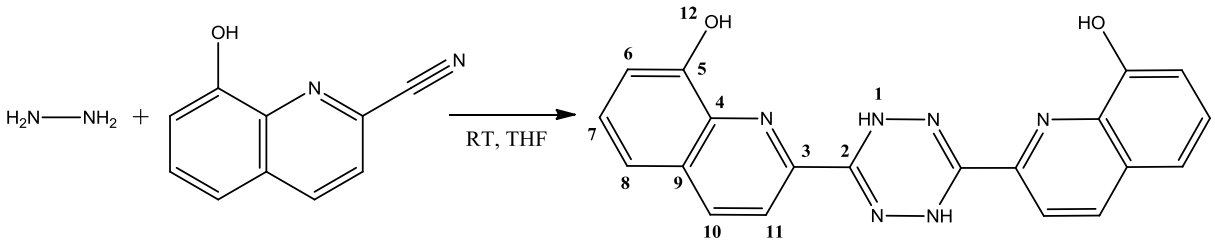
3,6-di(pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine (11.44 g, 48 mmol, 1eq) was suspended in glacial acetic acid (13 mL) and cooled to 0°C. Sodium nitrite (9.94 g, 144 mmol, 3eq) was dissolved in 20 mL deionized water and was added dropwise to the reaction. The resulting nitrous gases (caution!) were removed through a gas outlet and a violet coloured precipitate formed. After 2h of stirring, this precipitate was collected by filtration, washed with cold ethanol and dried in vacuo. The violet solid was purified by recrystallization in EtOH. The solution was filtered and dried in vacuo. Yield: 5.2 g (45.89%).

TLC: R_f = 0.49 (DCM/MeOH, 20:1, (v:v))

^{1}H-NMR: (δ, 20°C, $CDCl_3$, 300.36 MHz): 8.99 (d, $^3J_{HH}$ = 4.5 Hz, 2H, py^6), 8.76 (d, $^3J_{HH}$ = 7.9 Hz, 2H, py^3), 8.02 (ddd, $^3J_{HH}$ = 7.9, 7.8, 1.6 Hz, 2H, py^4), 7.59 (dd, $^3J_{HH}$ = 7.8, 4.5 Hz, 2H, py^5).

APT: (δ, 20°C, $CDCl_3$, 75.53 MHz): 163.9 (2C, tet^1), 151.1 (2C, py^6), 150.1 (2C, py^2), 137.5 (2C, py^4), 126.6, 124.6 (4C, py^{3,5}).

5.2.1.3. 2,2'-(1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl)bis(quinolin-8-ol)



Scheme 19: Synthesis of 2,2'-(1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl)bis(quinolin-8-ol)

8-hydroxyquinoline-2-carbonitrile (921 mg, 5.4 mmol, 1eq) was dissolved in hydrazine hydrate (848 ml, 13.5 mmol, 2.5eq, 50% aq. Soln.). THF (4 mL) was added and the reaction was stirred at room temperature. During that time, an orange precipitate formed in the THF phase. After 6h, deionized water (10ml) was added to the reaction. The THF was removed by evaporation and the reaction was cooled in the fridge for 30 min. The formed precipitate was removed by filtration, washed with cold ethanol and dried in vacuo. Yield: 850 mg (85%).

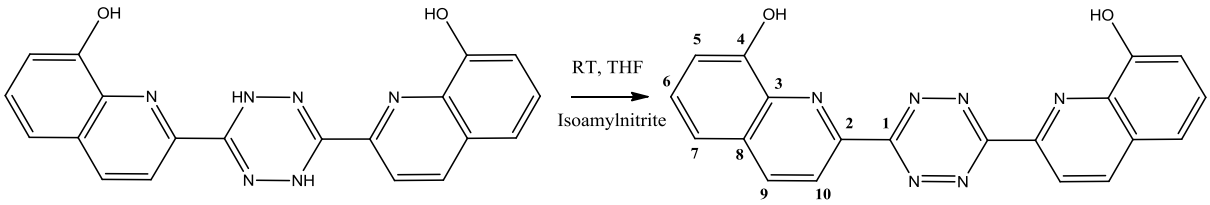
TLC: R_f = 0.50 (DCM/MeOH, 1:2, (v:v))

^{1}H-NMR: (δ, 20°C, DMSO-d_6, 300.36 MHz): 10.19 (s, 2H, tet^1), 8.42 (d, 2H, qui^{10}), 8.07 (d, 2H, qui^{11}), 7.53(t, 2H, qui^7), 7.45(d, 2H, qui^8), 7.17 (d, 2H, qui^6), 4.35 (s, 2H, qui^{12})

APT: (δ, 20°C, DMSO-d_6, 75.53 MHz): 153.6 (2C, qui^3), 146.4 (2C, qui^5), 145.1 (2C, tet^2), 137.1 (2C, qui^{10}), 136.5 (2C, qui^4), 128.9 (2C, qui^7), 128.8 (2C, qui^9), 118.3, 117.5, 111.9 (2C, qui^{6,8,11})

EI-mass spectra: m/z = [M^+] 370.1178 (calculated: m/z = [M^+] 370.12)

5.2.1.4. 2,2'-(1,2,4,5-tetrazine-3,6-diyl)bis(quinolin-8-ol)



Scheme 20: Synthesis of 2,2'-(1,2,4,5-tetrazine-3,6-diyl)bis(quinolin-8-ol)

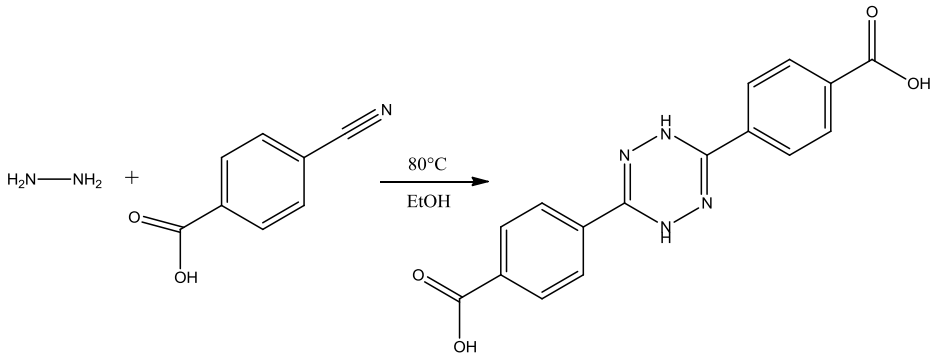
2,2'-(1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl)bis(quinolin-8-ol) (50 mg, 0.14 mmol, 1eq) was dissolved in THF (1.5 mL) and isoamylnitrite (90 µL, 0.68 mmol, 5eq) was added. The mixture was stirred overnight at room temperature. The THF was removed by evaporation and the solid residue was dried in vacuo. Yield: 40 mg (81%).

^{1}H-NMR of 2,2'-(1,2,4,5-tetrazine-3,6-diyl)bis(quinolin-8-ol) in DMSO-d_6 gave a spectrum of very poor quality.

APT: (δ, 20°C, DMSO-d_6, 75.53 MHz): 163.3 (2C, tet^1), 154.3 (2C, qui^2), 148.2 (2C, qui^4), 139.1 (2C, qui^3), 137.7 (2C, qui^9), 129.8 (2C, qui^6), 129.7 (2C, qui^8), 120.9, 117.9, 112.6 (2C, qui^{5,7,10})

EI-mass spectra: m/z = [M^+] 368.1022 (calculated: m/z = [M^+] 368.10)

5.2.1.5. 4,4'-(1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid



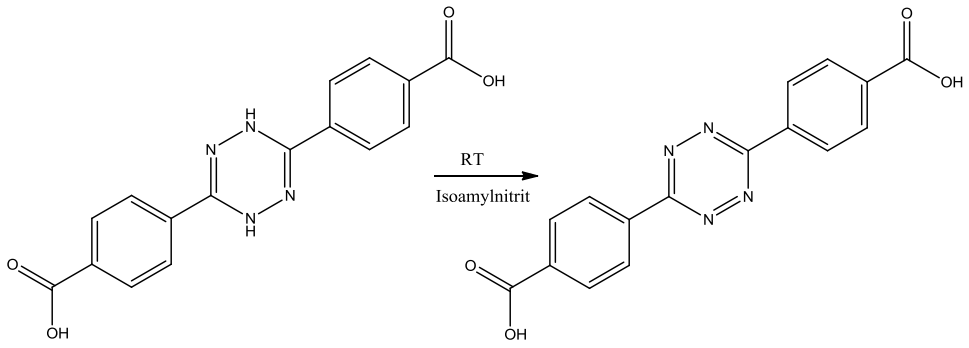
Scheme 21: Synthesis of 4,4'-(1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid

4-cyanobenzoic acid (1 g, 6.8 mmol, 1eq) was dissolved in dried EtOH (4 mL) and stirred at 80°C. To the white suspension hydrazine hydrate (1.065 mL, 16.99 mmol, 2.5eq, 50%aq. Soln.) was added and stirred for 6h. During that time, a yellow precipitate formed which was collected by filtration, washed with cold EtOH and dried in vacuo. Yield: 702 mg (64 %).

The determination of the product was done by further chemical reactions.
^{1}H-NMR of 4,4'-(1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid in DMSO-d_6 gave a spectrum of very poor quality (due to solubility).

^{1}H-NMR: (δ, 20°C, DMSO-d_6, 300.36 MHz): 9.11 (s, 2H, N-H), 8.04 – 7.75 (8H)

5.2.1.6. 4,4'-(1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid



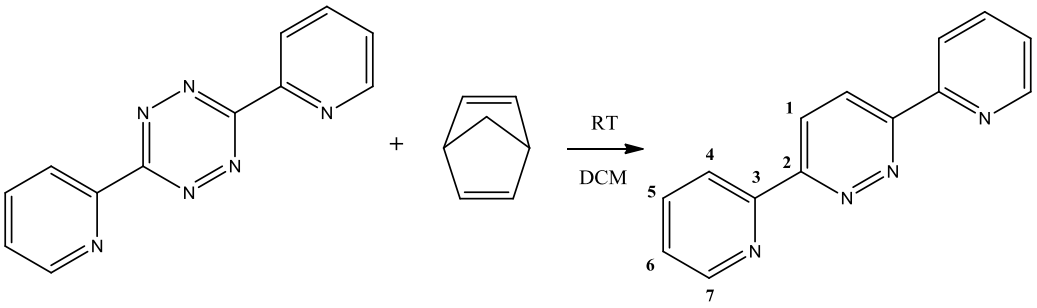
Scheme 22: Synthesis of 4,4'-(1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid

4,4'-(1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl)dibenzoic acid (410 mg, 1.26 mmol, 1eq) was suspended in THF (1.5 mL). Isoamylnitrit (84.6 µL, 6.32 mmol, 5eq) and acetic acid (3 mL) were added. The mixture was stirred over night at room temperature. The THF was removed by evaporation and the precipitate dried in vacuo. Yield: 611 mg (88%).

4,4'-(1,4-dihydro-1,2,4,5-tetrazine-3,6-diyl)dibenzoic wasn`t soluble enough to allow NMR characterization. The identification of the product was done by further chemical reactions.

5.2.2. Pyridazine synthesis

5.2.2.1. 3,6-di(pyridin-2-yl)pyridazine[16]



Scheme 23: Synthesis of 3,6-di(pyridin-2-yl)pyridazine

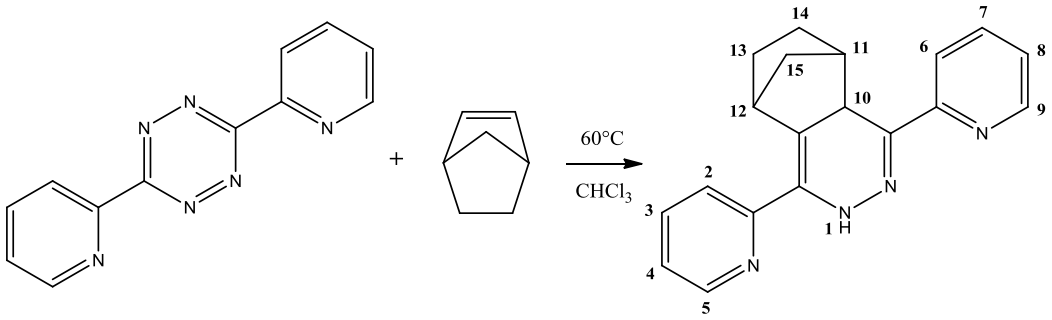
bipy-Tz (0.5 g, 2.1 mmol, 1eq) was dissolved in DCM (7 mL) and norbornadiene (1 mL, 5.9 mmol, 2.85eq) was added. The mixture was stirred overnight at room temperature. Then, DCM was removed by evaporation and the precipitate was dried in vacuo. The brown solid was purified by recrystallization from EtOH. The solution was filtered and dried in vacuo. Yield: 271 mg (55%).

TLC: R_f = 0.31 (DCM/MeOH, 20:1, (v:v))

^{1}H-NMR: (δ, 20°C, $CDCl_3$, 300.36 MHz): 8.78-7.74 (4H, $py^{4,7}$), 8.69 (s, 2H, pyd^1), 7.84 (t, 2H, py^5), 7.41(t, 2H, py^6).

APT: (δ, 20°C, $CDCl_3$, 75.53 MHz): 158.2 (2C, pyd^2), 153.5 (2C, py^3), 149.5 (2C, py^7), 137.2 (2C, py^5), 125.2, 124.8, 121.7 (2C, pyd^1, $py^{4,6}$).

5.2.2.2. 1,4-di(pyridin-2-yl)-2,4a,5,6,7,8-hexahydro-5,8-methanophthalazine[16]



Scheme 24: Synthesis of 1,4-di(pyridin-2-yl)-2,4a,5,6,7,8-hexahydro-5,8-methanophthalazine

bipy-Tz (500 mg, 2.1 mmol, 1eq) was dissolved in $CHCl_3$ (15 mL) and norbornene (0.576 mg, 6.12 mmol, 2.88eq) was added. The mixture was stirred for 5h at 60°C. Then, $CHCl_3$ was removed by evaporation. The solid was purified with column chromatography with DCM: MeOH 80:1 (v:v) as eluent. Yield: 203 mg (32 %).

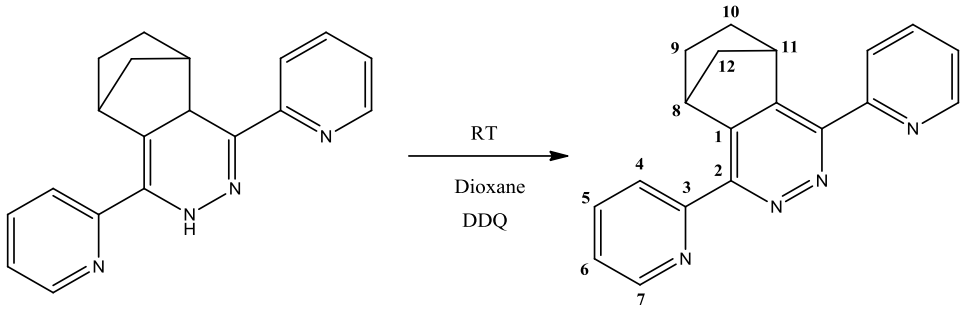
TLC: R_f = 0.34 (AlO_2; DCM/MeOH, 20:1, (v:v))

Table 9: weighed portions of norbonene/bipy-Tz

bipy-Tz	norbonene	solvent	base	Tz:N:B	time	comment
[g]	[mg]			[mol]	[h]	
0.02	7.96	THF	KOtBu	1:1:1	0.1	decomposition
0.02	7.96	THF	NaOH	1:1:1	32	ox. Product
0.02	7.96	THF	DBU	1:1:1	48	mixed product
0.02	7.96	THF	Et_3N	1:1:1	60	red. Product
0.02	7.96	THF	-	1:1	60	red. Product
0.02	7.96	THF/H_2O	NaOH	1:1:1	60	hydrolysed
0.02	-	THF/H_2O	NaOH	1:1:1	60	hydrolysed
0.01	3.99	dry iPrOH	NaOH	1:1:1	60	undefined
0.01	3.99	dry MeOH	NaOH	1:1:1	60	undefined
0.2	79.6	dry THF	NaOH	1:1:1	60	ox. Product
0.2	79.6	dry DCM	NaOH	1:1:1	24	undefined

^{1}H-NMR: (δ, 20°C, $CDCl_3$, 300.36 MHz): 8.66 (1H, N-H), 8.60 (tet), 7.73 (tet), 7.68 (tet), 7.55 (tet), 7.20 (tet), 3.45 (1H, nor^{11}), 3.30 (1H, nor^{12}), 2.60 (nor^{10}), 2.44 (nor), 1.93 (nor), 1.48 (nor), 1.35 (nor), 1.01 (nor).

5.2.2.3. 1,4-di(pyridin-2-yl)-5,6,7,8-tetrahydro-5,8-methanophthalazine[16]



Scheme 25: Synthesis of 1,4-di(pyridin-2-yl)-5,6,7,8-tetrahydro-5,8-methanophthalazine

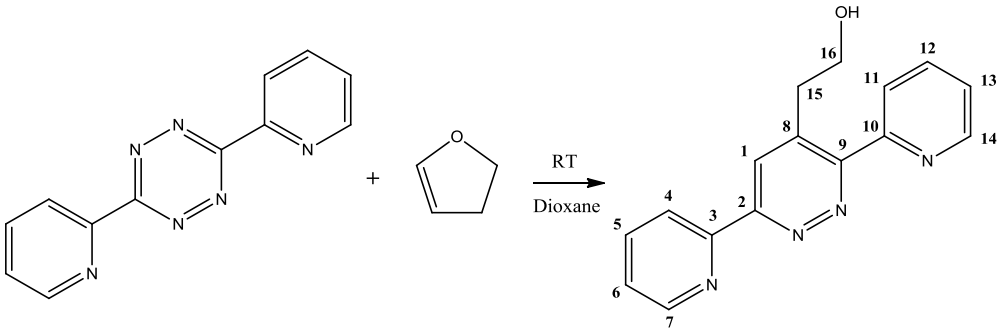
1,4-di(pyridin-2-yl)-2,4a,5,6,7,8-hexahydro-5,8-methanophthalazine (626 mg, 2.1 mmol, 1eq) was dissolved in dioxane (10 mL) and DDQ (2.86 g, 12.6 mmol, 6eq) was added. The mixture was stirred overnight at room temperature. Then, the solid was filtered off and the filtrate extracted with 1M NaOH, dest. H_2O and brine. The organic phase was dried with Na_2SO_4 and then filtered. After that the solvent was removed by evaporation and the solid dried in vacuo. Yield: 477 mg (75%).

TLC: R_f = 0.73 (DCM/MeOH, 10:1, (v:v))

^{1}H-NMR: (δ, 20°C, $CDCl_3$, 300.36 MHz): 8.77, 8.57 (4H, $py^{4,7}$), 7.88 (t, 2H, py^5), 7.34 (t, 2H, py^6), 4.51 (dd, 2H, $nor^{8,11}$), 2.14, 1.83, 1.63, 1.38 (6H, $nor^{9,10,12}$)

APT: (δ, 20°C, $CDCl_3$, 75.53 MHz): 156.0 (2C, pyd^2), 152.1 (2C, pyd^2), 149.2 (2C, py^7), 148.1 (2C, pyd^1), 136.7 (2C, py^5), 123.6, 123.0, (4C, $py^{4,6}$) 48.2 (1C, nor^{12}), 42.5 (2C, $nor^{8,11}$), 25.3 (2C, $nor^{9,10}$).

5.2.2.4. 2-(3,6-di(pyridin-2-yl)pyridazin-4-yl)ethanol



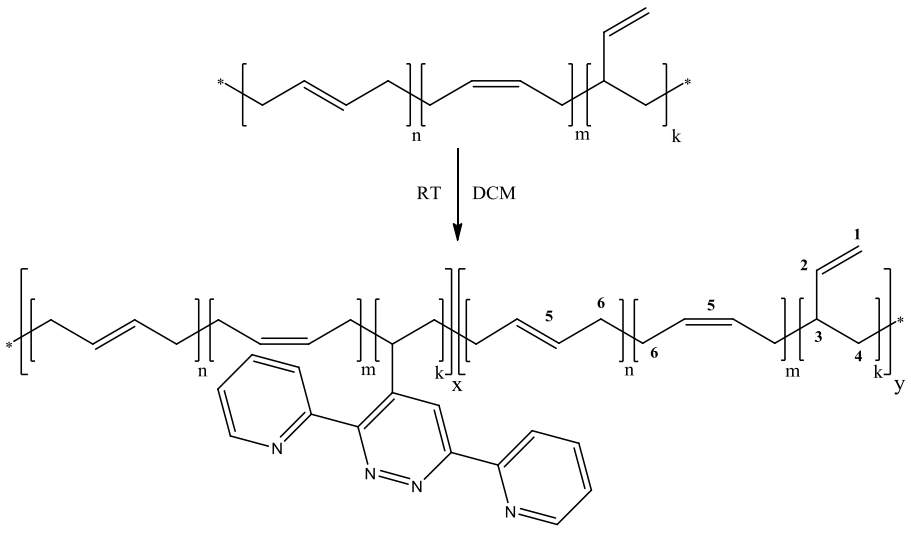
Scheme 26: Synthesis of 2-(3,6-di(pyridin-2-yl)pyridazin-4-yl)ethanol

bipy-Tz (0.2 g, 0.85 mmol, 1eq) was dissolved in dioxane (10 mL) and 2,3-dihydrofuran (185 µL, 2.45 mmol, 2.88eq) was added. The mixture was stirred over night at room temperature. The dioxane and excess 2,3-dihydrofuran were removed by evaporation and the product was dried in vacuo. Yield: 236.6 mg (100%).

^{1}H-NMR: (δ, 20°C, $CDCl_3$, 300.36 MHz): 8.75 (4H, $py^{7,14}$), 8.62 (s, 1H, pyd^1), 8.69, 8.32 (4H, $py^{4,11}$), 8.00, 7.92 (dd, 4H, $py^{5,12}$), 7.49, 7.42 (dd, 4H, $py^{6,13}$), 4.17 (t, 2H, CH_2^{16}), 3.18 (t, 2H, CH_2^{15}).

APT: (δ, 20°C, $CDCl_3$, 75.53 MHz): 159.0, 157.8, 155.0, 153.4 (2C, $pyd^{2,3}$, 2C, $py^{3,10}$), 149.6, 147.6 (2C, $py^{7,14}$), 140.6 (1C, pyd^8), 138.2, 137.4 (2C, $py^{5,12}$), 126.7, 125.9, 125.0, 124.2 (4C, $py^{4,6,11,13}$), 122.0 (1C, pyd^1), 63.6 (1C, CH_2^{16}), 34.7 (1C, CH_2^{15}).

5.2.2.5. Modification of polyisopren (Lithene) with bipy-Tz



Scheme 27: Synthesis of bipy-Tz modified Lithene AH

Lithene AH[70] (0.2 g, 3.7 mmol, 1eq) was dissolved in DCM (14 mL) and bipy-Tz was added. The mixture was stirred until the click reaction was complete. Then, DCM was removed by evaporation and the product dried in vacuo. The colour of the product depends on the amount of bipy-Tz (yellow-brown).

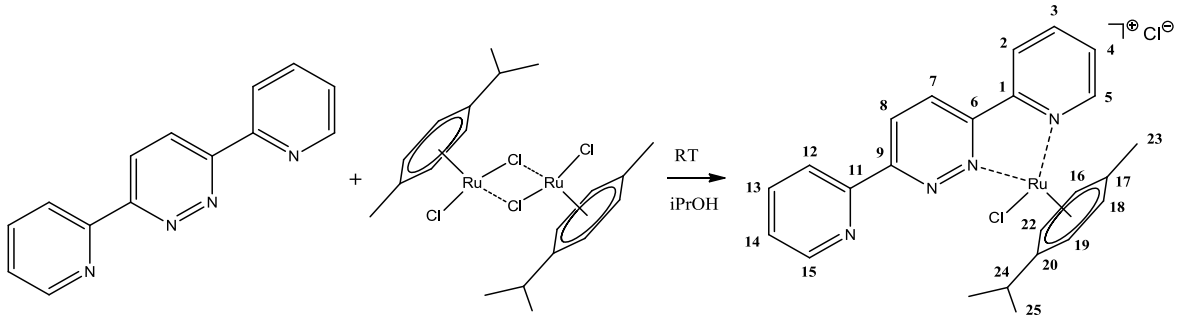
Table 10: weighed portions of Lithene/bipy-Tz

x (bipy-Tz)		Time	comment
[eq]	[mg]	[days]	
0.1	87	5	bipy-Tz reacted (yellow)
0.3	262	7	bipy-Tz reacted (yellow-brown)
0.5	436	10	bipy-Tz reacted (brown)

^{1}H-NMR: (δ, 20°C, $CDCl_3$, 300.36 MHz): 8.54 - 7.67 (9H, tet), 5.79-5.56 (4H, cis-trans[5]), 5.35 (1H, vinyl[2]), 4.96 (2H, vinyl[1]), 2.65 (1H, CH[3]), 2.03 (4H, CH_2[6]), 1.54 (2H, CH_2[4])

5.2.3. Ruthenium(II) Complexes

5.2.3.1. bipy-pyridazin complex (**com1**)



Scheme 28: Synthesis of bipy-pyridazin complex

3,6-di(pyridin-2-yl)pyridazine (50 mg, 0.21 mmol, 1eq) was dissolved in DCM (6 mL) and dichlorobis(p-cymene)ruthenium(II)-dimer (65 mg, 0.11 mmol, 0.5eq) was added. The mixture was stirred for 40h at room temperature under nitrogen atmosphere. During that time, a dark yellow precipitate formed. The DCM was removed by evaporation and the precipitate was dissolved in DCM and reprecipitated with Et_2O. The solution was filtered and the precipitate dried in vacuo. Yield: 78.2 mg (70 %).

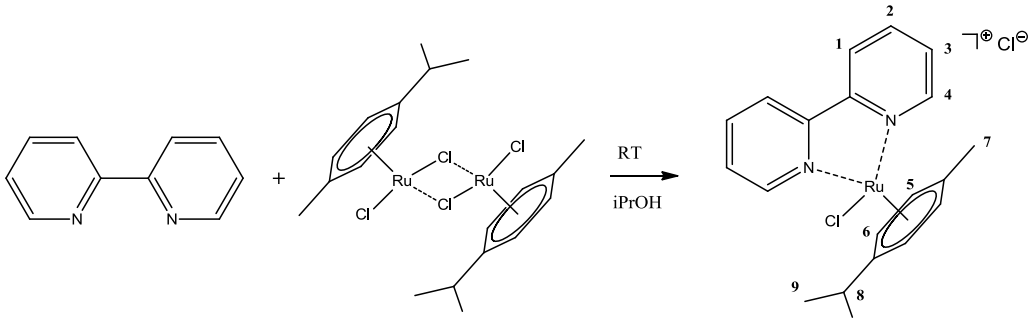
TLC: R_f = 0.09 (DCM/MeOH, 5:1, (v:v))

[70] http://www.synthomer.com/index.php?id=76&tx_productdatabase_pi1[view]=1&tx_productdatabase_pi1[mat]=2072&L= (19.10.2013)

^{1}H-NMR: (δ, 20°C, $CDCl_3$, 300.36 MHz): 10.05 (d, 1H, py^5), 9.11 (d, 1H, py^{15}), 9.00 (d, 1H, py^{12}), 8.81 (d, 2H, $tet^{7,8}$), 8.59 (d, 1H, py^2), 8.13 (t, 1H, py^{13}), 8.00 (t, 1H, py^3), 7.88 (t, 1H, py^{14}), 7.54 (dd, 1H, py^4), 6.30, 6.13, 6.05 (4H, $cym^{16,18,19,22}$), 2.85 (m, 1H, cym^{24}), 2.28 (s, 3H, cym^{23}), 1.16 (d, 6H, cym^{25}).

APT: (δ, 20°C, $CDCl_3$, 75.53 MHz): 160.4 (1C, q), 158.4 (1C, q), 157.6 (1C, CH), 152.2 (1C, q), 150.8 (1C, q), 150.5 (1C, CH), 139.9 (1C, CH), 137.7 (1C, CH), 129.86 (1C, CH), 129.3 (1C, CH), 127.9 (1C, CH), 126.4 (1C, CH), 126.0 (1C, CH), 122.1 (1C, CH), 106.4 (1C, q), 103.5 (1C, q), 89.5 (1C, CH), 87.9 (1C, CH), 86.8 (1C, CH), 86.2 (1C, CH), 31.3 (1C, cym^{24}), 22.6 (1C, cym^{25}), 19.0 (1C, cym^{23}).

5.2.3.2. bipy complex (**com2**)



Scheme 29: Synthesis of bipy complex

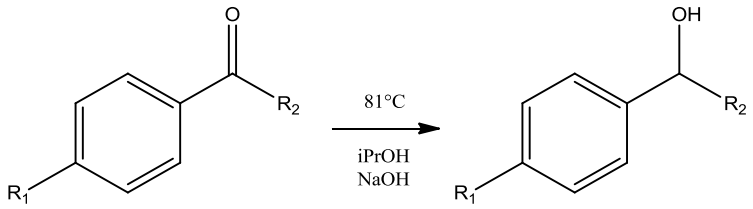
Bipyridine (50 mg, 0.32 mmol, 1eq) was dissolved in iPrOH (6 mL) and dichlorobis(p-cymene)ruthenium(II)-dimer (98 mg, 0.16 mmol, 0.5eq) was added. The mixture was stirred for 40h at room temperature under nitrogen atmosphere. During that time, a brown precipitate formed. The iPrOH was removed by evaporation and the precipitate was dissolved in DCM and reprecipitated with Et_2O. The solution was filtered and the precipitate dried in vacuo.

Two different complexes because of the solvent[60] (1x Cl; 1x D_2O). Ratio: Cl/D_2O = 10/1

Cl: ^{1}H-NMR: (δ, 20°C, D_2O, 300.36 MHz): 9.44 (d, 2H, py^1), 8.39 (d, 2H, py^4), 8.22 (t, 2H, py^2), 7.75 (t, 2H, py^3), 6.12, 5.87 (4H, $cym^{5,6}$), 2.54 (m, 1H, cym^8), 2.21 (s, 3H, cym^7), 0.98 (d, 6H, cym^9).

D_2O: ^{1}H-NMR: (δ, 20°C, D_2O, 300.36 MHz): 9.56 (d, 2H, py^1), 8.42 (d, 2H, py^4), 8.27 (t, 2H, py^2), 7.80 (t, 2H, py^3), 6.22, 5.95 (2H, $cym^{5,6}$), 2.47 (m, 1H, cym^8), 2.21 (s, 3H, cym^7), 0.93 (d, 6H, cym^9).

5.2.4. Transfer Hydrogenation



Scheme 30: General reaction of transfer hydrogenation

General procedure

The respective ketone was dissolved in iPrOH, complex 1 and NaOH were added. The reaction was stirred for 24h at 81°C under nitrogen atmosphere. The iPrOH was removed and product was suspended in dest. H_2O. The reaction was acidified with 5%-HCl and extracted with DCM. The organic phase was dried with Na_2SO_4, filtered and dried in vacuo.

Reaction control via ^{1}H-NMR (δ, 20°C, [$CDCl_3$, DMSO-d_6], 300.36 MHz).

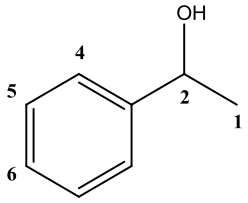
Table 11: yields of transfer hydrogenation

R_1	R_2	Educt	Complex 1	NaOH	iPrOH	comment
		[mg]	[com1:ketone]	[eq]	[ml]	
- H	- CH_3	515	1:100	0.02	4	no reaction
		515	1:100	0.15	4	conversion (96%)
		515	1:1000	0.15	4	conversion (94%)
		515	1:10000	0.15	4	conversion (93%)
		515	1:100000	0.15	4	conversion (93%)
- Cl	- CH_3	833	1:100	0.02	4	no reaction
		833	1:100	0.12	4	conversion (95%)
		833	1:1000	0.12	4	conversion (91%)
		833	1:10000	0.12	4	conversion (86%)
		833	1:100000	0.12	4	conversion (88%)
		833	1:1000000	0.12	4	conversion (88%)
		833	-	0.12	4	conversion (96%)
- OH	- CH_3	500	1:100	0.24	4	no reaction
- NO_2	- CH_3	500	1:100	0.12	4	polymerization
- H	- CH_2 - Ph	725	1:100	0.02	4	no reaction
		725	1:100	0.12	4	conversion (33%)
		725	1:100	0.36	4	conversion (94%)
		725	-	0.12	4	conversion (33%)

5.2.4.1. 1-phenylethanol

Yield: 80 - 85%.

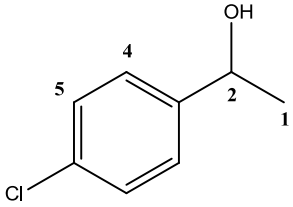
^{1}H-NMR: (δ, 20°C, $CDCl_3$, 300.36 MHz): 7.24 – 7.14 (5H, $ph^{4,5,6}$), 4.21 (q, 1H, 2), 1.36 (d, 3H, 1).



5.2.4.2. 1-(4-chlorophenyl)ethanol

Yield: 75 - 85%.

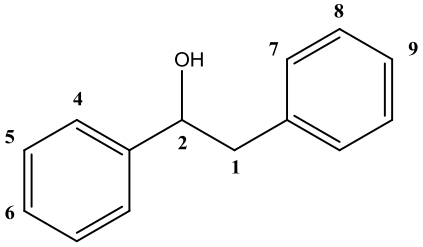
^{1}H-NMR: (δ, 20°C, DMSO-d_6, 300.36 MHz): 7.31 (4H, $ph^{4,5}$), 4.89 (q, 1H, 2), 1.48 (d, 3H, 1).



5.2.4.3. 1,2-diphenylethanol

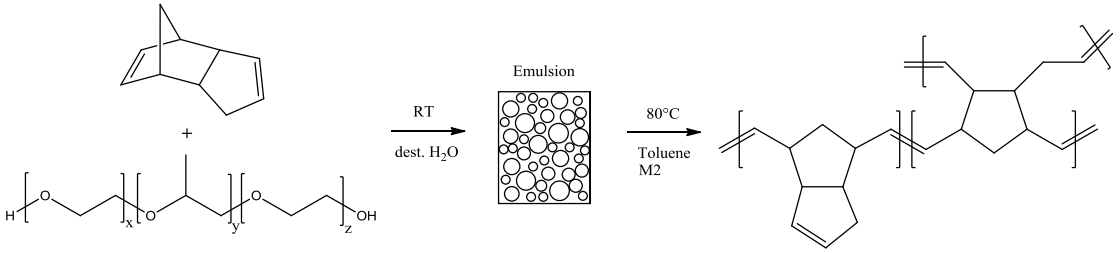
Yield: 33%.

^{1}H-NMR: (δ, 20°C, $CDCl_3$, 300.36 MHz): 8.07, 7.66, 7.55 (10H, $ph^{4,5,6,7,8,9}$), 4.76 (m, 1H, 2), 2.89 (m, 2H, 1).



5.2.5. Porous monoliths (polyHIPE)

5.2.5.1. Preparation of shoulder test bar with porosity of 80%[54]



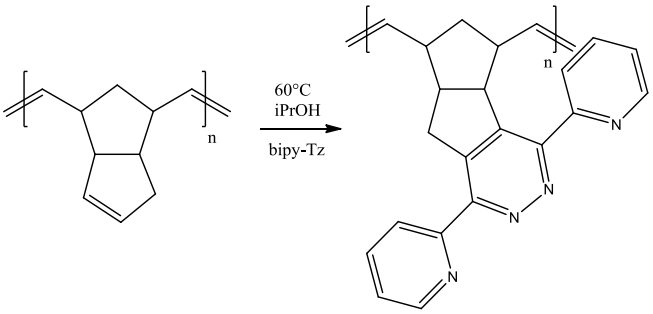
Scheme 31: Preparation of polyHIPEs

DCPD and surfactant (Pluronic L121) were put in a 250 mL 3-necked flask and stirred with an overhead stirrer. Dest. water was added dropwise. For each 10 mL H_2O the stirring speed was increased for 100 rpm. After 60min stirring at room temperature the initiator (M2), dissolved in toluene (60 µL/ 1 mL DCPD), was added to the suspension. After complete addition, the emulsion was stirred for 1h. The emulsion was filled in the defined sample mould and cured for 4h at 80°C. The shoulder test bars were put in acetone to extract the surfactant, residual monomer and free oligomers. After that the shoulder bars were dried under vacuo.

Table 12: pDCPD weighed portions

	DCPD	H_2O	M2		Surfactant	
	[g]	[mL]	[mg]	[M2:DCPD]	[mg]	[w%]
big	8.811	37.12	6.33	1:10000	441	5
small	4.405	18.61	3.16	1:10000	221	5

5.2.5.2. Modification of shoulder test bar with bipy-Tz



Scheme 32: Modification of pDCPD with bipy-Tz

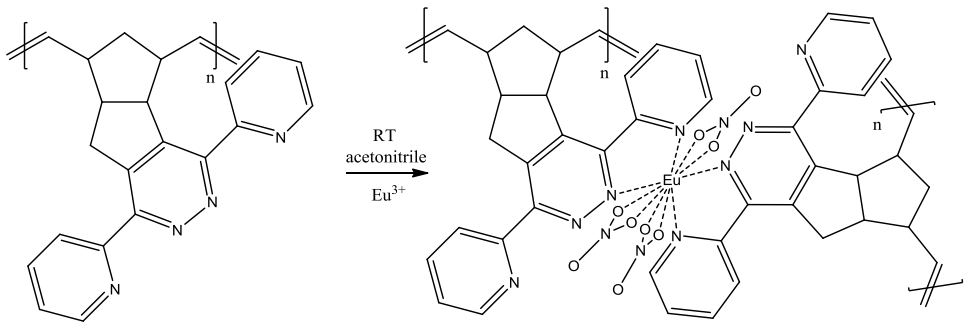
3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine (bipy-Tz) (0.1or 0.2eq referred to the double bonds) was dissolved in iPrOH (140 mL) and the shoulder test bar was put in the solution. After 48h-144h at 60°C the shoulder test bar was removed from the solution and put in acetone to remove free bipy-Tz from the surface. After that the shoulder bars were dried in vacuo. Due to immobilised pyridazine, colour of the shoulder bar changed from white to light yellow.

Table 13: properties of modified shoulder test bars

sample	solvent	bipy-Tz		bipy-Tz on pDCPD		increase weight	increase volume	Time	Eu(III)	mechanical properties tested
		[mg]	[eq]	[mg]	[%]	[%]	[%]	[h]		
48_1	iPrOH	-	-	-	-	-	-	-	-	yes
48_2	iPrOH	703	0.2	350	50	17.9	2.8	144	-	yes
53_2	iPrOH	641	0.2	139	22	7.8	2.8	48	-	yes
53_1	iPrOH	660	0.2	232	35	12.6	2.8	48	X	yes
60_1	iPrOH	647	0.2	183	28	10.0	2.6	48	X	yes
112_1	iPrOH	626	0.2	296	48	16.9	2.8	144	X	yes
112_1	iPrOH	622	0.2	146	23	8.4	2.7	48	X	yes
49_1	iPrOH /THF 3/1	641	0.2	260	41	28.5	10	48		no *

(* The measurement of the mechanical properties wasn't possible because of the deformation.)

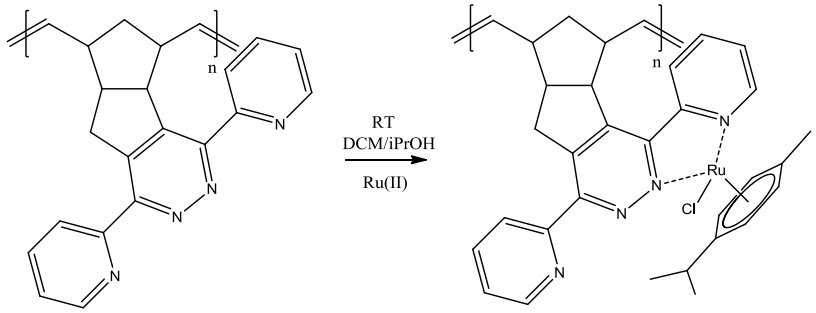
5.2.5.3. Modification of shoulder test bar with Eu(III)



Scheme 33: Modification of pDCPD/tetrazin with Eu^{3+}

Europium(III)nitrate pentahydrate (0.05eq to pDCPD) was dissolved in acetonitrile and the shoulder test bar was put in the solution. After 24h the shoulder test bar was removed from the solution and put in acetone to remove uncoordinated europium(III)nitrate pentahydrate from the surface. After that the shoulder bars were dried in vacuo. Due to immobilised Eu(III), the colour of the shoulder bar changed from light yellow to yellow-gold.

5.2.5.4. Modification of polyHIPE monolith with Ru(II)



Scheme 34: Modification of pDCPD/tetrazin with Ru(II)

Dichlorobis(p-cymene)ruthenium(II)-dimer (36 mg, 0.6 mmol, 0.05eq) was dissolved in DCM/iPrOH (2 mL/3.5 mL) and the polyHIPE (156 mg, 1.2 mmol, 1eq) was put in the solution. After 24h the shoulder test bar was removed from the solution and put in acetone to remove uncoordinated dichlorobis(p-cymene)ruthenium(II) from the surface. After that the monolith was dried in vacuo. The colour of the shoulder bar changed from light yellow to brown upon immobilisation of Ru(II).

6. List of Figures

7. List of Schemes

8. List of Tables