*Babeș-Bolyai University*
*Faculty of Chemistry and Chemical Engineering,*
*Department of Chemistry*

***PhD Thesis***

defended by Lakatos Eszter at Babeș-Bolyai University

# Terphenyl, pyrene and diketopyrrolopyrrole derivatives. Cyclophanes, host-guest supramolecular assemblies and organic solar cells

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| APCI | Atmospheric Pressure Chemical Ionization |
| Abs | Absorption |
| Bipy | 2,2'-bipyridine |
| BHJ | Bulk hetero junction |
| CD | Circular dichroism |
| CuAAC | Copper-catalyzed azide-alkyne cycloaddition |
| CV | Cyclic Voltammetry |
| DCM | Dichloromethane |
| DMF | *N*,*N*-Dimethylformamide |
| DMSO-$d_6$ | Dimethyl sulfoxide-$d_6$ |
| DME | Dimethoxyethane |
| DNA | Deoxyribonucleic acid |
| DCC | Dynamic Combinatorial Chemistry |
| DCL | Dynamic Constitutional Library |
| DLs | Dynamic Libraries |
| DNCL | Dynamic Non-covalent Libraries |
| DPP | Diketopyrrollopyrrole |
| eq. | Equivalent |
| ESI | ElectronSpray Ionization |
| EtOH | Ethanol |
| EQE | External quantum efficiency |
| FF | Fill factor |
| HOMO | Highest occupied molecular orbital |
| HRMS | High Resolution Mass Spectrometry |
| ITO | Indium tin oxide |
| $J_{sc}$ | Short circuit current |
| LDA | Lithium diisopropylamide |
| LED | Light-Emitting Diode |

| | |
|---|---|
| LUMO | Lowest unoccupied molecular orbital |
| m.p. | Melting point |
| *m/z* | Mass-to-charge ratio |
| MS | Mass Spectrometry |
| MeOH | Methanol |
| MeCN | Acetonitrile |
| MOF | Molecular organic framework |
| MOP | *(R)- or (S)-2-diphenylphosphino-2'-methoxy-1,1'-binaphthyl* |
| NFP | N-formylpiperidine |
| NMR | Nuclear magnetic resonance |
| NMP | N-methylpyrrolidone |
| OE | Organic electronics |
| OFET | Organic field effect transistor |
| OLED | Organic light-emitting diode |
| OPV | Organic photovoltaic |
| ORTEP | Oak Ridge Thermal Ellipsoid Plot Program |
| OSC | Organic solar cell |
| OTFT | Organic thin-film transistor |
| PCE | Power conversion efficiency |
| PEDOT:PSS | *poly(3,4-ethylenedioxythiophene) polystyrene sulfonate* |
| PEPPSI | *Bis(2,6-Diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride* |
| $PPh_3$ | Triphenyl phosphine |
| Pt | Platinum |
| PVD | Physical Vapor Deposition |
| RCAM | Ring closing alkyne metathesis |
| RCM | Ring closing metathesis |
| Rf | Retention factor |
| *r.t.* | Room temperature |
| QY | Quantum yield |
| SCE | Saturated calomel electrode |

| | |
|---|---|
| SMOSC | Single material organic solar cell |
| STM | Scanning tunneling microscopy |
| TBAF | Tetrabutylammonium fluoride |
| TLC | Thin layer chromoatography |
| TFA | Trifluoroacetic acid |
| THF | Tetrahydrofuran |
| TBTA | Tris(benzyltriazolmethyl)amine |
| TEM | Transmission electron microscopy |
| UV-Vis | Ultraviolet visible |
| $V_{oc}$ | Open circuit voltage |
| XRD | X-Ray Diffraction |
| δ | Chemical shift (NMR) |
| s | singlet |
| d | doublet |
| t | triplet |
| cv | quintet |
| m | multiplet |
| dd | doublet of doublets |
| br | Broad signal |

**Keywords**: *m*-terphenyl, pyrene, diketopyrrolopyrrole, cyclophanes, organic solar cells

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# General introduction

The thesis entitled '*Terphenyl, pyrene and diketopyrrolopyrrole derivatives. Cyclophanes, host-guest supramolecular assemblies and organic solar cells*' is divided in three main chapters discussing different subjects in the field of organic chemistry. All chapters are organized under the same idea: starting with a literature survey, followed by the original contributions, experimental data, and conclusions.

Part A is dedicated to the synthesis and characterization of some new *m*-terphenyl-based precursors. A literature survey on the synthesis of *m*-terphenyl unit, along with *m*-terphenyl-based macrocycles with emphasis on the macrocylization step, was conducted in the first part of this chapter. The initial purpose of these macromolecules was to obtain supramolecular aggregates *via* amidinium-carboxylate salt bridge formation. Synthetic limitation encountered throttled down the synthetic process. Finally, Suzuki and Sonogashira coupling reactions were used for the synthesis of macrocycle precursos. Preparation of a rigid and a semirigid macrocyle decorated with exo-oriented carboxylate group was planned. Copper catalyzed cycloaddition (CuAAC) was engaged in the formation of the semi rigid macrocycle reported herein.

Part B aimed at synthesis and characterization of new compounds based on pyrene, functionalized in the 1,3,6,8 positions. Pyrene derivatized with hexylcyanoacetate acceptor group connected by phenyl conjugating spacers were intended to be connected to non-fullerene electron acceptors. Their optoelectronic properties were examined by spectral and electrochemical techniques. Additionally, synthetic host molecules with pyrene backbone (1,6-pyrenophanes) were surveyed, designed and synthesized applying CuAAC 'click' reaction.

In Part C is presented the synthesis and valorization of a new donor-π-acceptor type molecule based on *1,4-diketopyrrolo[3,4-c]pyrrole* (DPP) moiety. In the first part of this section we surveyed the chemistry of DPP formation and exemplified the application of the DPP derivatives. The synthetic strategy was constructed on known procedures reported in the literature. The optoelectronic properties of the target compound were evaluated and the structure-property relationship was tested in organic solar cells with direct and inverted junctions.

# Part A. *m*-Terphenyl-based supramolecular structures

# II. Original contributions

## 1. Objectives

This part of the project targeted the synthesis of new macrocycles and cages with a *m*-terphenyl backbone. In order to act as "host-guest" systems, we ‘decorating’ these *m*-terphenyls with chemical functionalities, based on amidinium-carboxylate salt bridges or through other noncovalent interactions. In this regard, we envisioned macrocycles with exo-oriented carboxylic or amidine groups, which later to be used as templates for building cryptands, illustrated structure **I**-(Figure 10). Another idea was to make the cryptand to be template for the macrocyclization reaction (Structure **II**, Figure 10).

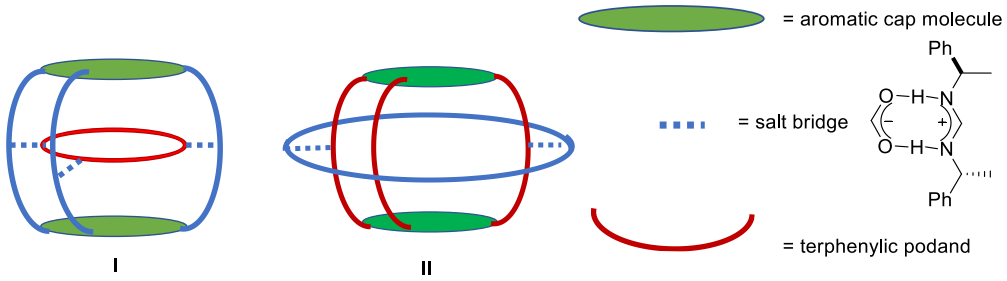



***Figure 10***-illustration of target structures

## 2. Results and discussions

The initial step towards formation of target structure **I**, and **II** was the selection and synthesis of the cap molecule, followed by the synthesis of the *m*-terphenyl unit, adequate for podand and macrocycle synthesis. From the range of strategies presented in the literature survey above, we chose the stepwise assembly of two different types of macrocyles with exo-oriented carboxylates: semirigid type **A** and rigid macrocyle **B** (Figure 11). Both strategies are based on multistep reaction paths in which only two molecules are necessary for the final cyclization step: Sonogashira cross-coupling reaction between **C** and **D**, and CuAAC ‘click’ reaction between two

complementary **C** molecules. To ensure solubility of the rigid cycle, we incorporated alkyl chains in the structure.

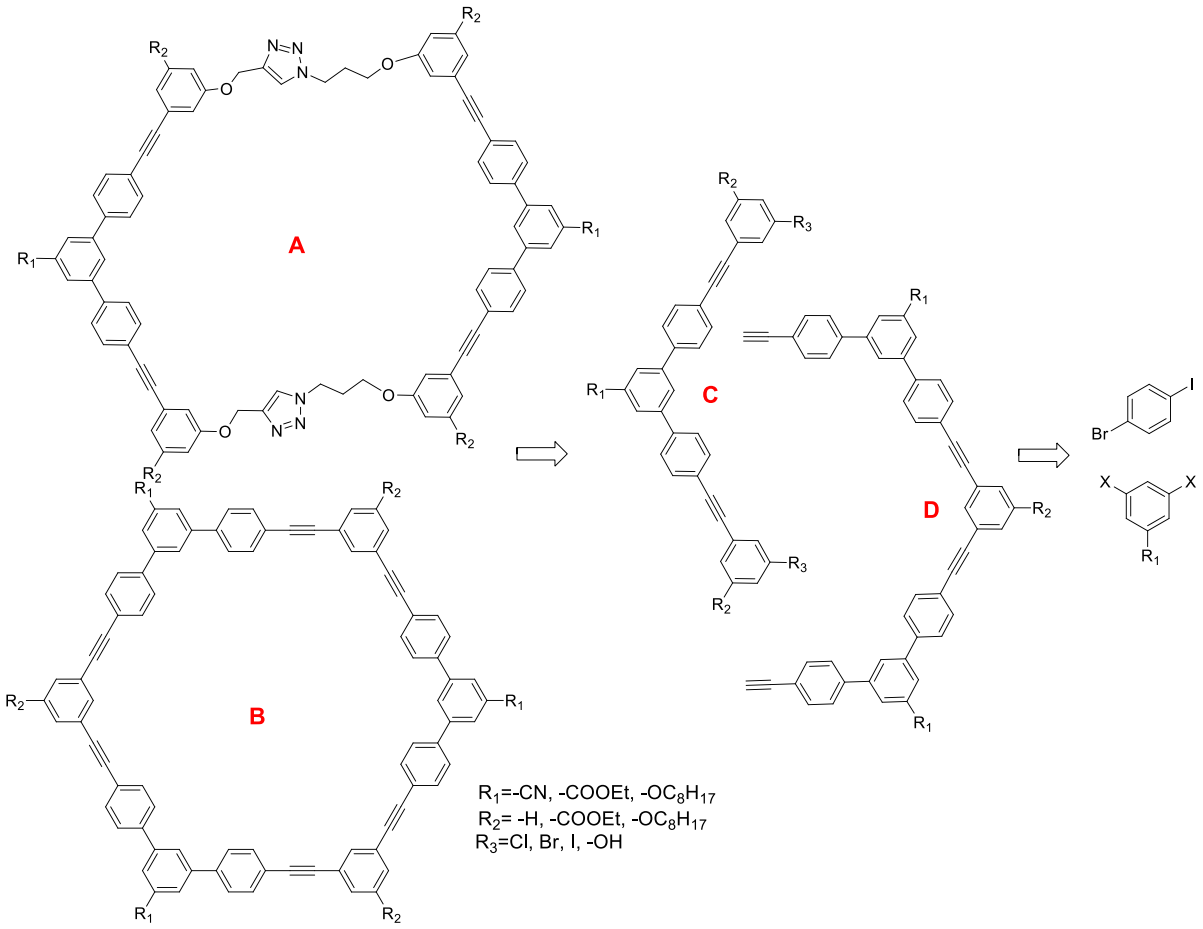



***Figure 11***-retrosynthetic scheme of target macrocycles

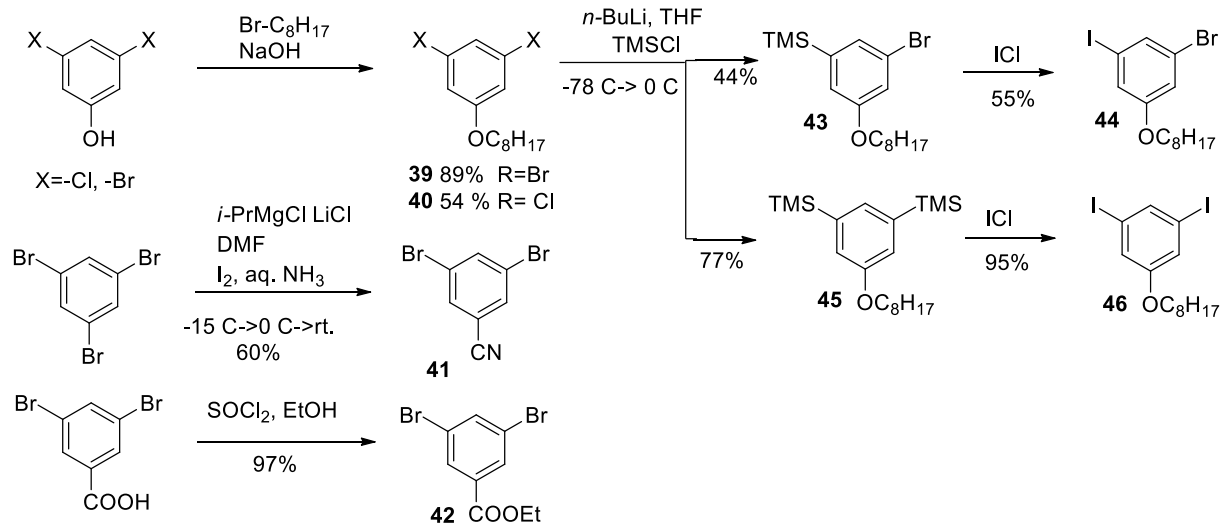
## 2.1. Synthesis of precursors

To serve as central phenyl units in the terphenyl moiety, a set of 1,3-dihalogenated benzenes were synthesized by adapting reported procedures for similar products (Scheme 7). O-alkylation of 3,5-dibromophenol with 1-bromooctane was performed in either ethanol or DMF, both furnishing yields above 80%[1].

For a better reactivity, bromine atoms were substituted with iodine in a two-step transformation. First, lithium-bromine exchange was performed in dry THF at -78℃ followed by treatment of lithiate with trimethylsilyl chloride. Afterwards, trimethylsilyl chloride was regained

[1] Kandre, R., Schlüter, A. D. *Macromol. Rapid Commun*. **2008**, 29, 1661–1665

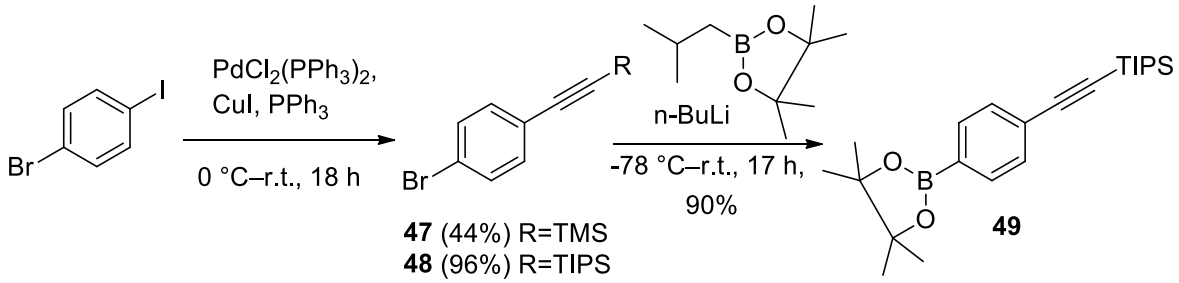
in reaction of **43** and **45** with iodine monochloride (ICl) that resulted the unsymmetric **44** in 55 %, and diiodobenzene **46** in 95 %.




***Scheme 7***- Synthesis 3,5-dihalogenated benzene derivatives

In order to avoid difficulties that carboxylic group can cause in the reaction sequence, we tried two different approaches: one in which the carboxylic group is obtained from a cyano group at a later stage on the synthetic path, and the other where the acid is transformed to ethyl-benzoate **41**[2]. All precursors were obtained in high yields and identified with NMR spectroscopy.

The ethynyl bearing phenyl rings were prepared by a regioselective Sonogashira-Hagihara reaction at r.t. [3] The bromine function was subsequently converted to the boronic ester **49** - (Scheme 8).

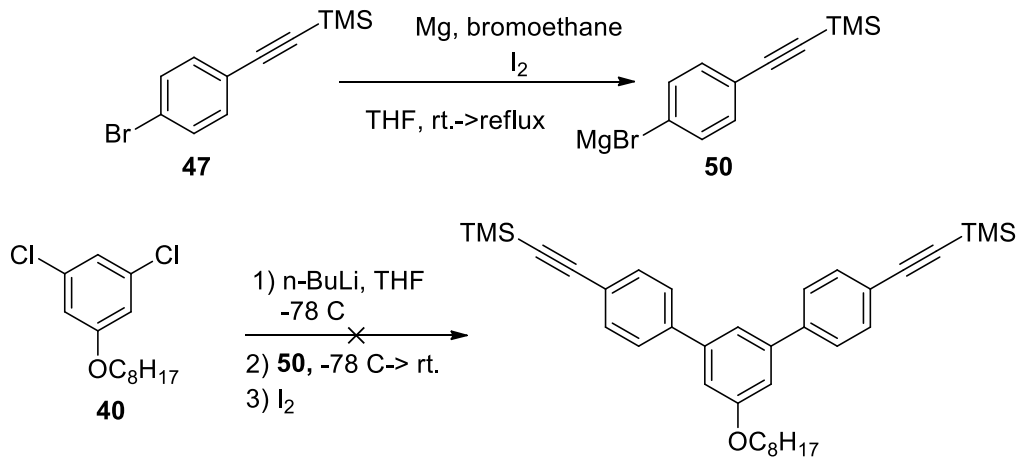



***Scheme 8***- Synthesis of boronic ester **49**

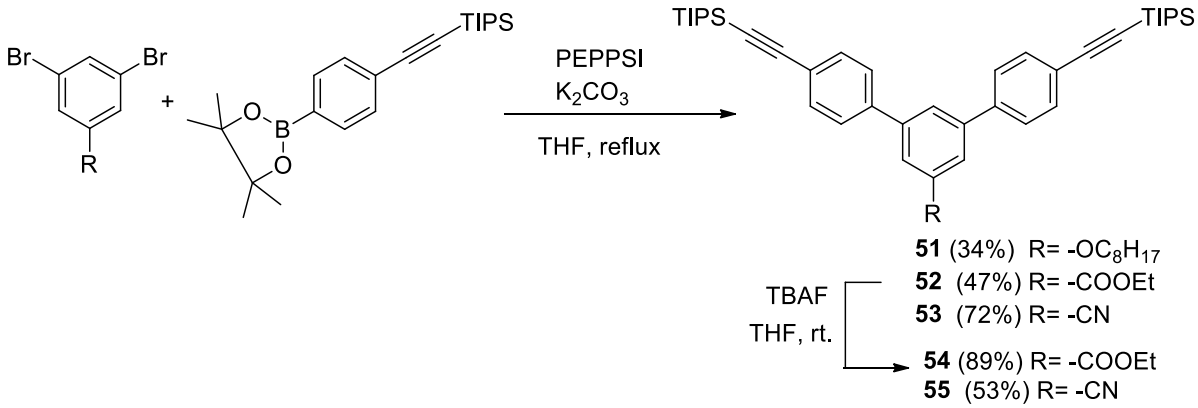
[2] Zalas, M., Gierczyk, B., Cegłowski, M., Schroeder, G. *Chem. Pap.* **2012,** 66, 733–740
[3] Lei, S., Ver Heyen, A., De Feyter, S., Surin, M., Lazzaroni, R., Rosenfeldt, S., Ballauff,, M., Lindner, P., Mçssinger, D., Hçger, S. *Chem. Eur. J***. 2009**, 15, 2518 – 2535

## 2.2. Synthesis of m-terphenyls

Presented in Scheme 9 is the reaction sequence inspired from the synthetic strategy used by Yashima.[Error! Bookmark not defined.] 4-trimethylsilylethynylphenylmagnesium bromide **50** was reacted with lithiated compound **40** followed by quenching with iodine. Unfortunately, all attemps to adapt the Hart coupling for our substrates failed. Neither NMR spectroscopy, nor mass spectrometry investigation indicated the formation of the desired *m*-terphenyl. Finally, we decided to change the strategy to the less sensible Suzuki coupling. So terphenyls were accessed through reaction of 3,5-dibromo(octyloxy)benzene **39** and boronic ester **49** using potassium carbonate base and [1,3-Bis(2,6-Diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride (PEPPSI) catalyst (Scheme 10).




***Scheme 9***-Synthetic approach to hart coupling reaction



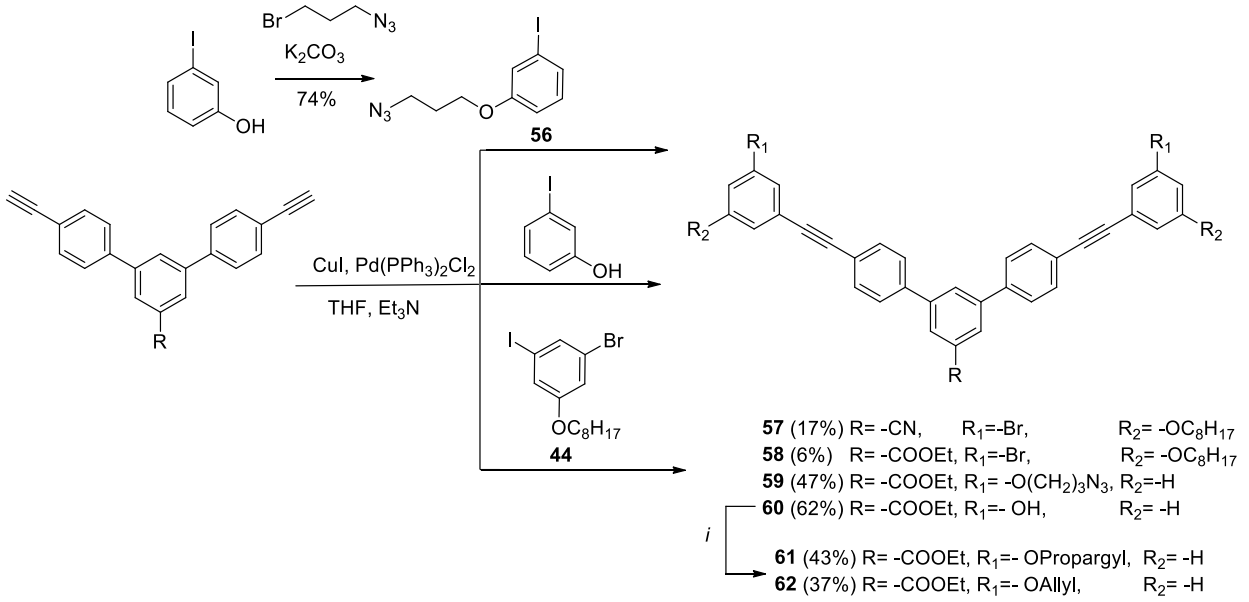

***Scheme 10***-Synthesis of *m*-terphenyls **51**-**55**

In order to optimize the reaction conditions for Suzuki coupling**,** we tried different base and solvent combinations, these are presented in Table 2. The best results were given by using 1,2-dimethoxyethane (DME) reacting media, potassium hydroxide base and PEPPSI catalyst.

***Table 2***- Reaction conditions and obtained yields for Suzuki cross-coupling

| Nr. Reaction | Base | Solvent | Yield |
|---|---|---|---|
| 1 | $Cs_2CO_3$ | THF | 29% |
| 2 | KOH | THF | 56% |
| 3 | $Cs_2CO_3$ | DME | 45% |
| 4 | KOH | DME | 77% |

In the next step alkyne deprotection was achieved by treating *m*-terphenyls with tetrabutylammonium fluoride (TBAF) in wet THF. Then the terminal alkyne was involved in Sonogashira coupling with a three different iodobenzene: 3-iodo-bromo-octyloxybenezene **44**, 3-iodophenol grafted with azide bearing propyl chain, and simple 3-iodophenol, whom hydroxyl function was later transformed to propargyl, respectively to allyl group (Scheme 11).




***Scheme 11***- Synthesis of macrocyclic precursors **57**-**62**

The structure of compounds **57-62** was confirmed by NMR spectroscopy as well as mass spectrometry. Comparison of $^1H$ NMR spectra recorded in $CDCl_3$ for compounds **59** *vs.* **61** is

presented in Figure 12. Signals assigned to the terphenyl unit appear under the same chemical shift and same number of resonances, namely a triplet a and dublet b corresponding to the central phenyl ring and a AB system as doublets c and d. Even the meta substituted phenyl rings show the similar pattern with just a slight downfield shift in the case of compound **61.** Two triplets i, k and a multiplet j are assigned to the azidoalkyl chain, while the propargyl function in compound **61** appears as a doublet i at 4.73 ppm and a triplet j at 2.56 ppm.

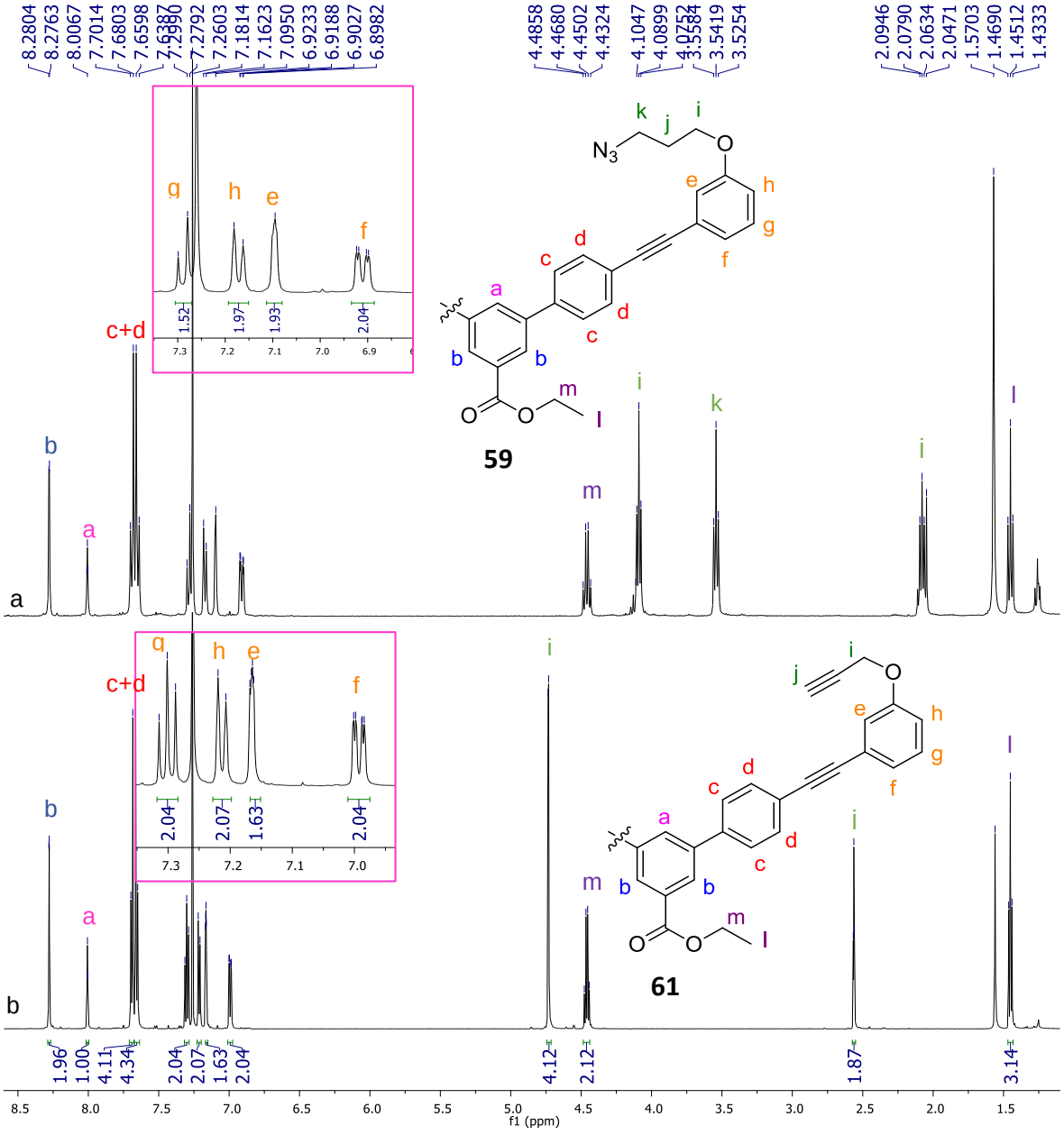



***Figure 11***-$^{1}$H NMR spectra of compound **59** (a) and compound **61** (b) recorded in $CDCl_3$, 600 MHz

## 2.3. Synthesis of macrocycles

As presented in the literature survey above, a certain degree of flexibility confers beneficial hosting abilities for macrocycles. Our research group already gained experience in the assembly of flexible macrocycles. A set of phentothiazine and thiophene containing macrocycles were obtained by Suzuki-Miyaura cross-coupling reaction. Flexibility of these structures was offered by ethylenoxide chains of various length.[45]

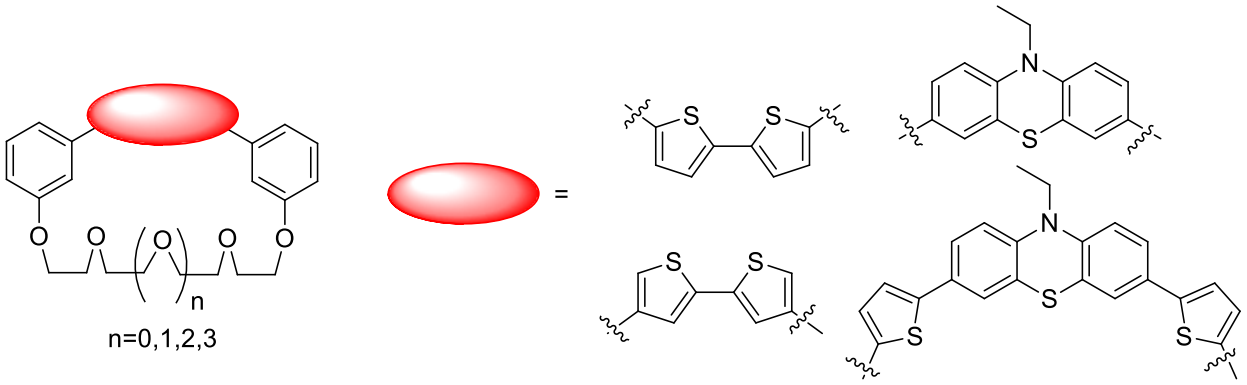
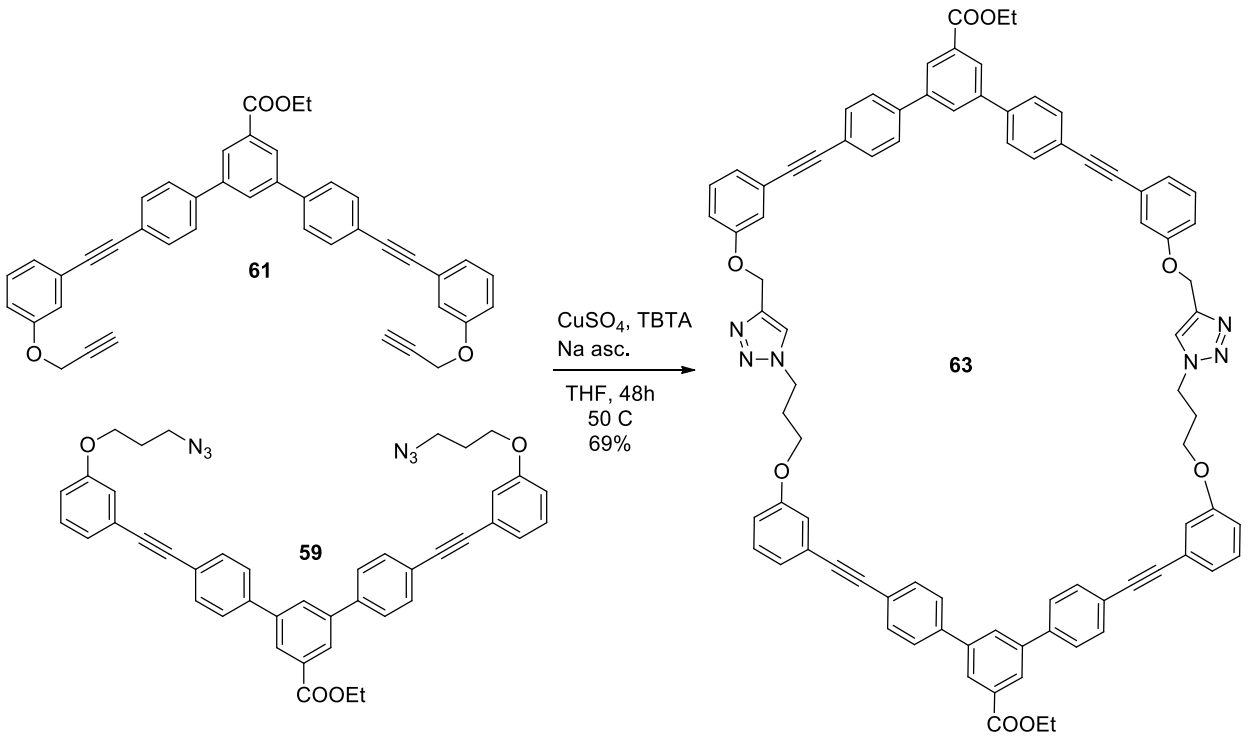



***Figure 12***-Chemical structure of macrocycles obtained via Suzuki coupling

In the present study, synthesis of the semirigid macrocyle *via* copper catalyzed azide-alkyne cycloaddition 'click' (CuAAC) gave exceptionally good yields. Using high dilution and traditional 'click' reagents, more precisely $CuSO_4$, tris(benzyltriazolmethyl)amine (TBTA) and sodium ascorbate yielded the target macrocycle in 69%. The macrocycle was separated on column chromatography with silicagel and further purified by recrystallization from toluene. (Scheme 12)

The $^1$H NMR spectrum of macrocycle **63** is presented in Figure 14. While signals corresponding for the central phenyl ring from the terphenyl had same chemical shifts in the macrocycle precursors **59** and **61**, the macrocycle **63** shows two sets of signals. Additionally, signals (i, j, k,i' ) assigned to aliphatic protons suffer a downfield shift.

[4] Medruț, I., Turdean, R., Gropeanu, R., Pop, F., Toupet, L., Hădade, N. D., Bogdan, E., Grosu, I. *Tetrahedron Lett.* **2013**, 54, 1107-1111
[5] Petran, A., Terec, A., Bogdan, E., Soran, A., Lakatos, E., Grosu, I. *Tetrahedron* **2014**, 70, 6803-6809




***Scheme 12***- synthesis of semi rigid macrocycle **63**

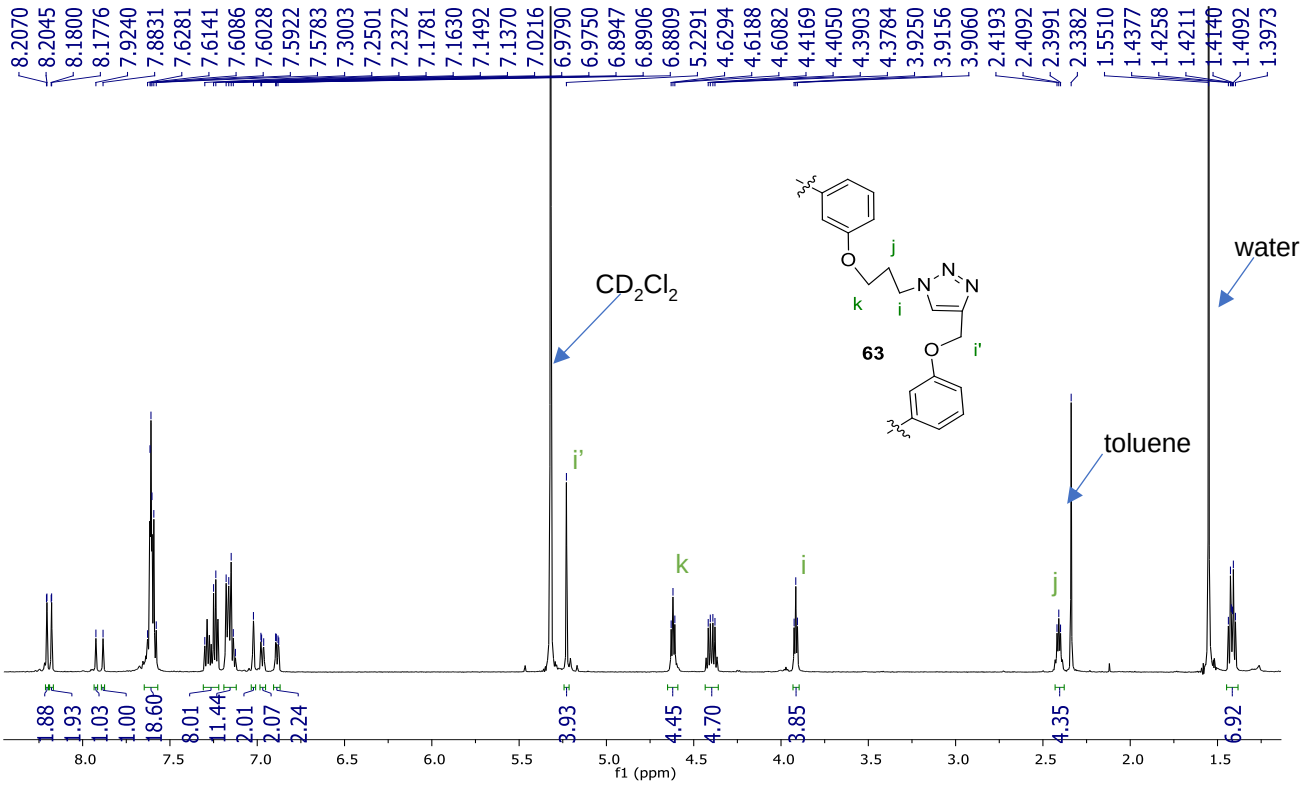



***Figure 14***-$^{1}$H NMR scpectrum of macrocycle **63** ($CD_2Cl_2$, 600 MHz)

# 3. Conclusions

In this chapter we report the synthesis of three new *m*-terphenyls prepared by Suzuki cross coupling. These were further functionalized with 3-iodophenol derivatives to give another six new building blocks for macrocycle and cage synthesis. Two tris(phenyl)benzene derivatives were synthesized to serve as cap molecules in cage synthesis.

A semirigid macrocycle **63** was synthesized by CuAAC 'click' reaction. The macrocyclization reaction was achieved in high yields. All compounds were analyzed by NMR and MS.
Other investigations on this macrocycle, as well as the synthesis of cage molecules are underway.

# Part B. Pyrenophanes and pyrene-based cages. Candidates for "host-guest" chemistry.

# II. Results and discussion

## 1. Objectives

The aim of this study was the synthesis and characterization of pyrene-based compounds, functionalized in the common 1-,3-,6-,8-positions. These would form the base of macrocyclic compounds like 1,6-pyrenophanes **I** and pyrene containing cages **II.** These macromolecules were designed to host small, neutral molecules, therefore investigation of their electronic and complexation properties was essential.


**I** **II**

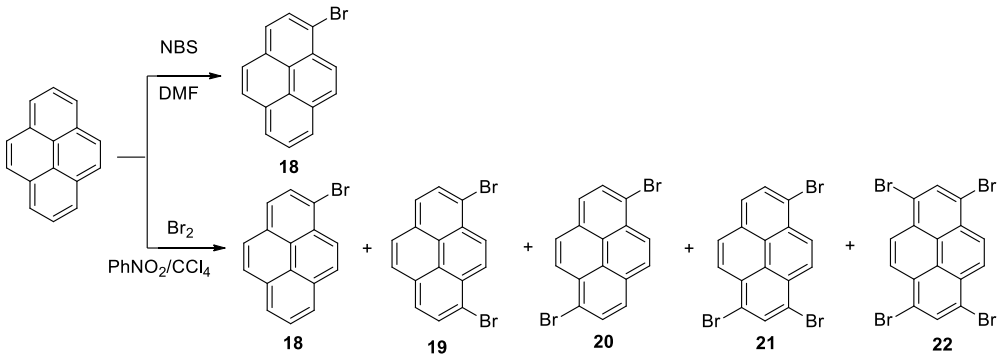
***Figure 7-*** General structure of target compounds

Copper catalyzed azide-alkyne click reaction (CuAAC)[6] was chosen for the main macrocyclization reaction, but other methods were tried too. We also wanted to take advantage of the π-stacking abilities of pyrene by using an electron deficient bridging unit, like naphthalene diimide, to facilitate the macrocyclization reaction.

[6] Meldal, M., Tornøe, C. W. *Chem. Rev.* **2008,** 108, 2952–3015

## 2. Synthesis of mono-, di-, tri-, and tetrasubstituted pyrene derivatives

Our synthetic sequence started by treatment of pyrene with molecular bromine in carbontetrachloride resulting a mixture of mono-, di-, trisubstituted pyrene. (Scheme 4).[7]



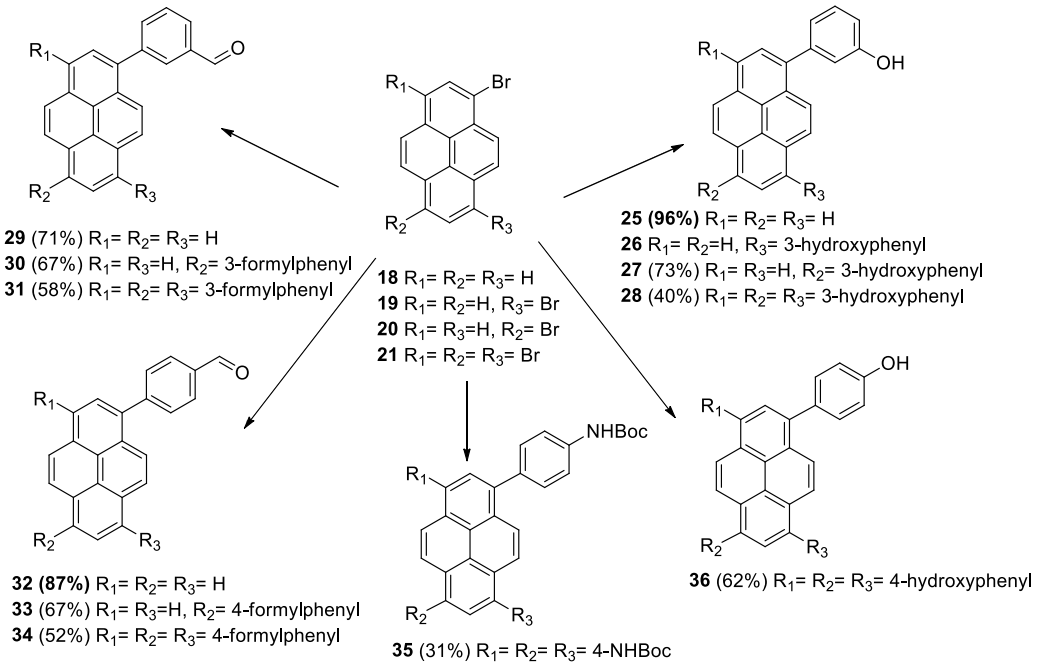

***Scheme 4***- Pyrene bromination

$^1$H NMR made on crude product afforded estimation of the molar ratio between the two isomers **19**:**20** =0.4-0.6:1. The resulting mixture was separated by fractional recrystallisation from toluene. Due to the more symmetrical structure, 1,6-dibromide is less soluble than 1,8-dibromide, so the pure isomer crystallized as long needles, and its purity was confirmed by $^1$H NMR. Since, removal of the last traces of 1,6-dibromide to obtain the pure 1,8-isomer is very difficult, researchers often opt for chromatographic separation of the desired isomer at a later stage of the synthetic route.[8] 1,3,6,8-tetrabromopyrene was synthesized by the same reaction, using excess of bromine and heating, while 1-bromopyrene was prepared by reacting pyrene with 1 eq. of freshly recrystallized N-bromosuccimide (NBS)[9]. Increasing the number of bromine atoms on the structure, the solubility of the bromo-substituted pyrenes decreased in the following order: **18**>**19**>**20**>**21**>**22**.

Bromurated pyrenes were subjected to Suzuki cross-coupling reaction with the corresponding phenyl boronic acids. (Scheme 5) The coupling reactions were conducted in toluene/ethanol or toluene/water mixture using tetrakis(triphenylphosphine)palladium(0)

[7] Grimshaw, J., Trocha-Grimshaw, J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1622-1623
[8]a) Leroy-Lhez, S., Fages, F**.** *Eur. J. Org. Chem.* **2005**, 2684–2688; b) Hirose, T., Takai, H., Watabe, M. Minamikawa, H.,Tachikawa, T., Kodama, K., Yasutake, M. *Tetrahedron* **2014**, 70, 5100-5108; c) Huang, C.-B., Chen, L-J., Huang, J., Xu, L. *RSC Adv*. **2014**, 4, 19538–19549
[9] Keshtova, M. L., Sharmab, G. D., Godovskiia, D. Yu., Belomoinaa, N. M., Gengc, Y., Zoud, Y., Kochurove, V. S., Stakhanova, A. I., Khokhlov, A. R. *Dokl. Chem.* **2014**, 456, 65-71.

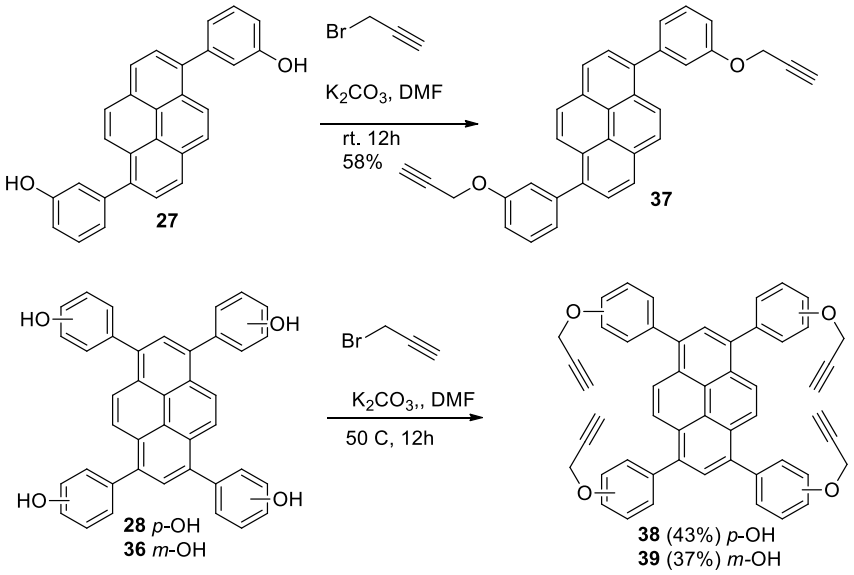
($Pd(PPh_3)_4$ catalyst and potassium carbonate or cesium carbonate base.[10] As one can observe, a decreasing tendency in yields showed, due to the decreasing solubility of bromopyrenes and the increasing number of reacting sites. The side products, especially in the case of tetrasubstituted pyrenes, also raised difficulties in purification. Often combined purification methods were used to isolate the pure compounds.




***Scheme 5***- Pyrene derivatives obtained by Suzuki cross coupling reaction

Introduction of a triple bond on the structure was essential for the click reaction to take place. Intermediates **27**, **28**, **36** were reacted with propargyl bromide to give alkyne containing derivatives (Scheme 6). Their structure was confirmed by NMR spectroscopy and mass spectrometry. $^1$H NMR fragments of disubstituted diol **27** (b) compared to product **37** (a) is presented in Figure 9 .Besides the 4 characteristic dublets corresponding to the pyrene ring, and the appearance of aliphatic signals assigned to protons from the propargyl substituent, a downfield shift of *m*-phenylene proton signals (a, b, c, d) can be observed in the spectrum of **37**.

[10] El-Assaad, T. H., Auer, M., Castañeda, R., Hallal, K. M., Jradi, F. M., Mosca, L., Khnayzer, R. S., Patra, D., Timofeeva, T. V., Brédas, J.-L., List-Kratochvil, E. J. W., Wex, B., Kaafarani, B. R. *J. Mater. Chem. C* **2016**, 4, 3041-3058




***Scheme 6***-Synthesis of compounds **37-39**

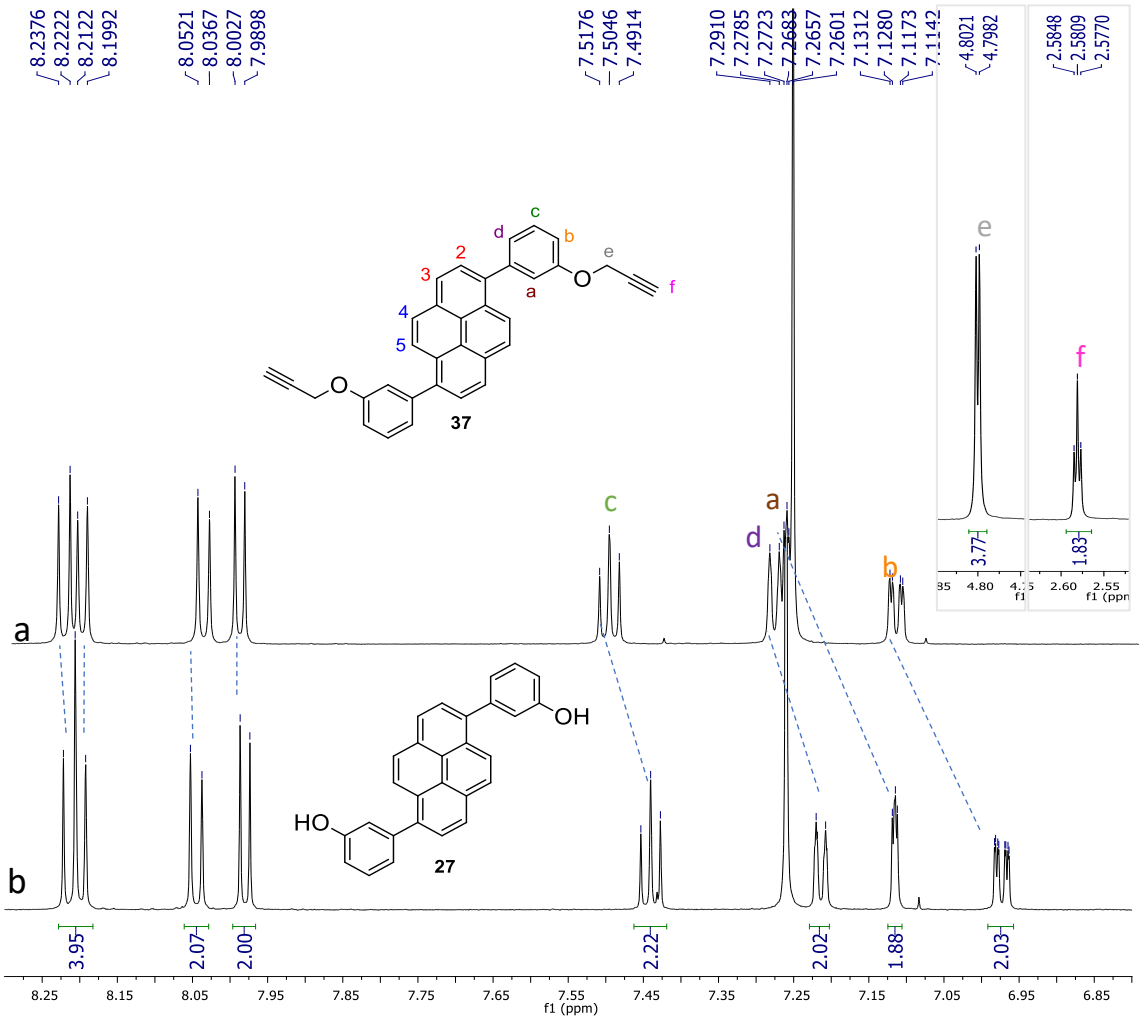
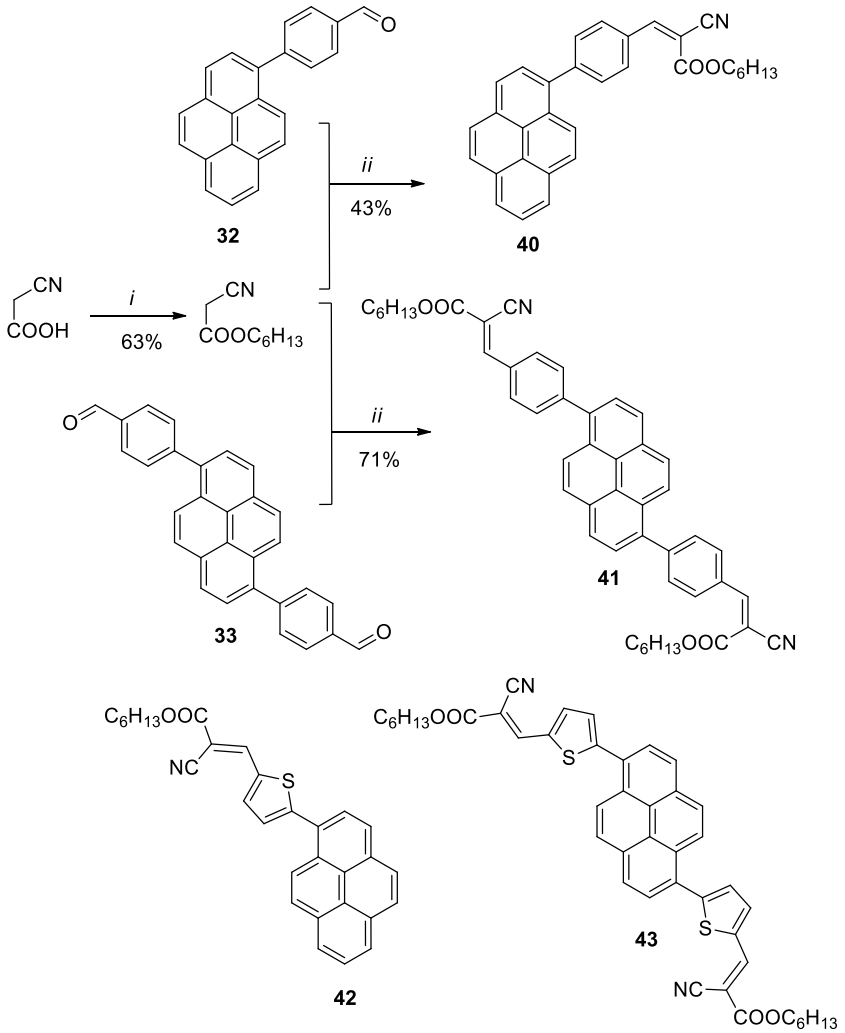



***Figure 9.*** Fragments of $^{1}$H NMR spectrum of compound **37** (a) and compound **27** (b) in $CHCl_{3}$,, 600 MHz**.**

In order to explore structure-property relationships in pyrene derivatives, we designed two series of mono-and disubstituted pyrenes as potential donor building blocks for single-material organic cells (SMOSCs) [11] [12] Besides compounds **40** and **41**, another set in which cyanoester electron acceptor groups are connected to the pyrene core *via* thienyl π-conjugating bridges was synthesized in our laboratory (**42** and **43,** Scheme 7). Unlike the already reported compounds[13], the solubility of these new molecules is ensured by the hexyl chains of the cyanoester in order to limit steric hindrance between the thiophene rings and the peripheral hydrogen atoms of pyrene.[14].




***Scheme 7-****i) 1-hexanol, $H_2SO_4$ ii)* $CHCl_3$, $Et_3N$, reflux

[11] Roncali, J. *Adv Energy Mater* **2011**, 1, 147-160.
[12] Roncali, J., Grosu, I. *Adv Sci* **2019**; 6:1801026
[13] Liu, M., Gong, X., Zheng, C., Gao, D. *Asian J Org Chem* **2017**, 6, 1903-1913.
[14] Diac, A., Szolga, L., Cabanetos, C., Bogdan, A., Terec, A., Grosu, I., Roncali, J. *Dyes Pigm.* **2019**; 171, 107748

***Table 1***-Optoelectronic properties of compounds **40**-**43**

| Compound | λmax (soln) [nm] | λmax (film) [nm] | ICT/π-π* | *E*pa [V] | *E*pc [V] | *E*g [eV] |
|---|---|---|---|---|---|---|
| **40** | 308, 377 | 385 | 0.64 | 1.33 | -1.35 | 2.48 |
| **41** | 336, 405 | 404 | 0.78 | 1.35 | -1.30 | 2.40 |
| **42** | 340, 424 | 440 | 1.02 | 1.32 | -1.30 | 2.20 |
| **43** | 340, 445 | 485 | 1.47 | 1.34 | -1.23 | 2.151 |

Esterification of cyanoacetic acid was achieved in 63% yield, following the reported procedure,[15] then Knoevenagel condensation of cyanoester with aldehydes **32** and **33** afforded target compounds **40** in 38% and **41** in 71% yield. $^{1}$H and $^{13}$C NMR and HRMS analysis were engaged to determine the purity of the target compounds. Figure 11. shows the normalized UV-Vis absorption spectra of the compounds in DCM solutions while the corresponding data are listed in Table 1. The spectrum of all compounds shows a first band in the 300-350 nm region assigned to the π-π* transition of the pyrene block followed by a broader band in the 400-500 nm range corresponding to an internal charge transfer (ICT). The spectra of the phenyl substituted compounds **40** and **41** show that the introduction of a second cyanoester acceptor unit on the pyrene block produces a bathochromic shift of the absorption maximum of both transitions together with an increase from 0.64 to 0.78 of the relative intensity of the ICT band *vs* the π-π* transition. Comparison of the data for compounds **40** and **41** to those of their thienyl analogs **42** and **43** shows that the replacement of the phenyl by the thienyl π-spacer produces a 47 nm bathochromic shift of the maximum of the ICT band for the mono-substituted compounds **42** *vs* **40** and 32 nm for the disubstituted compounds **43** *vs* **41**. Comparison of the relative intensity of the ICT *vs* π-π* bands for compounds **40**, **42** and **41**, **43** reveals an inversion of the ratio for the thienyl compounds. Taking this ratio as an indication of the strength of the ICT [16], suggests a stronger ICT for the thienyl compounds, consistent with a better conjugating effect of thiophene *vs* benzene[17].

[15] Zhou, L., Stewart, G., Rideau, E., Westwood, N. J., Smit, T. J. *J. Med. Chem.* **2013**, 56, 3, 796–806

[16] Idzik, KR., Licha, T., Lukes, V., Rapta, P., Fryfel, J., Schaffer, M., Taeuscher, E., Beckert, R., Dunsch, L. *J. Fluoresc*. **2014**, 24, 153-160.

[17] Kathiravan, A.; Srinivasan, V.; Khamrang, T.; Velusamy, M.; Jaccob, M.; Pavithra, N.; Anandan, S.; Velappan, K. *Phys Chem Chem Phys* **2017**; 19, 3125-3135

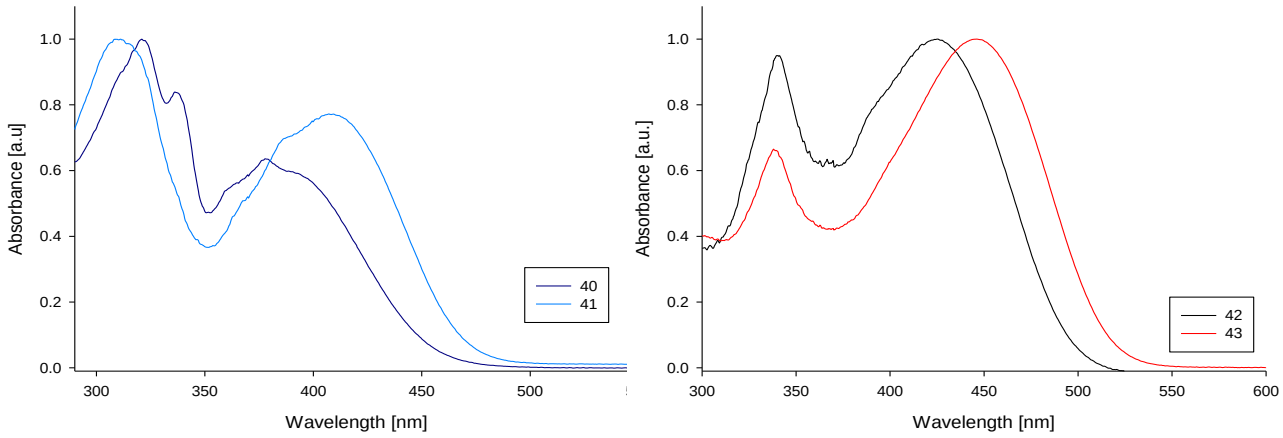



***Figure 11***-Normalized UV-vis spectra in DCM ($1x10^{-5}$ M) of compounds **40-43**

UV-Vis spectra for compounds **40-43** were recorded in solid state as well (Figure 12). Films were prepared from chloroform solutions on quartz substrate by using spin coating deposition technique. Absorption maximum of the ICT band in the solid state presents a bathochromic shift of 12 nm for compound **40** and no shift for **41**, while $\lambda$max of the thienyl compounds suffer a 16 nm redshift for compound **42** and 40 nm for **43**. These drastically different behaviors suggest that for the thienyl compounds, the passage from the solution to the solid-state results in a planarization of the conjugated structure, possibly assisted by the deformability of the thiophene ring[18] .

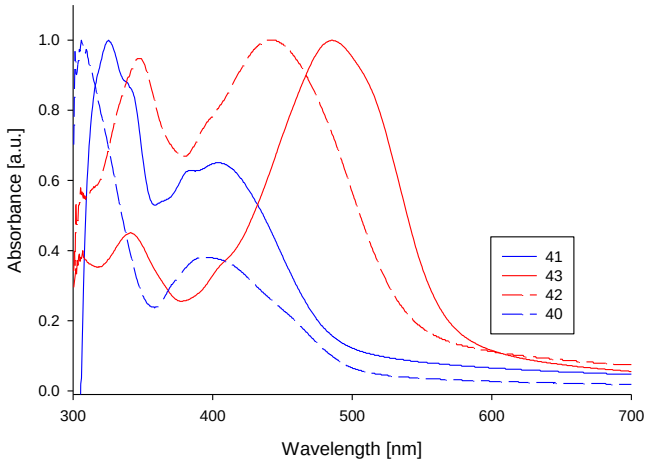



***Figure 12***- UV-Vis absorption spectra of spun-coated films

[18] Ashizawa, M., Yamada, K., Fukaya, A., Kato, R., Hara, K., Takeya, J., *Chem Mater* **2008**; 20, 4883-4890

The electrochemical properties of **40-43** were studied by cyclic voltammetry (CV) with tetrabutylammonium hexafluorophosphate as supporting eletrolyte in DCM at a scan rate of 100 mV/s. Voltammograms of compound **40-41** show reversible oxidation processes with very similar anodic potential peak ($E_{pa}$) at *ca*. 1.30 V. (Figure 13) In the negative potential region irreversible reduction process was observed peaking at about $E_{pc}$= -1.35 V for compound **40** and $E_{pc}$= -1.30 V for **41.** The small positive shift of the reduction wave for the di-substituted compounds is caused by the introduction of a second electron withdrawing cyanoester group. Little modifications encountered suggest that the type of connecting group and the number of electron-withdrawing cyanoester groups has little effect on the oxidation and reduction potentials, regardless the smaller HOMO-LUMO gap of the thienyl compounds indicated by the optical data.

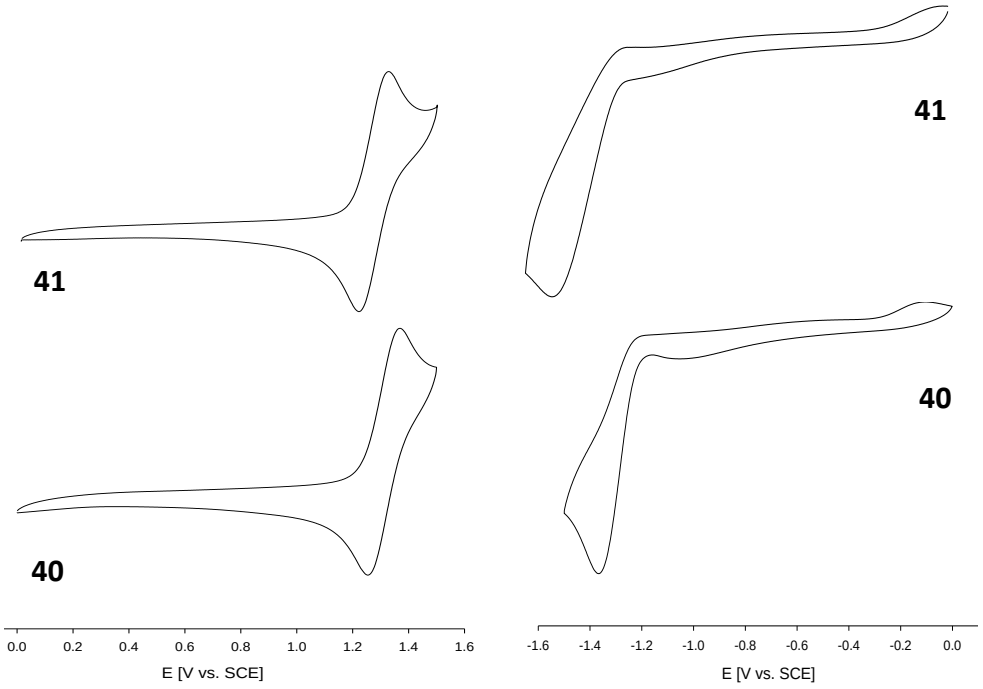



***Figure 13***- Voltammograms recorded in DCM/ $Bu_4NPF$ buffer at 100 mV/s scanning rate with SCE reference electrode and platinum wire counter electrode. Oxidation left, reduction right.

A cursory evaluation of the fluorescence efficiency in toluene relatively to diphenyl anthracene showed that all compounds present very low values, in the range of 2-5%, in agreement with recent results on related compounds. [19]

[19] Liu, M., Gong, X., Zheng, C., Gao, D. *Asian J. Org. Chem*. **2017**, 6, 1903 – 1913

To evaluate solvatochromism properties of compounds **40-43**, the absorption and emission spectra were recorded in solvents of increasing polarity. In Table 2 we listed the absorption and emission maxima obtained in toluene, THF, DCM, and acetone.

***Table 1***- Absorption and emission maxima in solvents of increasing polarity

| Compound | Solvent | $\lambda_{abs}$ [nm] | $\lambda_{em}$ [nm] | $\lambda_{em}$ [$cm^{-1}$] | *SS* [$cm^{-1}$] |
|---|---|---|---|---|---|
| **40** | toluene | 378 | 490 | 20408 | 6050 |
| | THF | 377 | 540 | 18518 | 8010 |
| | DCM | 370 | 577 | 17953 | 8580 |
| | acetone | 374 | 560 | 17758 | 8880 |
| **41** | toluene | 408 | 491 | 20366 | 4140 |
| | THF | 405 | 544 | 18382 | 6310 |
| | DCM | 412 | 555 | 18018 | 6250 |
| | acetone | 385 | 562 | 17793 | 8180 |

As one can observe, solvent polarity has minor influence on absorption maxima, whereas increase in solvent polarity produces a large bathochromic shift in emission maximum causing a large increase in Stokes shift between absorption and emission. In Figure 14 are presented normalized emission spectra of compound **41,** and photograph taken to show the variation in the emitting behaviour of **41** in solvents of increasing polarity under UV-light illumination (365 nm). Both **40** and **41** undergo a *ca.* 70 nm red shift of the emission maximum ($\lambda_{em}$) between toluene and acetone.

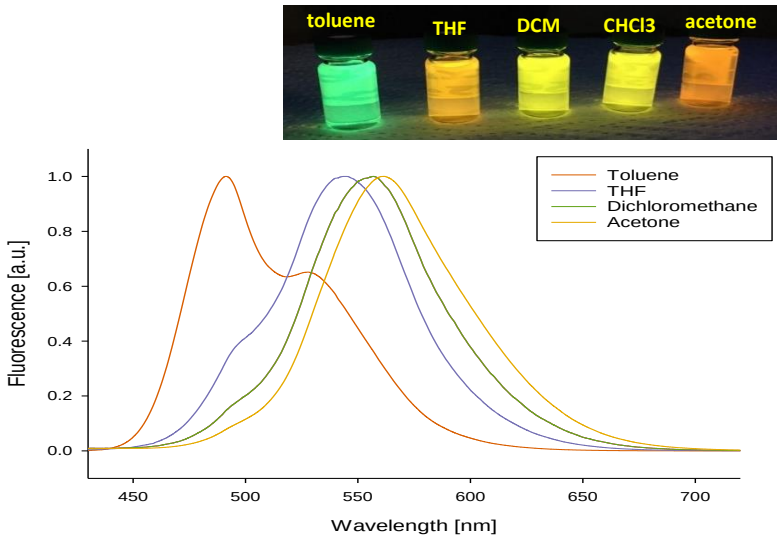
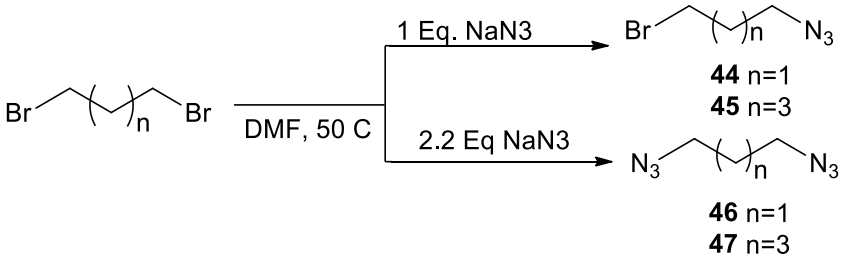



***Figure 14*** -Normalized emission spectra of compound **41** in different solvents.

The Stokes shift between the absorption and emission maxima increases by 2830 $cm^{-1}$ for **40** and with smaller values for **41**. These results suggest an increase of the dipole moment of the molecule between the ground and the excited state; the rearrangement of the solvent around the molecule leading to a decrease of the energy of the excited state.

## 3. Synthesis of azidoalkanes and naphtalenediimides.

To offer a certain degree of flexibility to our cyclophanes, 1,3-diazidopropane **46** and a longer, 5 carbon atom containing alkylazide **47** were chosen as bridging units (Scheme 8). Dibromoalkanes were reacted with either 1 or 2.2 equivalents of sodium azide, in N,N-dimethylformamide [20] Partial substitution was carried out by dropwise addition of the substrate to more diluted reactant. Monoazides were synthesized to be involved in subsequent chemical modifications. Their purification however was not entirely achievable by column chromatography.




***Scheme 8***- Synthesis of azides **44-47**

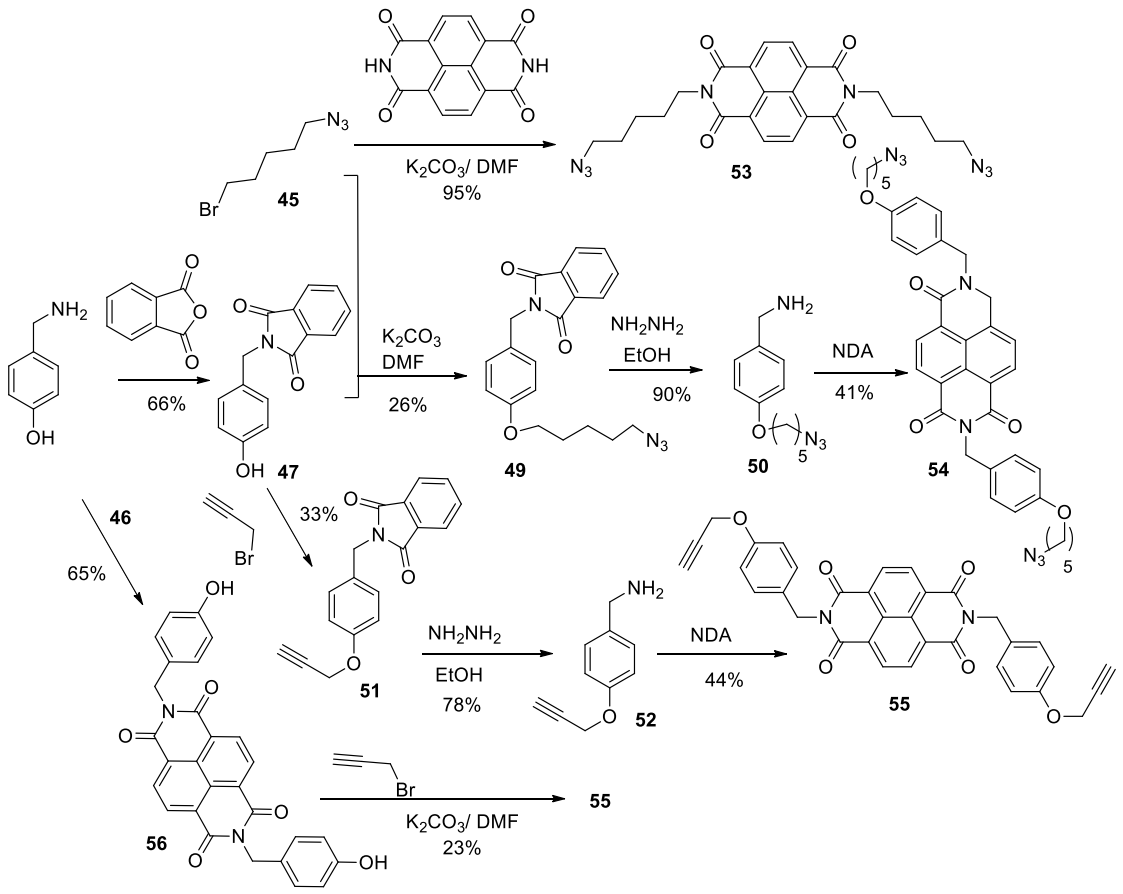
The concept behind donor-acceptor cyclophane, containing the naphthalene diimide core was established in previous works dedicated to NDI derivatives[21 22]. 1,4,5,8-naphthalenediimides (NDI) are planar, chemically robust, redox active compounds. The two, electron withdrawing imide group linked to the naphthalene core create a highly acidic π- surface. Inclusion of this π-electron deficient moiety into complex supramolecular architecture is guided by π-π stacking, charge transfer (CT) and van der Waals interactions. Our choice on NDIs as complementary π-electron acceptor for π-electron rich pyrene compounds hopefully ensures association in a

[20] Agnew, H. D., Rohde, R. D., Millward, S. W., Nag, A., Yeo, W-S., Hein, J. E., Pitram, S. M., Tariq, A. A., Burns, V. M., Krom, R. J., Fokin, V. V., Sharpless, K. B., Heath, J. R. *Angew. Chem. Int. Ed.* **2009**, 121, 5044 – 5048

[21] Diac, A., Matache, M., Grosu, I., Hădade, N. D. *Adv. Synth. Catal.* **2018**, 360, 817-845

[22] Hamilton, D. G., Sanders, J. K. M., Davies, J. E., Clegg, W., Teat, S. J. *Chem. Commun***., 1997,** 9, 897-898

geometry that favors [1+1] or [2+2] macrocyclization. Since N,N-functionalization has small effect on optical and electrochemical properties, embellishment with azide-alkyne functional groups was carried out through these positions. In this regard, a synthetic strategy presented in Scheme 9, was designed for obtaining NDI compounds **54-57.** Prior to O-alkylation, the amino group was protected with phthalic anhydride. Base-promoted substitution yielded compound **49** in 26%, and **51** in 33%. Treatment of 1,4,5,8-naphthalene tetracarboxylic acid dianhydride (NDA) with 4-hydroxybenzylamine or its functionalized derivative **50** or **52**, at high temperature in DMF, gave NDI derivatives **53-56** in good yields.[23] NMR spectroscopy and mass spectrometry were used for characterization. All spectral data obtained on **53-56** is in full agreement with the proposed structures.




***Scheme 9***- Synthesis of NDI derivatives

[23] Guha, S., Goodson, F. S., Roy, S., Corson, L. J., Gravenmier, C. A., Saha, S. *J. Am. Chem. Soc.* **2011**, 133, 39, 15256–15259

# 4. Synthesis of cyclophanes and cages with pyrene units

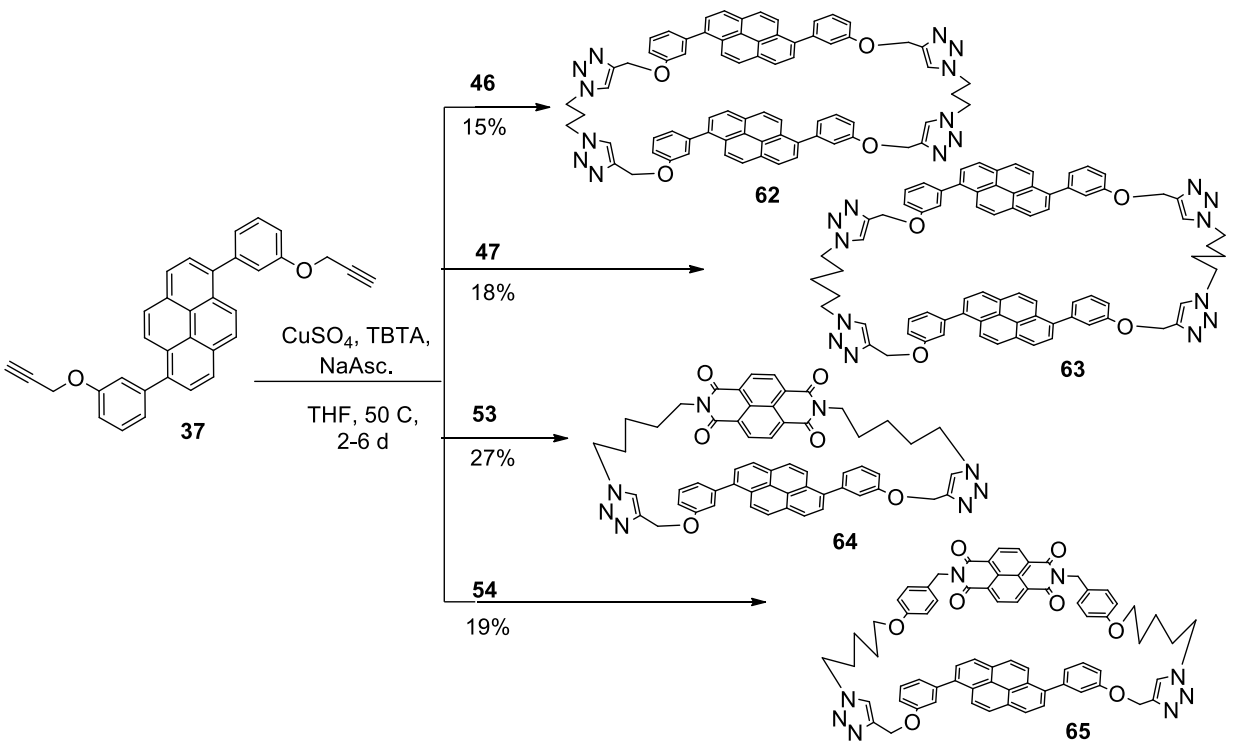
With our precursors available, we tried a few synthetic methodologies for constructing macrocycles and cages. The first idea was to apply the principles of constitutional dynamic chemistry (CDC) on pyrene-based aldehydes and amines. The imine bond formation is one of the most frequently used covalent reversible reactions in CDC. The only drawback to this exchange is the sensitivity to hydrolysis of the imine products, thus raising difficulties in the analysis of DCL. Several attempts to engage pyrenyl amine **57**-into imine exchange in anhydrous chloroform with aliphatic glutaric dialdehyde or phthaldehydes failed in oyr hands.

The CuAAC 'click' reaction has proved to be a powerful tool for designing multiple functionalized macrocycles. [24] Apart from inclusion complexes with neutral polycyclic aromatic hydrocarbons (PAHs), the click-derived macrocycles show a high-binding affinity towards anions and metal ions thanks to the 1,2,3-triazole-linker Our interest for the preparation of macrocycles **62-65** came from the porphyrin-[25], and $C_3$-symmetric 2,4,6-triaryl-1,3,5-triazine-based[26] organic cages, with two cofacial aromatic platforms brigded with click-derived triazole units. The 'click' macrocyclization reaction was carried out following classical reaction conditions with $CuSO_4$, tris(benzyltriazolylmethyl)amine (TBTA) as catalyst and sodium ascorbate in THF (Scheme 12). Chromatographic purification afforded cyclophanes **62-65** in reasonable yields.

[24] a) Xu, L., Li, Y., Li, Y. *Asian J. Org. Chem*. **2014**, 3, 582 – 602; b) Peng1, R., Xu1, Y., Cao, Q. *Chinese Chem. Lett.* **2018**, 29, 1465–1474

[25] a) Zhang, J., Li, Y., Yang, W., Lai, S-W., Zhou, C., Liu, H., Chec, C-M., Li, Y. *Chem. Commun.* **2012**, 48, 3602–3604; b) Kocher, L., Durot, S., Heitz, V. *Chem. Commun.*, **2015**, 51, 13181-13184

[26] Samanta, J., Natarajan, R. *Org. Lett.* **2016**, 18, 14, 3394–3397




***Scheme 12***- Synthesis of cyclophanes **62-65**

The drawn structures of pyrenophanes **62-65** were proved by NMR spectroscopy and mass spectrometry.

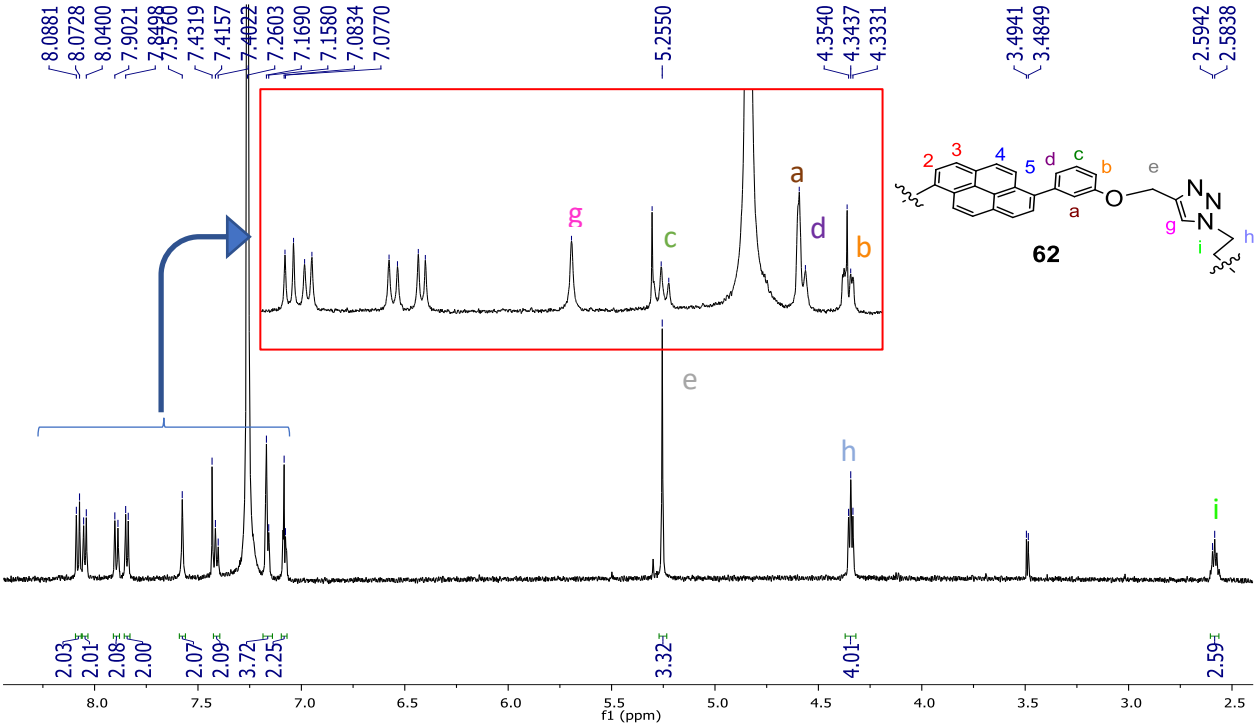



***Figure 15***-$^{1}$H NMR spectrum of pyrenophanes **62** recorded in $CDCl_3$, 600 MHz

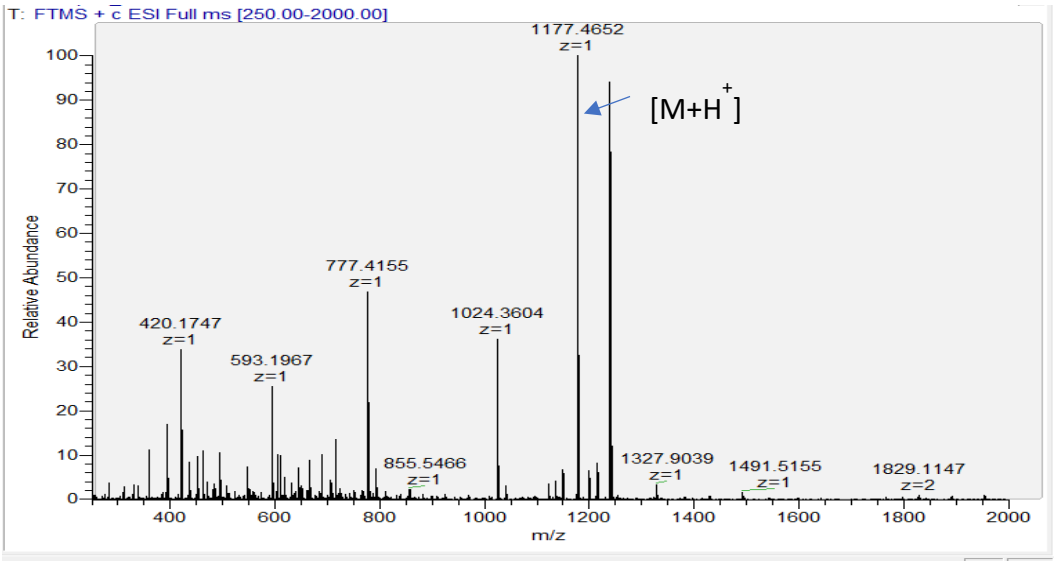



***Figure 16***-Mass spectrum of compound **62**

Mass spectrum of cyclophane **62** is also in full agreement with the assigned structure (Figure 16). The protonated molecular peak appears at 1177 *m/z*.

# 5. Conclusions

In summary, two solution processable D-π-A systems, consisting of the donor pyrene core connected to cyanoester by phenyl π-bridges, were synthesized for OPV purposes. Their optical, electrochemical and solvatochromism properties were investigated and compared to the thienyl counterparts. Cyclic voltammetry showed stable cation radicals that can be reversibly oxidized. UV-Vis absorption data showed larger band gaps and weaker internal charge transfer for benzene-brigded compounds probably due to the synergistic effect of the lower resonance energy of thiophene *vs* benzene and of the larger plasticity of the thiophene ring.

A set of mono-, di-, tetra-functionalized pyrene compounds have been synthesized. Suzuki coupling reactions on bromurated pyrenes gave the phenyl decorated pyrene moieties in good yields. These served as building blocks for obtaining macrocyclic compounds via CuAAC 'click' reaction. A total number of 5 pyreonphanes were synthesized and identified using NMR spectroscopy and mass spectrometry. Investigation of their photophysical, and complexation properties is underway.

# Part C. Diketopyrrolopyrole derivatives in single-material organic solar cell systems.

## II. Results and discussions

### 1. Objectives

Taking into account recent advances in Single-material organic cells (SMOSCs), we projected the synthesis of a *1,4-diketopyrroIo[ 3,4-c]pyrrole* (DPP)-based D-π-A- system that consist of an electron-rich hydrazone group, the conjugated π-system of diketopyrrolopyrrole as bridge, and an electron deficient dicyanovinyl end group (Figure 4).

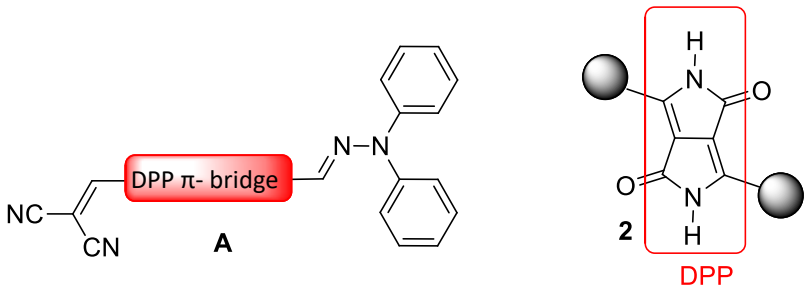



***Figure 4***- Structure of the target compound

Apart from the effectual synthesis we intended investigation of its photophysical properties as well as testing its efficiency in single material organic solar cell.

### 2. Synthesis of DPP-based single molecules

The DPP molecule, endowed with excellent chemical resistance, occurs in a broad spectrum of bright colors depending on the aryl group attached. The color in solid state differs from the color in very dilute solutions, which is ascribed to π-π interactions between layers in solid state arrangement. The intra- and intermolecular hydrogen bonding along with π-π stacking makes the DPP chromophore highly insoluble in common organic solvents, except in polar aprotic solvents ( DMF, NMP).

To achieve our A type structure (Figure 4) we first envisioned the target compound to be structure **I** (Figure 5), but synthetic difficulties encountered along the pathway shifted our design to structure **II**, then to target molecule **III**.

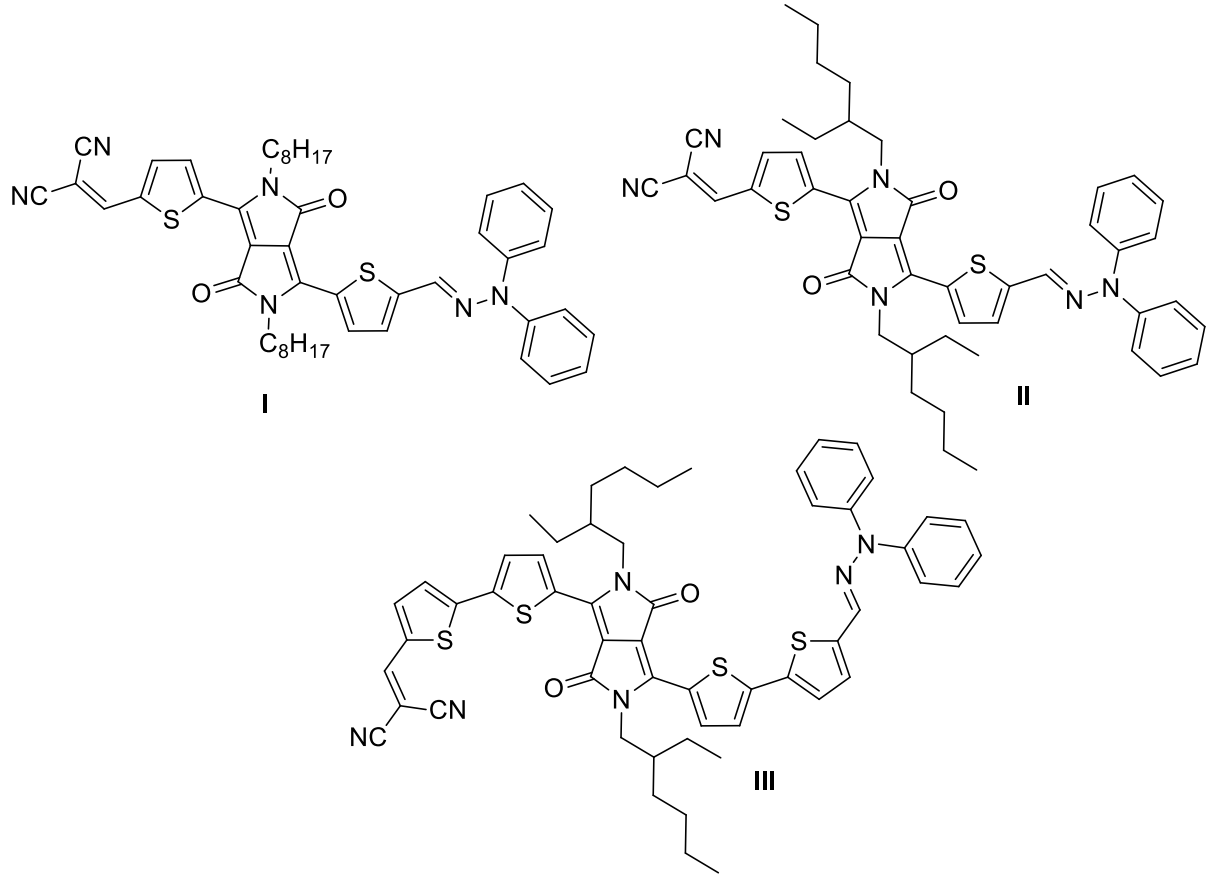


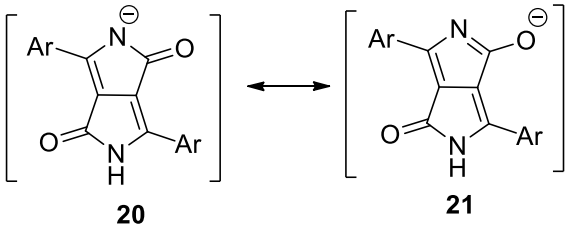

***Figure 5***- Proposed structure for A-type molecule

The synthetic route to *1,4-diketopyrrolo[3,4-c]pyrroles* it is well established and discussed in several articles.[2,27] Following the published synthetic procedures[8a, 28,29], the condensation of thiophene-2-carbonitrile with succinate **18** or **19** resulted the DPP core **12** as a bright red solid in yields up to 70 %. The structure off DPP **12** was confirmed by $^1$H RMN analysis in dmso-$d_6$.

The key step for obtaining solvent processable compounds for OPV and OE purposes is the substitution of the lactam-NH group with an alkyl chain or other solubilizing groups. Similar to other amides under basic conditions, the lactam group from the DPP core can undergo tautomerization, in other words the negative charge is distributed between the nitrogen and oxygen

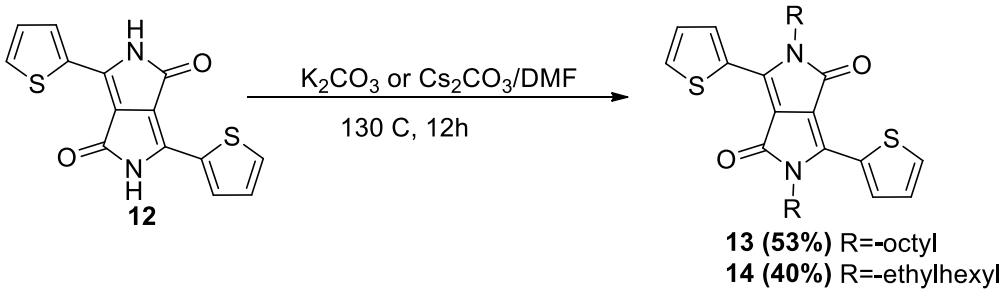
[27] Stas, S., Sergeyev, S., Geerts, Y. *Tetrahedron* **2010**, 66, 1837–1845
[28] Chen, X., Guo, K., Li, F., Zhou, L., Qiao, H. *RSC Adv*. **2014**, 4, 58027–58035
[29] Deng, L., Wu, W., Guo, H., Zhao, J., Ji, S., Zhang, X., Yuan, X., Zhang, C. *J. Org. Chem*. **2011**, 76, 9294−9304

atom of the amide group. (Scheme 7). This can cause competing side reaction during nucleophilic substitution with alkylbromides, and as a result lowering the reaction yield.




***Scheme 7***- mesomeric structures of deprotonated DPP

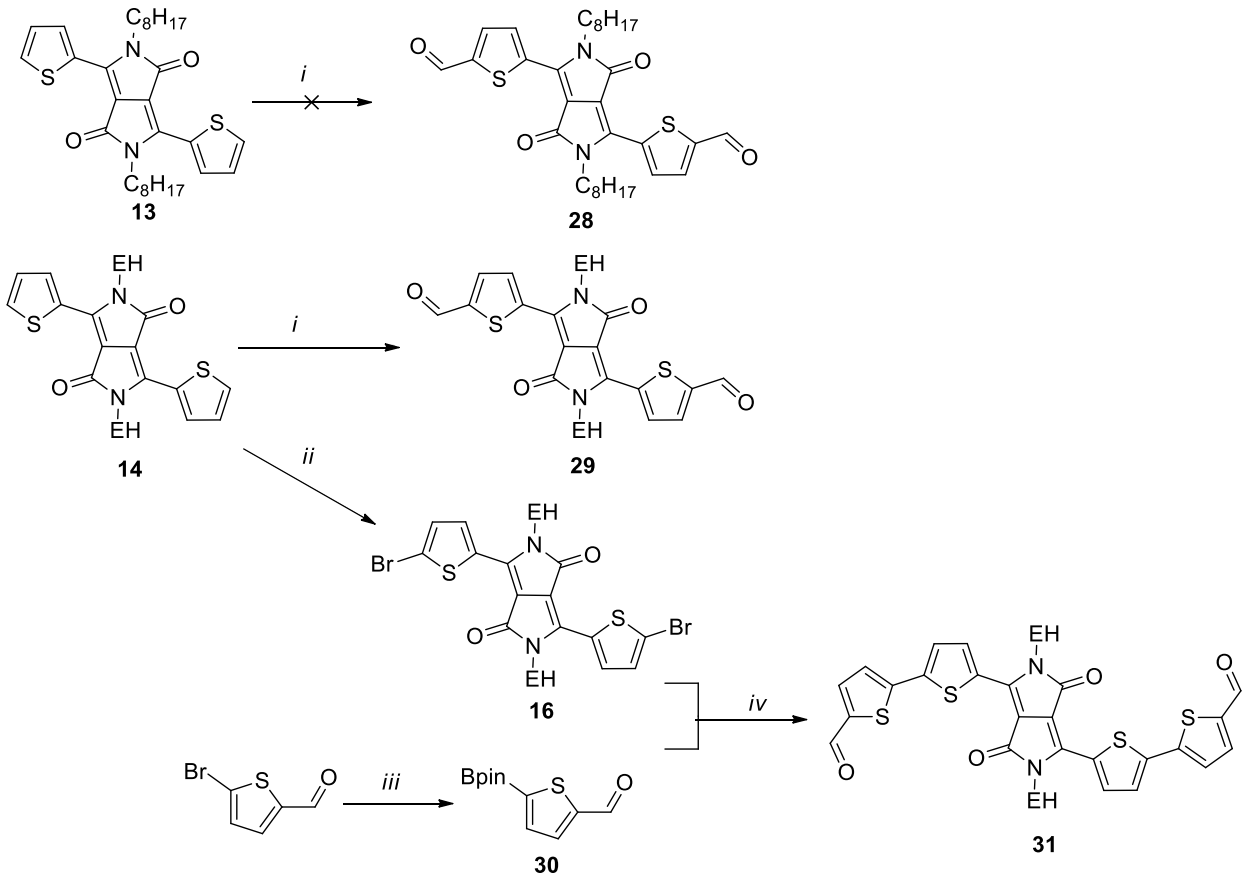
Applying the established method, our alkylation procedure started by heating up to 130℃ the mixture of DPP **12,** 3 equivalents of $K_2CO_3$/$Cs_2CO_3$, and catalytic amount of 18-crown-6 in dry DMF under argon atmosphere for 1 hour, followed by dropwise addition of the alkylbromide. The reaction mixture was stirred at this temperature for at least 12 hours then cooled to room temperature. The product was extracted with ethyl acetate or DCM and purified by recristallyzation. (Scheme 9).




***Scheme 9***-Conventional method for DPP alkylation

In several cases we observed the formation of O-alkylated side product, but isolation by column chromatography was performed just once, mainly because purification *via* recrystallization made an easier access to the desired N,N'-substituted compounds.

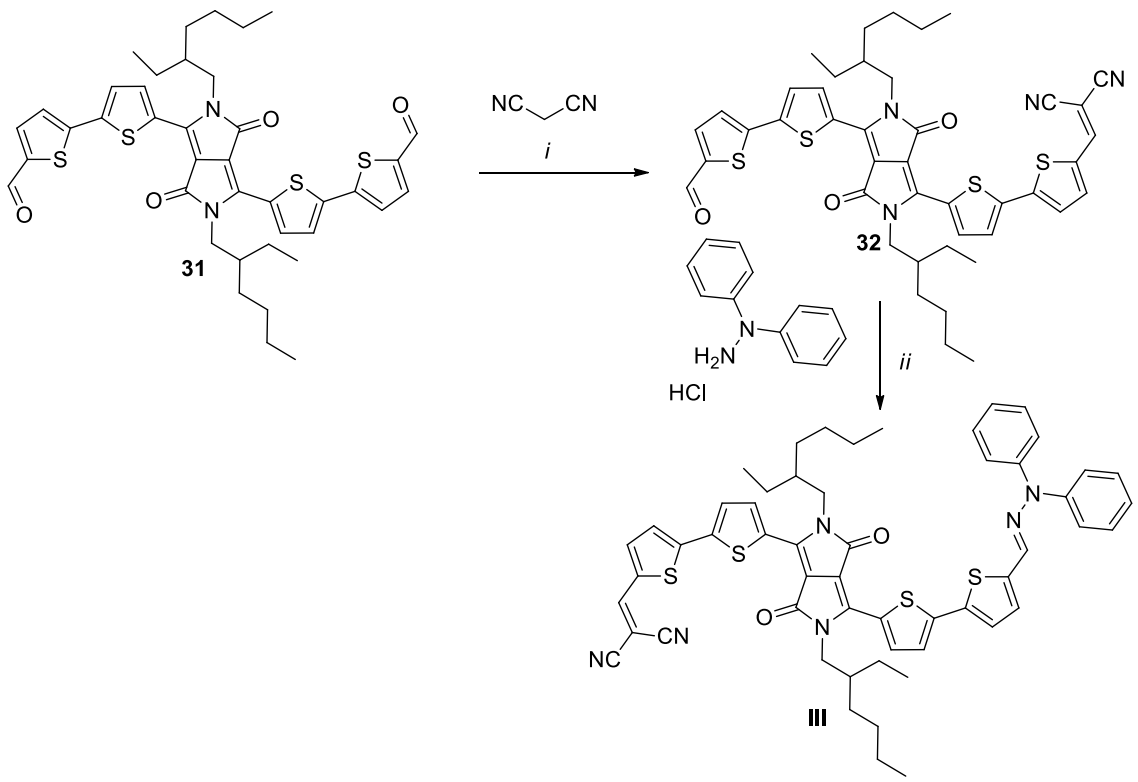
The next step towards our target A type compound (Figure 7) was the formylation reaction at the 5,5' position of the thiophene unit attached to DPP core. Derivative **13** was subjected to lithiation according to procedure by Janssen et al.**Error! Bookmark not defined.** Cooling the THF solution of compound **13** to -78 ℃ induced aggregation, hence the starting material was recovered in the form of a bright red precipitate. This problem made us reevaluate the structure of the target compound. Branched alkyl derivatized compounds increase the solubility, therefore we decided changing alkylating agent to 2-ethylhexyl bromide instead of the linear octyl bromide. We also thought of an easier way to endow our structure with formyl groups (Scheme 11).




***Scheme 11***- *i)* LDA, -78℃, 2h, DMF -78 ℃->0 ℃; *ii*) NBS, rt., 2h, 43%; *iii*) bispinacolatodiboron, KOAc, $Pd(PPh_3)Cl_2$, 1,4-dioxane, 80 ℃, 6h, 86 %; *iv*) $Pd(PPh_3)_4$, THF, $Na_2CO_3$, 12 h, reflux, 82%

In order to synthesize target compound III we first reacted compound **14** with NBS (*N*-bromosuccinmide) at room temperature. Then precursor **30** was synthesized by borylation of commercially available 2-bromothiophene-5-carbaldehyde. Finally, Suzuki coupling of compounds **16** and **30** was carried out in THF with $Na_2CO_3$ base and $Pd(PPh_3)_4$ catalyst. Obtained yields were similar to those from the literature, in some cases even improved. These are the following: 43% for **16**, 86% for **30** and 82% for **31**.

Knoevenagel condensation of dialdehyde **31** with malononitrile was perfomerd in dry $CHCl_3$ in the presence of triethylamine (Scheme 12). Monoaldehyde **32** was separated on column chromatography, and its structure was confirmed by NMR and mass spectrometry analysis.




***Scheme 12***- *i*) $CHCl_3$, $Et_3N$, rt; 12 h, 70%; *ii*) NaAc, DCE, rt., 6h 45%

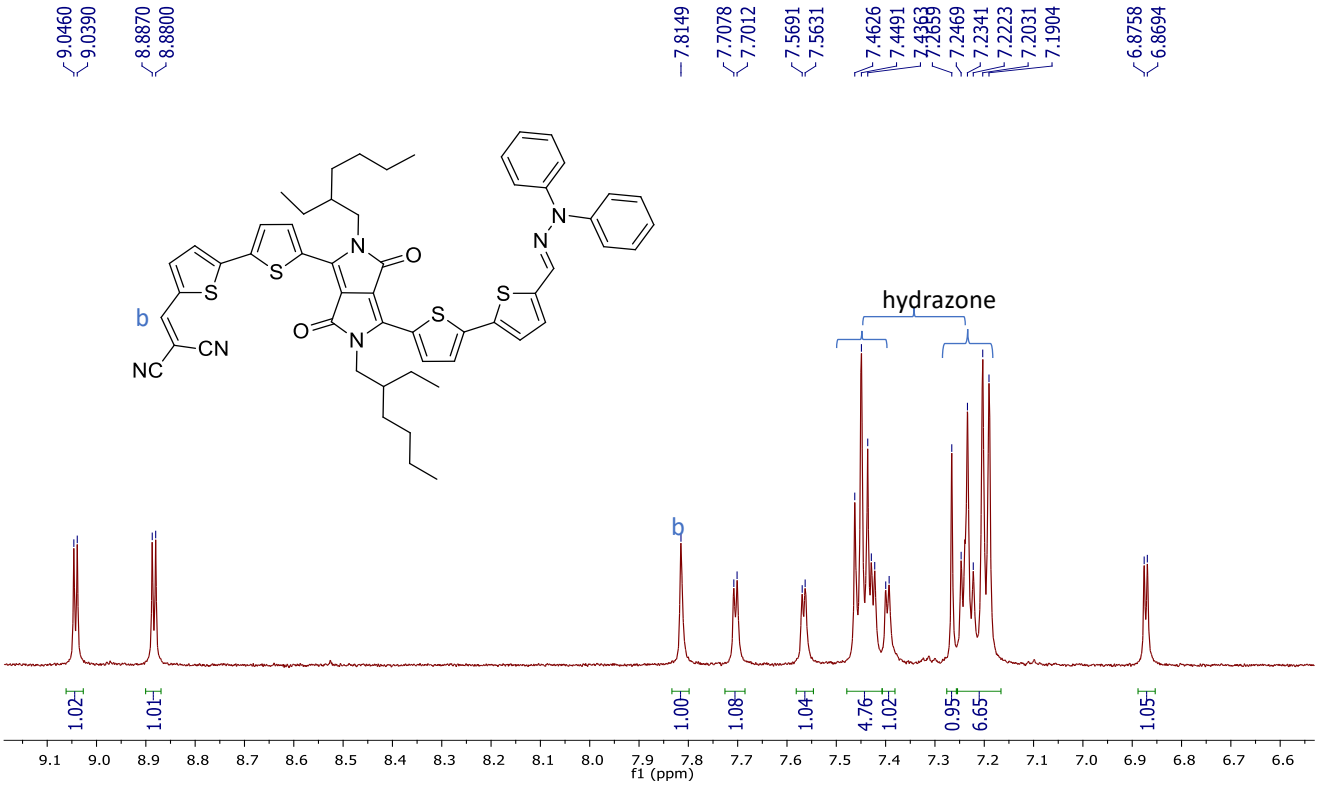
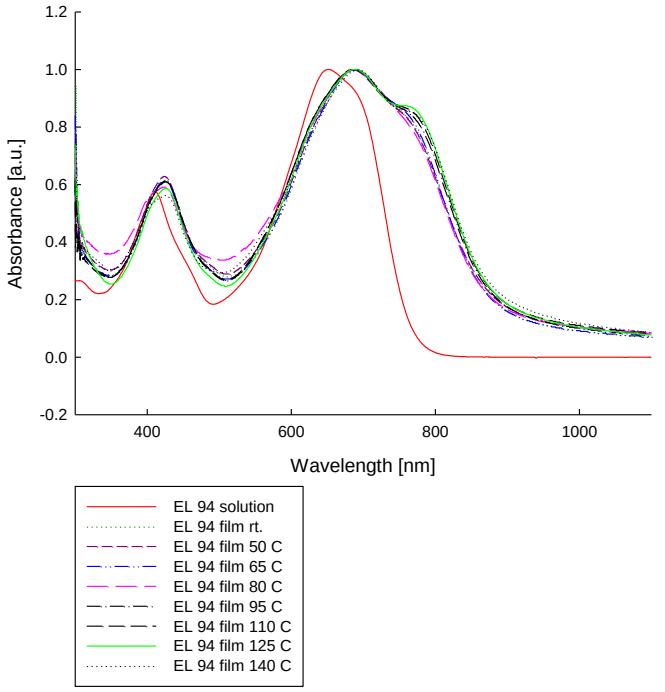



***Figure 8***- Aromatic region of $^1H$ NMR spectrum for target compound **III** ($CD_2Cl_2$, 400 MHz)

The last step consisted of condensation of intermediate **32** with 1,1-diphenylhydrazine hydrochloride. Chromatographic purification afforded analytical sample in good yields. In Figure 8 is presented the aromatic region of $^{1}$H NMR spectrum corresponding to compound **III**. The absence of signal for aldehydic proton at 9.89, and the presence of overlapped signals of the phenyl substituents indicates that the aldehyde group has been converted to the hydrazone end capped final product.

Mass spectrometry was used for analysing compound **III.** The mass spectrum is shown in Figure 10, ionic species detected at 959.3334 *m/z* corresponding to [M+H]+.

UV-vis absorption spectra were registered both in solution (DCM, $1x10^{-5}$ M), and in solid-state (spin-coated film on quartz) at different temperatures. As shown in Figure 9 the absorption maximum ($\lambda_{max}$) suffers a bathocromic shift from 652 nm to 690 nm. This deviation can be attributed to molecular stacking effects in solid state.



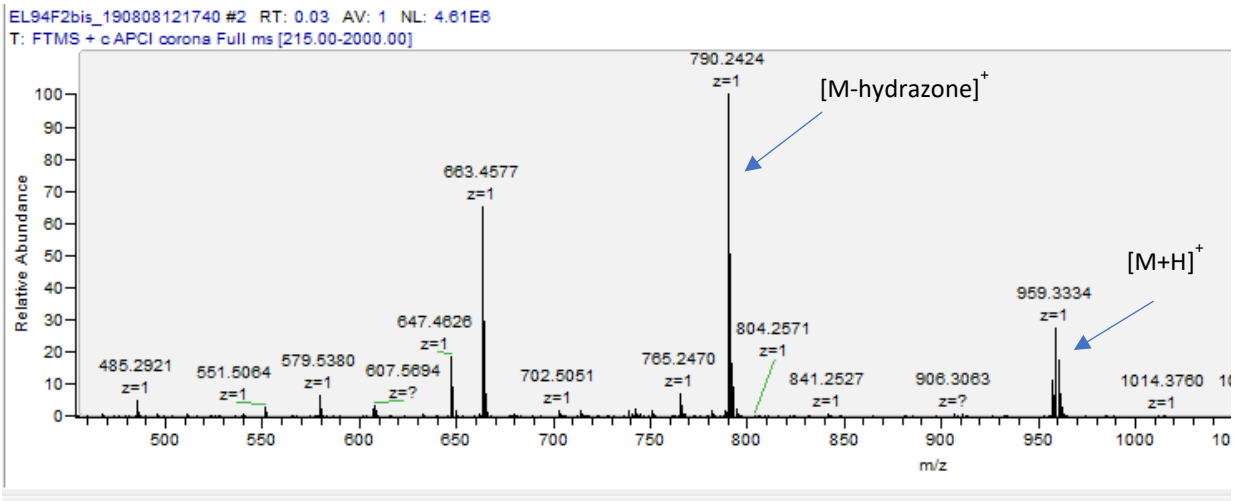




***Figure 10***- HRMS (APCI) spectrum of compound **III**

Redox properties were investigated by cyclic voltammetry using a conventional three electrode system. Energies of the frontier orbitals ($E_{HOMO}$ and $E_{LUMO}$) were calculated based on recorded voltammograms.

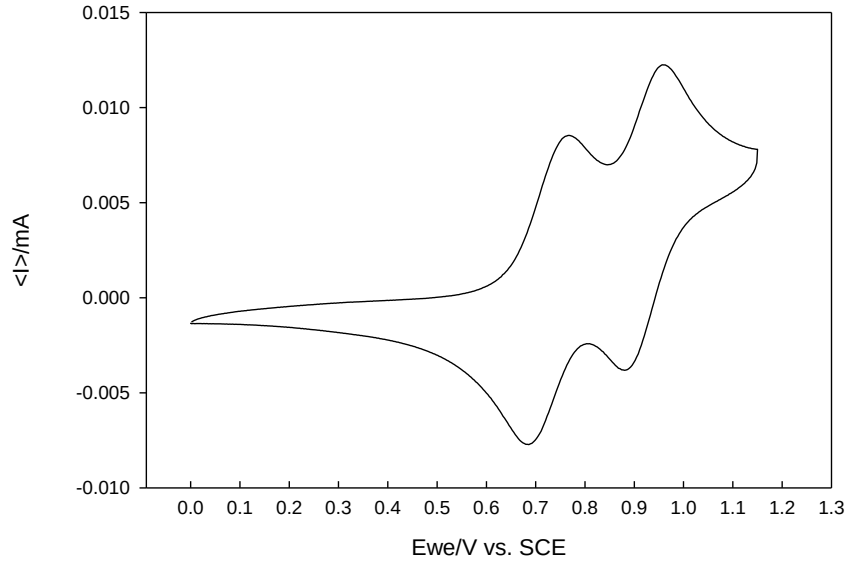



***Figure 11-*** Oxidation CV for **III** in 0.10 M $Bu_4NPF_6$/DCM, Pt electrodes, Ref. SCE, scan rate 100 mV $s^{-1}$.

Condensation side-product **33** and **34** presented in Figure 12, have also been isolated and characterized. Their optoelectronic properties are presented in Table 2

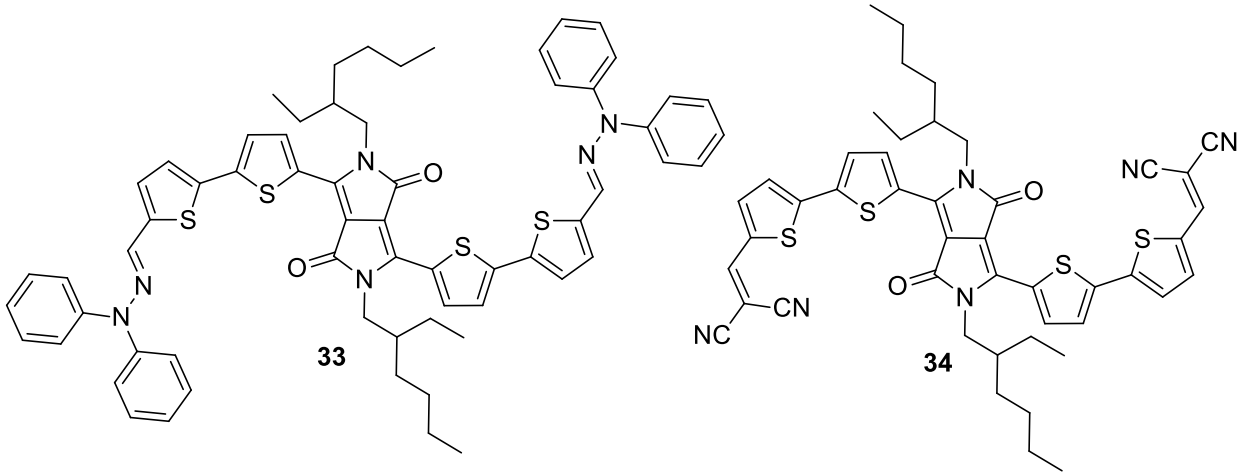



***Figure 12-*** Symmetric derivatives **33** and **34**

***Table 2***- UV-Vis absorption spectroscopy and cyclic voltammetry data

| Compound | $\lambda_{max}$ (solution) [nm] | $\lambda_{onset}$ [nm] | $E_g^{opt}$ [eV] | $\Delta E$ [eV] | $E_{pa}$ [V] | $E_{pc}$ [V] | $E_{HOMO}$ [eV] | $E_{LUMO}$ [eV] |
|---|---|---|---|---|---|---|---|---|
| **III** | 411, 652 | 766 | 1.61 | 1.90 | 0.76 | -0.93 | -5.61 | -3.71 |
| **33** | 401, 626 | 731 | 1.69 | 1.98 | 0.64 | -1.22 | -5.51 | -3.53 |
| **34** | 439, 643 | 755 | 1.64 | 1.92 | 0.98 | -0.85 | -5.84 | -3.91 |

# 3. Device assembling and testing

We carried out OPV measurements for the newly synthesized D-π-A structure **III** and compared results with those of the symmetric side-product **33** and **34.** To verify the suitability of these compounds for active layer in OSCs, we fabricated cells with three different cell structures: direct bilayer, direct BHJ (bulk-heterojunction) and inverted BHJ. More than that, because the compound **III** shows a single-like structure (Donor-π-Acceptor) from the OSC point of view (having a donor functional group on one side and an acceptor functional group on the other side) we tested out in direct single cell too. The cell structure for each of these are presented in Table 3.

***Table 2***- OSCs constructed with compounds **III, 33** and **34**

| **OSC type** | **Cell structure** | **Active Layer** |
|---|---|---|
| Direct Single | ITO/PEDOT:PSS/Active Layer/Al | Compound III |
| Direct Bilayer | ITO/PEDOT:PSS/Active Layer/Al | Compound III/C60 |
| Direct BHJ | ITO/PEDOT:PSS/Active Layer/Al | Compound (III): $PC_{61}BM$ |
| Inverted BHJ | ITO/ZnO/Active Layer/$MoO_3$/Al | Compound (**III/33/34**): $PC_{61}BM$ |

First, compound **III** was tested in Direct Single composition. Despite of the good deposition of the active layer, the results showed no useful electrical characteristics, which means that the compound cannot act as a single material in the OSCs.

Based on these results, compound **33** and **34** were tested without going through the Direct junctions that are very sensitive to environmental changes. The highest efficiency (PCE=1.17%) obtained was with **Inverted BHJ** in 1:3 weight ratio with $PC_{61}BM$.

In Table 3 are collected the best results obtained for the DPP-based OSCs.

**Table 3-** Electrical characteristics

| **Comp.** | **OSC type** | **Weight ratio** | **Active Material Thickness [nm]** | **Best OSC electrical characteristics** | | | | **Measurement Conditions** |
|---|---|---|---|---|---|---|---|---|
| | | | | **$V_{OC}$ [V]** | **$J_{SC}$ [mA/cm$^2$]** | **FF [%]** | **PCE [%]** | |
| **III** | **Direct Bilayer** | N/A | 50 | 0.65 | 0.95 | 48.22 | **0.30** | Ambient |
| **III** | **Direct BHJ** | 1:1 (**III:**$PC_{61}BM$) | 70 | 0.76 | 2.80 | 29.24 | 0.63 | Ambient |
| | | 1:2 (**III:**$PC_{61}BM$) | 70 | 0.79 | 4.16 | 32.67 | **1.08** | Ambient |
| | | 1:3 (**III:**$PC_{61}BM$) | 70 | 0.77 | 3.41 | 32.81 | 0.86 | Ambient |
| **III** | **Inverted BHJ** | 1:1 (**III:**$PC_{61}BM$) | 70 | 0.82 | 3.34 | 30.46 | 0.83 | 90°C |
| | | 1:2 (**III:**$PC_{61}BM$) | 70 | 0.55 | 5.06 | 37.58 | 1.05 | 90°C |
| | | 1:3 (**III:**$PC_{61}BM$) | 70 | 0.80 | 5.52 | 32.30 | **1.43** | 90°C |
| | | 1:4 (**III:**$PC_{61}BM$) | 70 | 0.80 | 4.56 | 31.67 | 1.15 | 90°C |
| **33** | **Inverted BHJ** | 1:3 (**33:**$PC_{61}BM$) | 80 | 0.72 | 4.89 | 33.50 | **1.17** | 90°C |
| **34** | **Inverted BHJ** | 1:1 (**34**:**III**) | 80 | 0.71 | 0.47 | 32.25 | **0.11** | 110 C |

# 4. Conclusions

This study targeted the synthesis of a new D-π-A type *1,4-diketopyrroIo[ 3,4-c]pyrrole* derivative for OPV purposes. The DPP core was obtained *via* classical succinate method. To ensure solvent processability, 2-ethylhexyl chains were grafted onto the central DPP unit. Another thiophene unit was introduced on each side of the DPP core *via* Suzuki coupling. The target compound was prepared by successive condensation with malononitrile followed by condensation with *N*,*N*-diphenyl hydrazine. The symmetric side products were also purified and characterized by NMR, MS, UV-Vis and CV measurement.

The target compound **III** was tested as active material in **Direct Single**, **Direct Bilayer**, **Direct BHJ** and **Inverted BHJ** organic solar cells. The symmetric **33** and **34** were tried in the latter one too. **Inverted BHJ** structure offered the best power conversion efficiency (1.43%) from all the structures analyzed, with more than 30% compared to the **Direct BHJ** structure (1.08%) and almost more than 5 times compared the Direct Bilayer structure (0.3%). In all the cases, 90ºC thermal annealing had the optimum improvement of the efficiency.

The synthesis of another D-π-A type DPP derivative with perylene-3,4:9,10-tetracarboxylic acid bisimide electron acceptor side group is underway. We presume that the strong electron deficiency of the perylene core could improve the target molecule's optoelectronic properties for single material cell application.

# PUBLICATIONS

1. Thiophene-based macrocycles via the SuzukieMiyaura cross coupling reaction
   Anca Petran, Anamaria Terec , Elena Bogdan, Albert Soran, Eszter Lakatos,Ion Grosu
   *Tetrahedron* **2014**, 70, 6803-6809
   doi:/10.1016/j.tet.2014.07.061
2. Mono- and di-substituted pyrene-based donor-p-acceptor systems with phenyl and thienyl p-conjugating bridges
   Monica Irina Nan, Eszter Lakatos, Gavril-Ionel Giurgi, Lorant Szolga, Riccardo Po, Anamaria Terec, Siriporn Jungsuttiwong, Ion Grosu, Jean Roncali *Dyes and Pigments*, 181:108527
   doi:10.1016/j.dyepig.2020.108527