



UNIVERSIDADE DE ÉVORA
ESCOLA DE CIÊNCIAS E TECNOLOGIA
DEPARTAMENTO DE QUÍMICA

Diketopyrrolopyrroles for dye-sensitized solar cells

Vítor Alexandre da Silva Almodôvar

Orientação: Professor Doutor Augusto C. Tomé

Mestrado em Química

Área de especialização: Química de Materiais

Dissertação

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"Everything happens on time. Everything happens, exactly when it should happen. "

Albert Einstein

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Resumo

Com foco nos últimos seis anos, o sistema bicíclico dicetopirrolopirrol tem sido cada vez mais utilizado como "bloco de construção" de materiais (polímeros e moléculas pequenas) para utilização em células solares. Isso deve-se principalmente à sua alta estabilidade ambiental (principalmente fotoestabilidade) e capacidades de transferência de carga. Apesar dos estudos serem ainda recentes, os resultados já alcançados mostraram o tremendo potencial dos dicetopirrolopirróis em células solares.

O trabalho descrito nesta tese de Mestrado envolveu a síntese de vários derivados de dicetopirrolopirrol com o objetivo de introduzir unidades fotossensibilizantes ligadas covalentemente ao sistema dicetopirrolopirrol. Os novos compostos podem vir a incorporar um grupo carboxílico para suportar o corante na superfície de um óxido semicondutor das células solares sensibilizadas por corantes (DSSCs).

A primeira parte do trabalho consistiu na alquilação ou arilação dos grupos NH de dicetopirrolopirróis comerciais. Posteriormente, foram estudados métodos de funcionalização dos grupos arilo nas posições 3 e 6 dos DPP por reações catalisadas por paládio ou por clorossulfonação. Todos os dicetopirrolopirróis sintetizados foram caracterizados por ressonância magnética nuclear, espectrometria de massa e espectrofotometria de UV-visível. Alguns compostos foram também caracterizados por fluorescência.

Palavras-chave: dicetopirrolopirrol, DPP, DSSC, reações catalisadas por paládio

Abstract

With a focus on the last six years, the bicyclic diketopyrrolopyrrole (DPP) system has been increasingly used as an active building block in materials (polymers and small molecules) used in solar cells. That is mainly due to its high environmental stability (mainly photostability) and charge transfer capabilities. Despite its infancy, the results already achieved have shown the tremendous potential of diketopyrrolopyrroles in solar cells.

The work reported in this Master thesis involved the synthesis of several diketopyrrolopyrrole derivatives aiming introducing photosensitizing units covalently linked to the diketopyrrolopyrrole system. The new compounds may be functionalized with carboxylic groups to support the dye firmly at the surface of a semiconductor oxide of dye-sensitized solar cells (DSSCs).

The first part of the work consisted in the alkylation or arylation of the NH groups of commercially available DPP. Then, new methods for the functionalization of the aryl groups at 3 and 6 positions of DPP were studied, mainly by palladium catalysed reactions or by chlorosulfonation. All diketopyrrolopyrrole derivatives synthesized were characterized by nuclear magnetic resonance, mass spectrometry and UV-vis spectrophotometry. Some compounds were also characterized by fluorescence.

Keywords: diketopyrrolopyrrole, DPP, DSSC, palladium-catalysed reactions

Table of Contents

List of abbreviations and symbols	iii
List of figures	vi
List of schemes	vii
List of tables	ix
1. Introduction	11
1.1. A brief history of Diketopyrrolopyrroles (DPP)	13
1.2. Synthesis	14
1.2.1. Reformatsky route	14
1.2.2. Succinic ester route	15
1.2.3. Succinic amide route of DPP	16
1.2.4. Other routes	16
1.3. Molecular structure and properties	17
1.3.1. Spectroscopic properties	17
1.3.2. Single crystal X-ray diffraction	18
1.4. Chemical properties of DPP derivatives	19
1.4.1. <i>N</i> -alkylation	20
1.4.2. <i>N</i> -arylation	21
1.4.3. Reactions at the aromatic substituents at the 3 and 6 positions of DPP	22
1.4.4. Modifications at the carbonyl groups	24
2. Applications of diketopyrrolopyrroles	25
2.1. Application of DPP derivatives in DSSC	25
2.1.1. Basic operating principle	27
2.2. DPP as fluorescent probes	28
2.3. DPP in photodynamic therapy	29
2.4. Others applications	30
3. Results and discussion	33
3.1. Synthesis and characterization of DPP derivatives	35
3.1.1. <i>N</i> -alkylation of DPP	35
3.1.2. <i>N</i> -Arylation of DPP	45
3.1.3. Reactions at the aromatic groups of DPP	47
3.1.4. Synthesis of DPP-sulfonamide	52
4. Photophysical properties	54
5. Conclusions and future prospects	59

6. Experimental section	63
6.1. Materials and methods	65
6.2 Synthesis and characterization	66
7. References	77

List of abbreviations and symbols

δ - chemical shift

ϵ - molar absorbance coefficient

η - yield

λ - wavelength

$\Delta\lambda$ - Stokes' shift

^{13}C **NMR** - carbon nuclear magnetic resonance

^1H **NMR** - proton nuclear magnetic resonance

A - absorbance

Ar - aryl group

BODIPY - boron-dipyrromethene

Cu(II)-TPP - 5,10,15,20-tetraphenylporphyrinatocopper(II)

d - doublet

dd - double doublet

D-A-D - donor–acceptor–donor

DCC - *N,N'*-dicyclohexylcarbodiimide

DCE - dichloroethane

DCM - dichloromethane

DDQ - 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

DMF - *N,N*-dimethylformamide

DMAP - 4-(dimethylamino)pyridine

DMSO - dimethyl sulfoxide

DPP - diketopyrrolopyrrole (2*H*,5*H*-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione)

DSSCs - dye-sensitized solar cells

EFG - electrophilic functional group

ESI - electrospray ionization

HOMO - highest occupied molecular orbital

IR - infrared

J - coupling constant

LUMO - lowest unoccupied molecular orbital

LR - Lawesson reagent

m - multiplet

M - metallic ion

(M+H)⁺ - protonated molecular ion

MS - mass spectrometry

mPEG - methoxypoly(ethylene glycol)

m/z - mass/charge ratio

NFG - nucleophilic functional group

NMR - nuclear magnetic resonance

OSC - organic semiconductor

OFET - organic field-effect transistor

PAI - photoacoustic imaging

Pc - phthalocyanine

PDT - photodynamic therapy

Ph - phenyl

PYRO - pyromellitimide

PS - photosensitizer

ROS - reactive oxygen species

r.t. - room temperature

s - singlet

t - triplet

TDPP - thienyl-substituted diketopyrrolopyrrole

TFA - trifluoroacetic acid

THF - tetrahydrofuran

TLC - thin layer chromatography

TMS - tetramethylsilane

TOF - time-of-flight

TPP - 5,10,15,20-tetraphenylporphyrin

UV-vis - ultraviolet-visible light

Xphos - 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl

List of figures

Figure 1. Absorption spectra of DPP **2** in solution (DMSO) and in solid state.

Figure 2. Absorption and emission spectra of DPP **2** in solution and in solid state.

Figure 3. Crystal structure of DPP **2**.

Figure 4. Schematic drawing of a DSSC showing the principle of operation.

Figure 5. ^1H -NMR spectrum of di-alkylated DPP **2a** in CDCl_3 .

Figure 6. ^1H -NMR spectrum of di-alkylated DPP **3a** in CDCl_3 .

Figure 7. ^1H -NMR spectrum of di-alkylated DPP **3b** in CDCl_3 .

Figure 8. ^1H -NMR spectrum of di-alkylated DPP **4b** in CDCl_3 .

Figure 9. ^1H -NMR spectrum of di-alkylated DPP **6** in CDCl_3 .

Figure 10. ^1H -NMR spectrum of di-Boc DPP **7** in CDCl_3 .

Figure 11. ^1H -NMR spectrum of compound **8** in CDCl_3 .

Figure 12. ^1H -NMR spectrum of compound **9** in CDCl_3 .

Figure 13. ^1H -NMR spectrum of compound **10** in CDCl_3 .

Figure 14. ^1H -NMR spectrum of compound **11** in CDCl_3 .

Figure 15. ^1H -NMR spectrum of compound **12** in CDCl_3 .

Figure 16. Jablonski diagram representing energy levels and spectra.

Figure 17. Absorption spectra of **4b** (green), **11** (yellow) and **12** (red) in DMF.

Figure 18. Compounds **4b**, **11** and **12** in solid state and in solution (DMF) under natural light and UV light.

Figure 19. Absorption (solid lines) and emission spectra (dashed lines) of compounds **4b** (green), **11** (yellow) and **12** (red).

List of schemes

Scheme 1. First synthesis of DPP.

Scheme 2. Postulated mechanism of DPP formation under Reformatsky conditions.

Scheme 3. Reformulated mechanism of DPP formation via Reformatsky reaction.

Scheme 4. Succinic ester route to DPP.

Scheme 5. Mechanism of DPP formation via the succinic ester route.

Scheme 6. Succinic amide route to DPP.

Scheme 7. Formation of tetraphenyl DPP.

Scheme 8. Potentially reactive centres in a diaryl-DPP derivative.

Scheme 9. Mesomeric structures of deprotonated DPP.

Scheme 10. *N*-alkylation of DPP.

Scheme 11. *N*-arylation with 1-fluoro-2,4-dinitrobenzene.

Scheme 12. *N*-arylation with 1-fluoro-2-nitro-4-(trifluoromethyl)benzene.

Scheme 13. Different methods to obtain *N*-aryl-DPP.

Scheme 14. Sulfonation, bromination, and chlorination of DPP **2**.

Scheme 15. Coupling reactions with brominated DPP.

Scheme 16. Synthesis of DPP derivatives via direct arylation.

Scheme 17. Various transformations of carbonyl groups of DPP.

Scheme 18. New DPP derivative (DPP-PYRO).

Scheme 19. Irreversible sensor for fluoride.

Scheme 20. TPA-DPP.

Scheme 21. (ZnPc)₂-DPP.

Scheme 22. Starting materials.

Scheme 23. *N*-alkylation of DPP with 1-iodopentane.

Scheme 24. *N*-alkylation of DPP with 2-ethylhexylbromide.

Scheme 25. NH substitution of DPP with propargyl bromide.

Scheme 26. Synthesis of DPP with *N*-*t*-butyloxycarbonyl protecting groups.

Scheme 27. Synthesis of ClCH₂-TPP.

Scheme 28. Synthesis of a diketopyrrolopyrrole covalently linked to a porphyrin.

Scheme 29. Mono-arylation of DPP **3b**.

Scheme 30. *N*-arylation of DPP.

Scheme 31. Attempted palladium-catalysed borylation of **2b** with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

Scheme 32. Palladium-catalysed borylation of **4b**.

Scheme 33. Functionalization of boronate **10**.

Scheme 34. Synthesis of a DPP-sulfonamide.

List of tables

Table 1. Arylation of DPP.

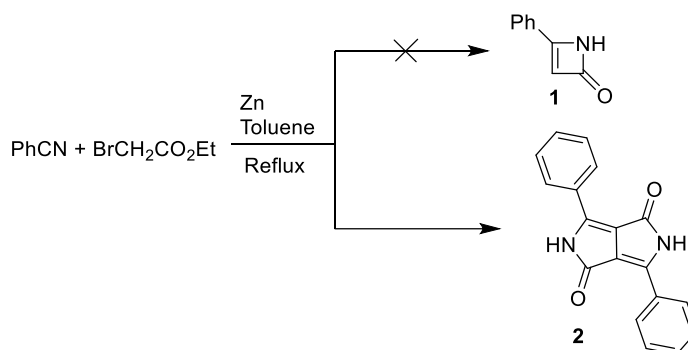
Table 2. Optical properties of DPP derivatives.

1. Introduction

Introduction

1.1. A brief history of Diketopyrrolopyrroles (DPP)

Diketopyrrolopyrroles* are one of the most recently discovered groups of organic pigments. Discovered in the early 1970's, their first synthesis was reported by Donald Farnum and co-workers, with the structure having a phenyl group attached to each of the lactam rings (compound **2**).¹⁻³



Scheme 1. First synthesis of DPP.¹

3,6-Diphenyldihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**2**) (Scheme 1) was synthesized for the first time in an attempted Reformatsky reaction of benzonitrile, ethyl bromoacetate, and zinc to obtain the 2-azetinone (**1**). Instead, a red pigment **2** was obtained in 5-20% yield (Scheme 1). The authors noted the unusual properties of compound **2**, such as a bright red colour and very low solubility and perceived it could be considered an organic pigment.³

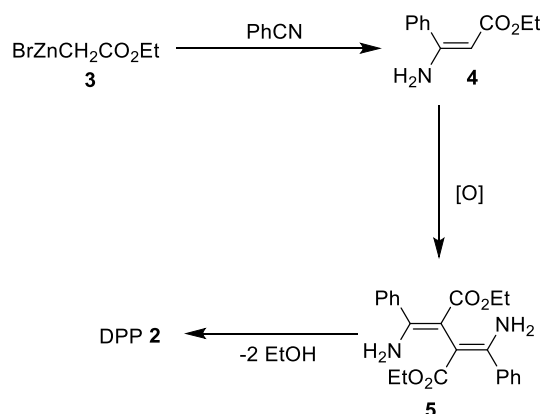
The physical properties of the DPP such as melting point (≥ 350 °C), high insolubility and red colour remained unremarked until researchers from Ciba-Geigy (now Ciba Specialty Chemicals) took notice of this reaction in a compilation of interesting reactions published by Ranganathan in 1980.⁴ The chemistry and the applicatory properties were developed, and six years later the first DPP pigment was introduced in the market. Since then, several other DPP pigments have been developed and introduced in the market for conventional pigment applications like paints, plastics, fibres and inks. In recent years, interest in the DPP chromophore for non-conventional applications has grown increasingly, and large numbers of patent applications in different areas have been filed.^{4,5}

*According to the IUPAC nomenclature rules, diketopyrrolopyrroles are, in fact, dioxopyrrolopyrroles.

1.2. Synthesis

1.2.1. Reformatsky route

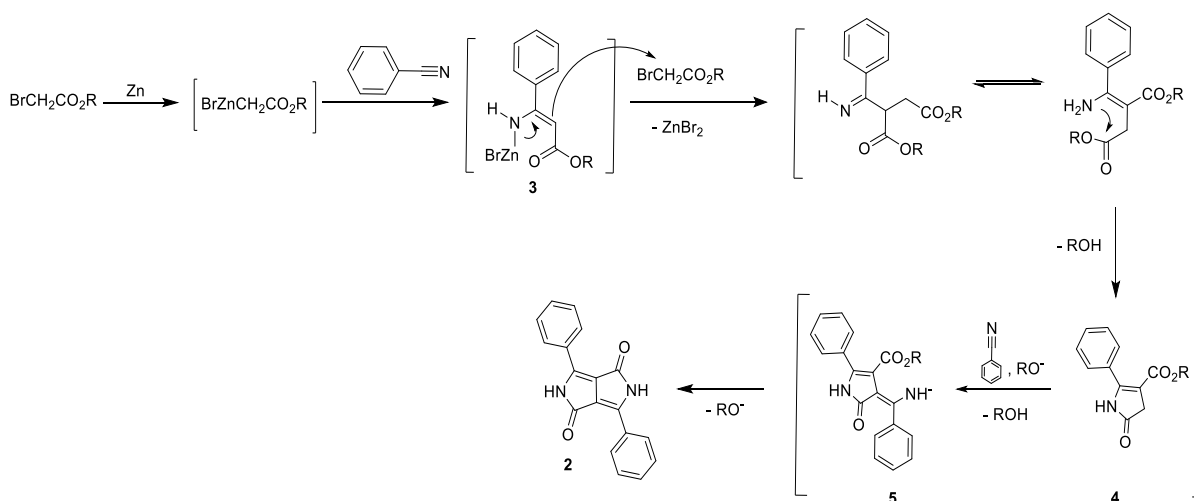
To explain the formation of product **2**, Farnum *et al.* proposed a reaction mechanism (Scheme 2) that involved the addition of an organozinc compound (**3**) to benzonitrile, which led to ethyl 2-aminocinnamate (**4**). Subsequently, **4** undergo an oxidative dimerization to compound **5**, which, after the loss of two ethanol molecules, gives the final pigment **2**.^{1,3}



Scheme 2. Postulated mechanism of DPP formation under Reformatsky conditions.³

In 1988, new investigations on the Reformatsky route were published. Synthesis of crucial intermediates and cross over experiments using two different benzonitrile strongly indicated that the reaction did not proceed via an oxidative dimerization mechanism.³

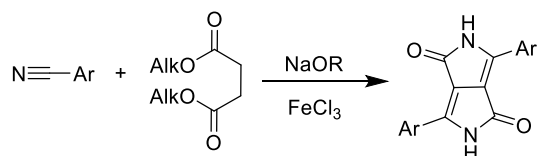
The first step is considered to involve the condensation of the Reformatsky reagent with benzonitrile to yield the Zn-salt **6**. C-alkylation of **6** by bromoacetate, followed by ring closure, is believed to lead to the hitherto elusive key intermediate **7**, a pyrrolinone ester. Condensation with a second molecule of benzonitrile and subsequent cyclization of intermediate **8**, which could be isolated and also mentioned by Farnum, finally affords the DPP **2** (Scheme 3).³



Scheme 3. Reformulated mechanism of DPP formation via Reformatsky reaction.³

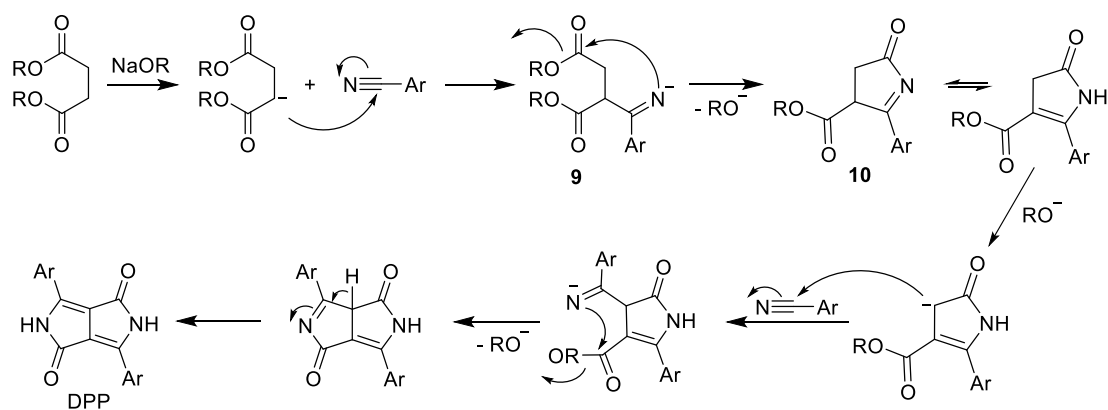
1.2.2. Succinic ester route

A new route to DPP pigments was published in 1983.^{3,5} This route involved the condensation of aromatic nitriles with succinate esters under basic conditions (succinic method) (Scheme 4).⁵



Scheme 4. Succinic ester route to DPP (the mechanism for this reaction is depicted in Scheme 5).⁶

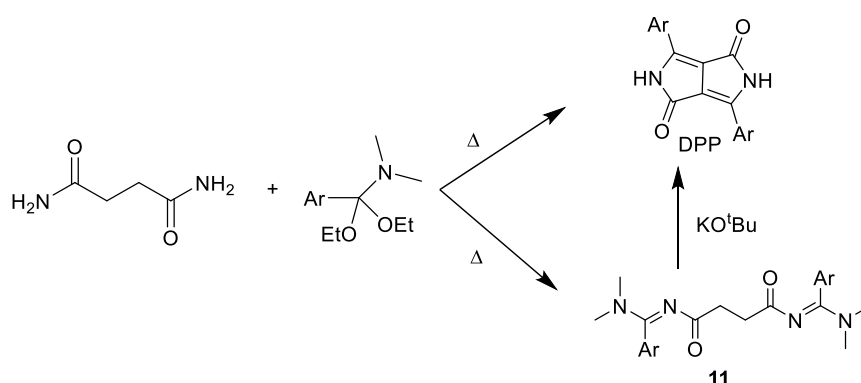
The initially formed enamine ester **9** undergoes self-condensation to give pyrrolinone ester **10**, which further undergoes condensation with another molecule of aromatic nitrile and subsequent cyclization to give the desired DPP core (Scheme 5).⁶



Scheme 5. Mechanism of DPP formation via the succinic ester route.⁶

1.2.3. Succinic amide route of DPP

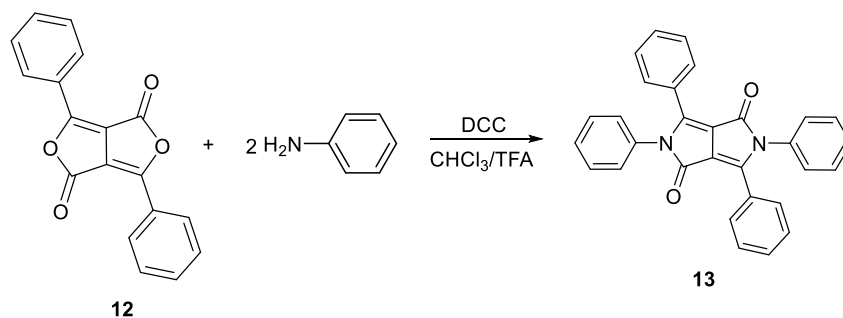
Another synthesis of DPP, that has been reported by Gompper and co-workers, involves the reaction of succinamide with *N,N*-dimethylbenzamide diethyl acetal, giving rise to two products, the DPP and compound **11** which can condense to obtain DPP **2** (Scheme 9).⁷



Scheme 6. Succinic amide route to DPP.⁷

1.2.4. Other routes

During investigations to synthesize *N,N'*-diphenyl-DPP, Langhals and co-workers were able to condense the diketofurofuran **12** with anilines in the presence of dicyclohexylcarbo-diimide (DCC) and isolate the tetraphenyl-DPP **13** in 46% yield (Scheme 7).⁸ This procedure was applied in the synthesis of tetraaryl-DPP suitable for the preparation of cross-linked polymers based on DPP.⁹



Scheme 7. Formation of tetraphenyl DPP.

1.3. Molecular structure and properties

1.3.1. Spectroscopic properties

The diketopyrrolopyrrole **2** is a bicyclic 8π electron system containing two lactam units. The characteristic physical properties of DPP are the high melting point (≥ 350 °C), low solubility (≤ 110 mg/L in dimethylformamide (DMF) at 25 °C) and an absorption in the visible region (400–600 nm) with a molar extinction coefficient of 33 000 ($\text{dm}^2 \text{mol}^{-1}$). In solution, DPP **2** gives a yellow fluorescing solution, whereas in solid state it is a vivid red. Figure 1 shows the absorption spectra of **2** in solution (DMSO) and in solid state.^{5,10–12}

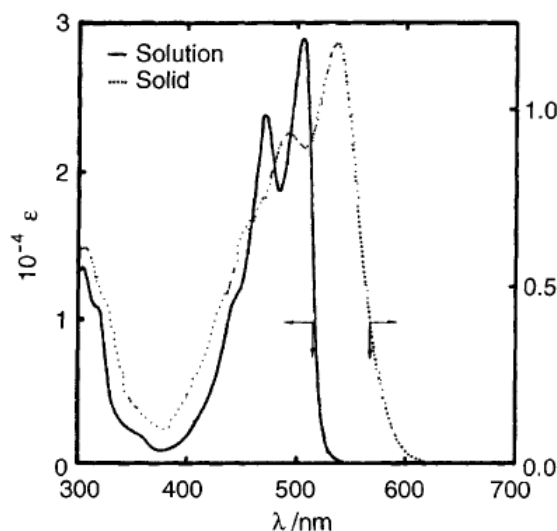


Figure 1. Absorption spectra of DPP **2** in solution (DMSO) and in solid state.¹⁰

Like many other pigment classes, DPP pigments are fluorescent in solution. The Stokes shifts are in the range 10–70 nm and the fluorescence quantum yields *ca.* 60%. In the solid state, some DPP show a minor fluorescence. Through *N*-substitution, both the solubility and the Stokes shift can be increased (Figure 2).^{8,13}

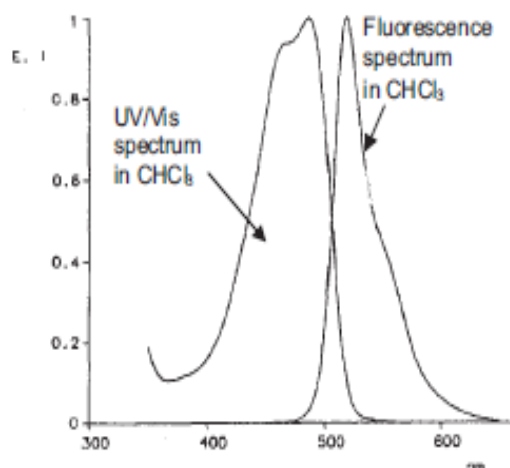


Figure 2. Absorption and emission spectra of DPP **2** in solution and in solid state.⁸

1.3.2. Single crystal X-ray diffraction

The intra- and intermolecular arrangements of DPP molecules in a DPP crystal have been investigated by single crystal X-ray diffraction. Mizuguchi and co-workers obtained single crystals of DPP **2** suitable for X-ray analysis.¹⁴ Figure 3 presents the structure of DPP **2** with selected bond lengths and interatomic distances. The bicyclic dilactam system of DPP is practically flat (the deviation of atoms from the calculated plane is ≤ 0.01 Å). The dihedral angle between the planes of benzene rings and the central DPP unit is just 7° , despite the steric hindrance between the *ortho* hydrogen atoms at phenyl substituents (H2, H6), and the carbonyl oxygen atom (O) on one side and the amide hydrogen atom (H1) on the other side (Figure 3). The distances H1–H2 (2.19 Å) and H6–O (2.32 Å) are in fact noticeably shorter than the corresponding sums of the van der Waals radii of the individual atoms (2.4 and 2.6 Å, respectively). This indicates a relatively strong π -conjugation between the phenyl groups and the DPP core. This is also supported by the fact that the C3–C4 bond length, which connects the benzene ring with the central DPP unit, is only 1.46 Å (Figure 3). The value is much shorter than that for standard single bonds between the sp^2 carbon atoms (~ 1.50 – 1.54 Å), suggesting that the C3–C4 bond has partly a double bond nature. This also applies for the C2–C2' bond located in the centre of the molecule (1.42 Å, Figure 3).^{2,14,15}

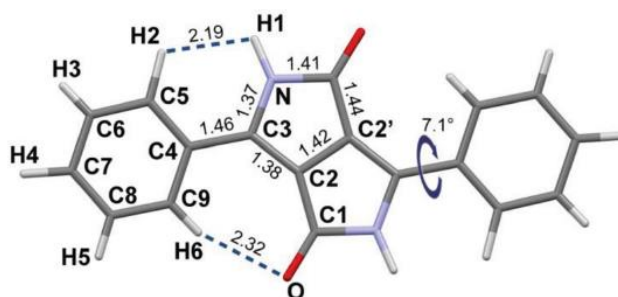
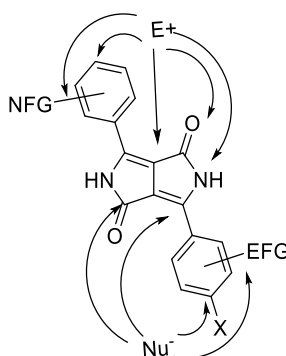


Figure 3. Crystal structure of DPP 2.^{2,14}

1.4. Chemical properties of DPP derivatives

Diaryl DPP molecules reveal several centres of reactivity (Scheme 8). Two main considerations motivated the investigation of this type of compound. The most important one is the easy access to specific DPP by the succinic ester route suggesting the attractive possibility of exploiting their chemical reactivity towards transformations into derivatives of improved performance or of novel application properties. The second consideration is the desirable acquirement of a basic knowledge of the chemistry of the hitherto sparsely studied chromophore.^{2,3}



X = e.g. halogen

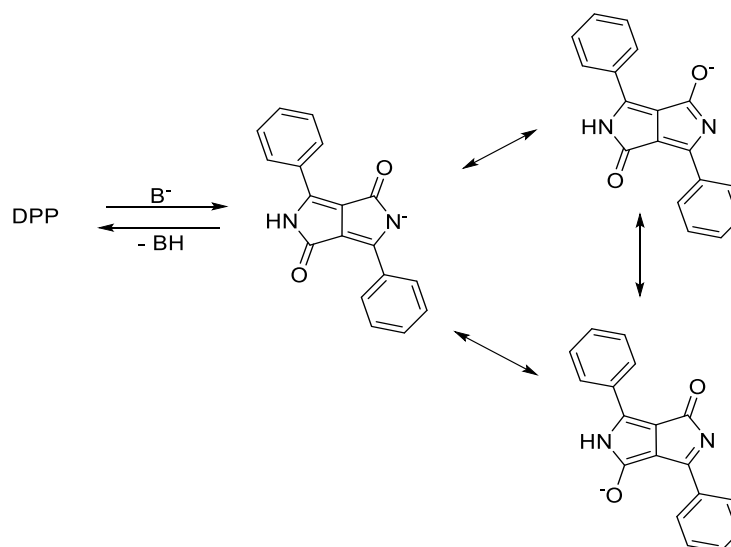
NFG = nucleophilic functional groups, e.g. -OH, -SH, -NR¹R²

EFG = electrophilic functional groups, e.g. -CN, -COX

Scheme 8. Potentially reactive centres in a diaryl-DPP derivative.³

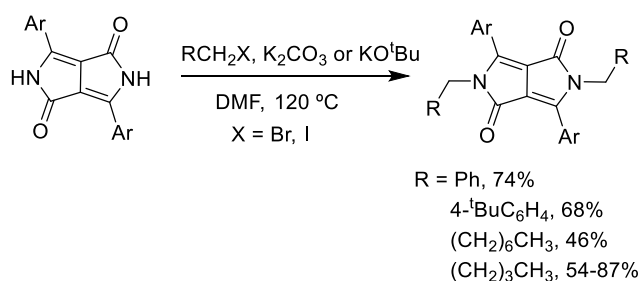
1.4.1. *N*-alkylation

Under basic conditions, DPP can be deprotonated to give ambidentate anions, being the negative charge distributed between the oxygen and nitrogen atoms of the amide group (Scheme 9).^{2,16}



Scheme 9. Mesomeric structures of deprotonated DPP.²

According to the literature, the alkylation of DPP is usually performed in DMF at temperatures above 100 °C, using potassium carbonate as a base and a large excess of alkylating agent (Scheme 10). For this reaction it is necessary to use solvents that are capable of dissolving DPP. Polar, aprotic solvents are particularly good for that purpose and, among them, DMF is the most widely used. Due to the effective stabilization of anions, it can be expected that DPP would readily undergo an alkylation reaction in basic medium conditions. After the *N*-alkylation, the biggest change for DPP is the loss of intermolecular hydrogen bonding.^{1,17-19}

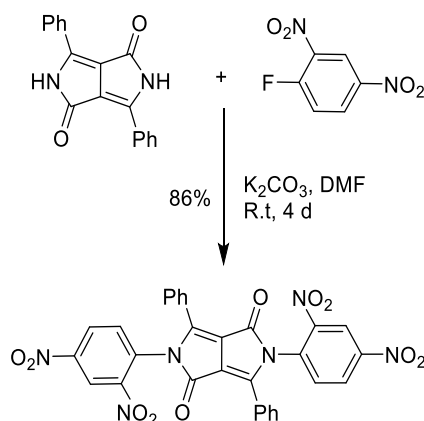


Scheme 10. *N*-alkylation of DPP.

Recent papers show that the dialkylation of DPP can take place not only at the nitrogen but also at the oxygen atoms of DPP. The alkylation on these two types of atoms leads to three dialkyl DPP isomers, including the *O,O*-dialkyl DPP isomer.^{16,20}

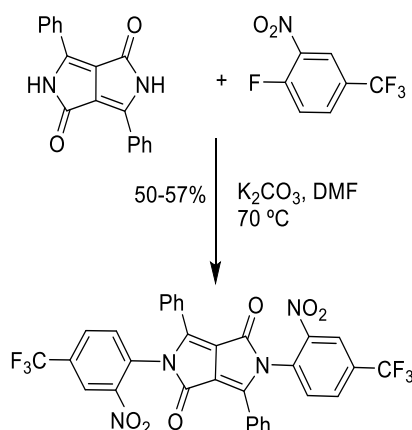
1.4.2. *N*-arylation

Reported examples of *N*-arylation of DPP are very scarce. The reaction of DPP with 1-fluoro-2,4-dinitrobenzene in DMF, in presence of potassium carbonate, is a well-known example, and the *N,N'*-diaryl DPP is obtained in very good yield under mild conditions (Scheme 11).^{21,22}



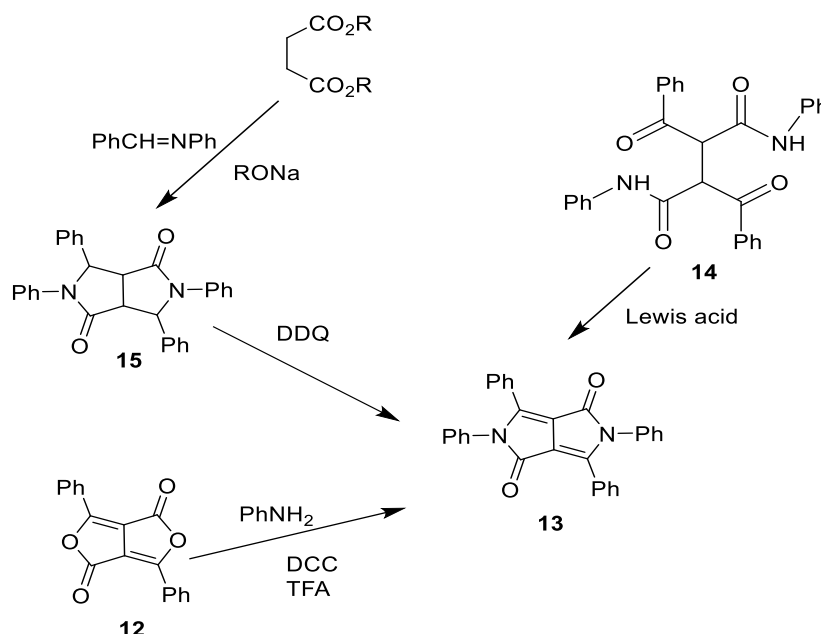
Scheme 11. *N*-arylation with 1-fluoro-2,4-dinitrobenzene.²¹

Recently, Wurthner and co-workers showed that the nucleophilic aromatic substitution (S_NAr) reaction of DPP can also be performed using 1-fluoro-2-nitro-4-(trifluoromethyl)benzene as the arylating agent (Scheme 12).²³



Scheme 12. *N*-arylation with 1-fluoro-2-nitro-4-(trifluoromethyl)benzene.²³

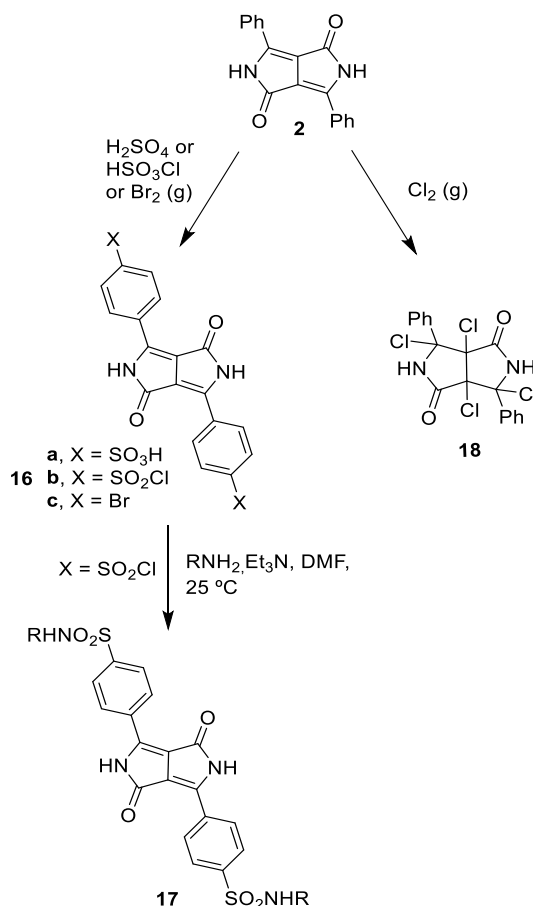
However, *N,N'*-diaryl-DPP may be obtained in certain cases from the corresponding furo[3,4-*c*]furans **12** by reaction with aniline derivatives (Scheme 13), by cyclisation of bis-anilides **14** or by oxidation of the tetrahydro-DPP precursor **15** with 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ) (Scheme 13).^{21,24}



Scheme 13. Different methods to obtain *N,N'*-diaryl-DPP.

1.4.3. Reactions at the aromatic substituents at the 3 and 6 positions of DPP

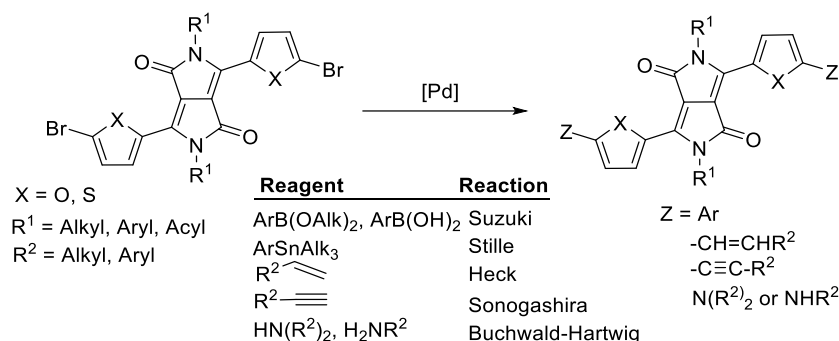
The majority of DPP found in the literature possess aromatic substituents at the 3 and 6 positions. The aryl substituents may participate in various types of reactions, namely in electrophilic aromatic substitutions. For example, diphenyl DPP **2** can be sulfonated with fuming sulfuric acid, which leads to DPP containing sulfonic groups at the *para* position of the benzene rings (**16a**). Recently it was also reported the synthesis of DPP containing chlorosulfonyl groups (**16b**) and their conversion into sulfonamides (**17**).²⁵ DPP **2** also reacts with gaseous bromine and chlorine. However, the two reactions take a completely different course (Scheme 14). In the case of **16c**, it can be obtained simply from *p*-bromobenzonitrile using the succinic method.^{1,3}



Scheme 14. Sulfonation, chlorosulfonation and subsequent formation of sulfonamides, bromination and chlorination of DPP **2**.^{1,25}

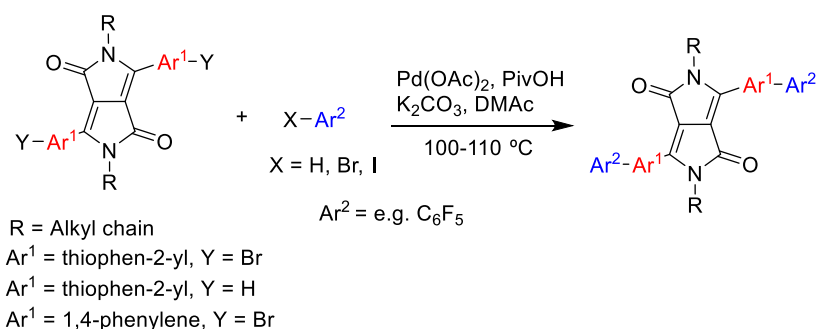
The bromination is much more useful in DPP which possess simple heteroaromatic substituents such as thiophene, furan or selenophene at the 3 and 6 positions (Scheme 15). Due to the relatively high electron density of these heterocycles, the compounds readily react with NBS to give the corresponding dibromo derivatives in good yields.²⁶⁻²⁸

Bromoaryl-DPP can serve as starting materials in Pd-catalyzed cross-coupling reactions that include the Suzuki reaction with organo-boron compounds²⁸⁻³⁰, the Stille reaction with organotin derivatives³¹⁻³⁴, Heck coupling with alkenes³⁵⁻³⁷, the Sogonashira reaction with alkynes³⁸⁻⁴⁰ and Buchwald-Hartwing amination with primary and secondary amines^{41,42} (Scheme 15). All these reactions lead to the expansion of the DPP chromophore, because the DPP core and the newly introduced substituents are π -conjugated.²⁹⁻⁴²



Scheme 15. Coupling reactions with brominated DPP.

In addition to the above-mentioned reactions, the direct C–H activation of aryl groups at 3 and 6 positions of DPP has been reported. These reactions possess numerous advantages over traditional cross-coupling reactions such as: avoidance of the use of organometallic reagents in the starting materials leading to simpler byproducts and higher atom economy, fewer synthetic steps, higher global yields, better compatibility with chemically sensitive functional groups and simpler catalytic systems free of phosphine ligands. With these advantages, DPP-containing thiophene derivatives should be ideal candidates for the exploration of direct arylation reactions (Scheme 16).⁴³⁻⁴⁸



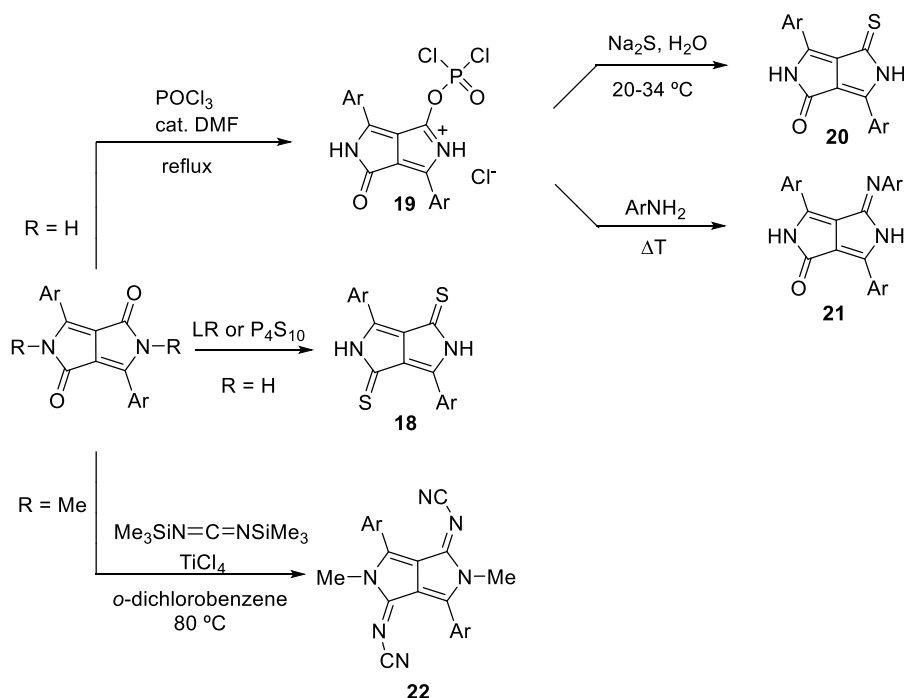
Scheme 16. Synthesis of DPP derivatives via direct arylation.

1.4.4. Modifications at the carbonyl groups

Carbonyl groups of DPP are important electrophilic centres, and can be subjected to numerous transformations (Scheme 17). DPP react with thiation reagents, such as phosphorous pentasulfide (P_4S_{10}) and Lawesson's reagent (LR) to give blue-green dithioketopyrrolopyrroles, where DPP is converted to a dithiolactam **18**.⁴⁹ Another transformation is the activation of the carbonyl groups using phosphoryl chloride. Heating DPP with an excess of POCl_3 and a catalytic amount of DMF leads to the formation of a phosphorylated salt (**19**) in good yield. This salt, which is significantly more reactive toward nucleophiles than the starting DPP, undergoes a

reaction with an aqueous solution of sodium sulfide to give monothiocarbonyl DPP derivatives (**20**). At elevated temperatures, this salt also reacts with aromatic amines. In this case there is substitution of the dichlorophosphate group by the amine nitrogen atom, leading to dye **21** that contain an amidine unit (Scheme 17).^{2,3}

Oxygen atoms of DPP can be replaced through the reaction with bis(trimethylsilyl)carbodiimide. Using this reagent, methylated DPP can be converted into bis(cyanoimine) derivatives **22** with a relatively good yield.^{2,50}



Scheme 17. Various transformations of carbonyl groups of DPP.

2. Applications of diketopyrrolopyrroles

Diketopyrrolopyrroles and their derivatives represent a class of brilliant red and strongly fluorescent high performance pigments that have exceptional light, weather, and heat stability. So, the DPP core is at the heart of many chemical structures for application in materials technology, from car-paint pigments to small molecule and polymeric organic photovoltaics.⁵¹⁻⁵³ Recently it was reported the potential application of DPP in photodynamic therapy.⁵³⁻⁵⁵

2.1. Application of DPP derivatives in DSSC

Dye-sensitized solar cells (DSSC) have received considerable attention as promising candidates for renewable energy systems in recent years, due to their high conversion efficiency and low cost of production.⁵⁶

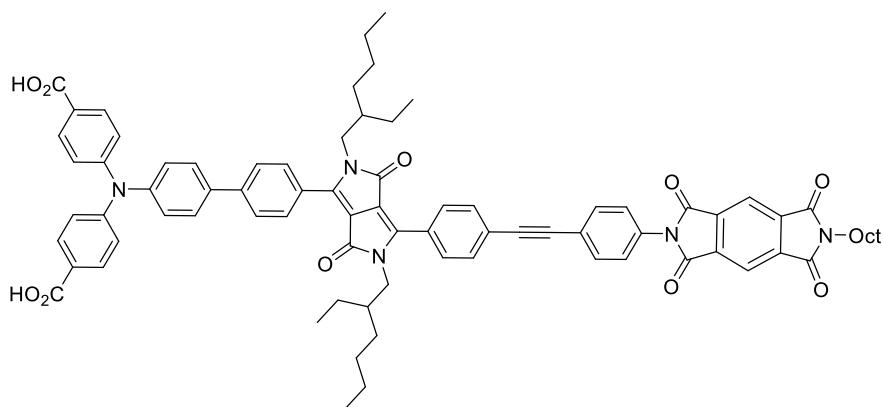
The dye-sensitized solar cells are a technically and economically credible alternative concept to present p–n junction photovoltaic devices. These systems, in contrast to the conventional systems, separate the functions of light absorption and charge carrier transport. Light is absorbed by a sensitizer, which is anchored to the surface of a wide band semiconductor. Charge separation takes place at the interface via photo-induced electron injection from the dye into the conduction band of the solid. Carriers are transported in the conduction band of the semiconductor to the charge collector. The conjugation of sensitizers with a broad absorption band with oxide films of nanocrystalline morphology permits to harvest a large fraction of sunlight.⁵⁷

Current sensitizers are mainly focused on metal complexes (ruthenium and zinc porphyrin or phthalocyanine) but their limited sources and the high cost of the efficient ruthenium-based sensitizers drove research attention towards metal free organic sensitizer.⁵⁷

It is possible to list a number of desirable properties for a photosensitizer: strong light absorption in visible and near-IR region (for efficient light harvesting); good solubility in organic solvents (for easy deposition from stock solutions in few hours or less); presence of suitable peripheral anchoring ligands such as –COOH (to promote the effective interaction of the dye with the oxide surface and thus the coupling of donor and acceptor levels); suitable disposition of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the dye molecule (to permit quantitative injection of charges from the electronically excited state); good thermal stability and good chemical stability (to retain the chemical identity over repetitive oxido-reduction cycles).⁵⁷

DPP pigments, with a conjugated bicyclic planar structure and the electron-withdrawing characteristics, are widely used as π -conjugated units in D- π -A organic dyes due to their excellent photochemical, mechanical and thermal stability as well as high carrier mobility.⁵⁸⁻⁶²

The photovoltaic performance of DPP-based sensitizers has been greatly improved since these dyes were first reported by Tian *et al.* in 2010.⁶³ Scheme 18 shows a new DPP derivative (DPP-PYRO) recently synthesized more specifically for solid-state p-type DSSC.⁶⁰



Scheme 18. A new DPP derivative (DPP-PYRO).⁶⁰

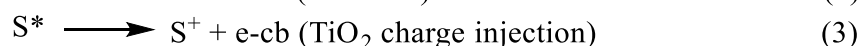
2.1.1. Basic operating principle

DSSC use the same basic principles of photosynthesis to generate electricity from sunlight. Each plant leaf is a photochemical cell that converts solar energy into organic matter. Although only 0.02–0.05% of the incident solar energy is converted by the photosynthesis process, the food being produced is 100 times more than what is needed for mankind.⁶⁴

Exposure of this solar cell assembly to visible light leads to a sequence of reactions. Figure 4 shows schematically these processes. Firstly it is considered the reactions that take place at the anode, where the absorption of the light by the dye S leads to formation of its electronically excited state S^* (eq. 1):⁵⁷



The molecule in the excited state can decay back to the ground state (eq. 2) or undergo oxidative quenching, injecting electrons into the conduction band of TiO_2 (eq. 3).



The injected electrons travel through the mesoporous network of particles to reach the back-collector electrode to pass through the external circuit. The oxidized dye is reduced rapidly to the ground state by the donor (iodide) present in the electrolyte (eq. 4):



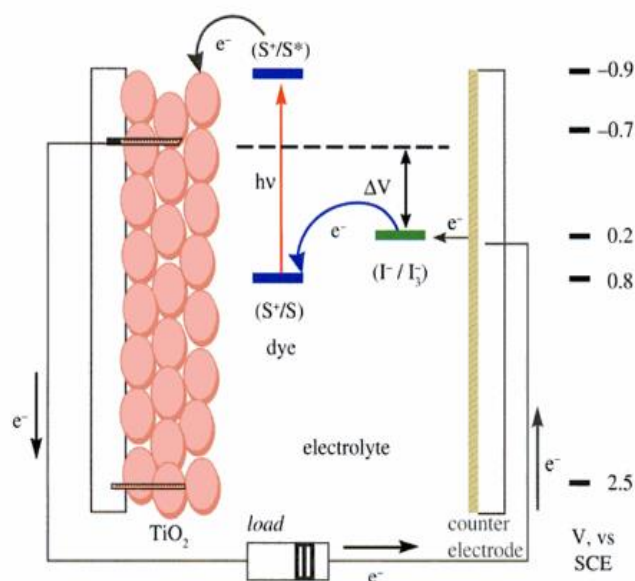
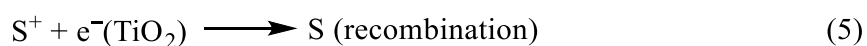
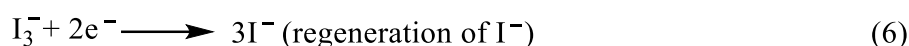


Figure 4. Schematic drawing of a DSSC showing the principle of operation.⁵⁷

In the absence of a redox mediator to intercept and rapidly reduce the oxidized dye (S^+) (eq. 5), recombination with the electrons of the titania layer takes place, without any measurable photocurrent:



The electrons reaching the counter-electrode through the external circuit reduce in turn the I_3^- so that the entire sequence of electron transfer reactions involving the dye and the redox mediator is rendered cyclic:

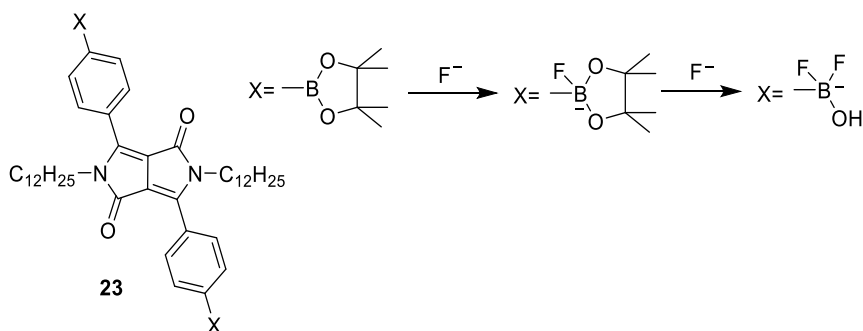


If cited reactions alone take place, the overall effect of irradiation with sunlight is to drive the electrons through the external circuit, i.e., direct conversion of sunlight to electricity.⁵⁷

2.2. DPP as fluorescent probes

In 2010, Tian and co-workers found that mono-*N*-alkyl DPP derivatives can serve as selective sensors sensitive to fluoride ions. In the presence of fluoride anions, the hydrogen abstraction occurs from the *N*-unsubstituted amide group of DPP, which causes significant changes in the optical properties. The solution colour changes from orange to red, whereas the fluorescence changes from yellow to red.⁶⁵ Unfortunately, the authors did not examine the behaviour of compounds in the presence of other ions, e.g., hydroxide or cyanide. But, according to the results from a basic titration of DPP

solution described by Mizuguchi¹⁰ it can be expected that the influence of hydroxide ions on the optical properties of dyes should be similar to the results obtained with fluorides. In the last years, the study of DPP-based polymers as fluoride probes has been developed and new compounds have emerged and studied such as compound **23**.⁶⁵⁻⁶⁸



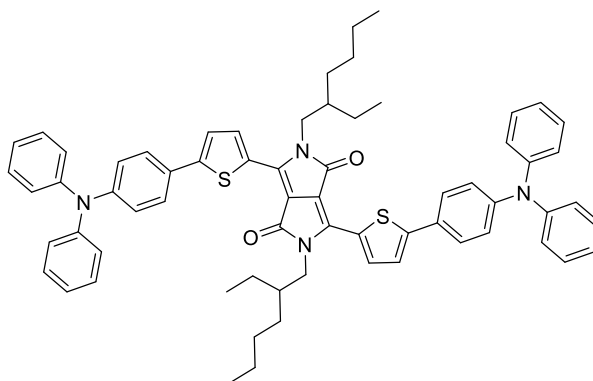
Scheme 19. Irreversible sensor for fluoride.⁶⁶

2.3. DPP in photodynamic therapy

Photodynamic therapy (PDT) is a new emerging method of cancer treatment that is attracting more and more attention as it is non-invasive, causes fewer side effects than other therapeutic modalities, is associated with negligible drug resistance and exhibits low systemic toxicity. Typically, a photosensitizer (PS) is excited by light irradiation and an electron in the ground state jumps into a high energy orbital. It further decays into a lower triplet state, sensitizing triplet oxygen to singlet oxygen and other reactive oxygen species (ROS) that kill tumor cells.⁵³⁻⁵⁵

Recently, DPP-based dyes have received attention for biological applications. Shi *et al.*, demonstrated that thienyl-substituted diketopyrrolopyrroles (TDPP) have lower ΔE_{ST} values, which can significantly enhance reactive ROS generation. They demonstrated that TDPP conjugated with methoxy poly(ethylene glycol) (mPEG) has excellent water solubility, biocompatibility, photostability, and significantly inhibited tumor growth upon irradiation with light both *in vitro* and *in vivo*, which show the great potential of its application in clinical cancer therapy.⁵⁴

Scheme 20 shows a donor–acceptor–donor (D–A–D) structured small molecule (TPA-DPP) recently designed and synthesized for photoacoustic imaging (PAI) guided photodynamic/photothermal synergistic therapy.⁵⁵

Scheme 20. TPA-DPP.⁵⁵

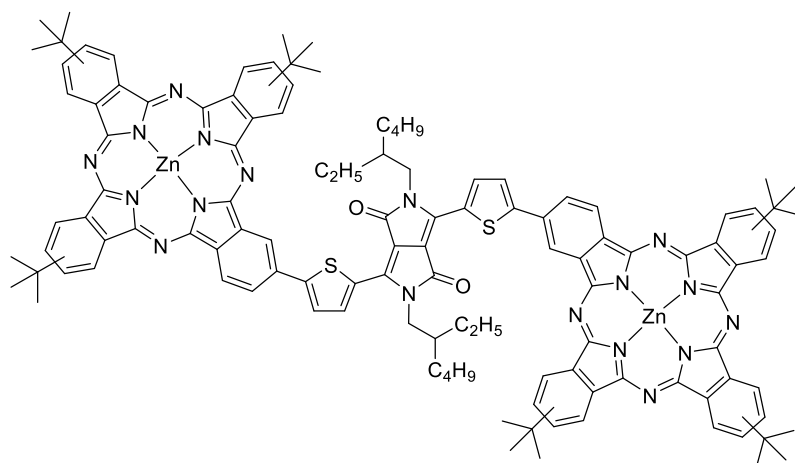
2.4. Others applications

Due to their intense emission and very high photostability, *N*-alkyl DPP derivatives can be applied as lasing media in dye lasers. For preparation of solid state dye lasers, several *N,N'*-dimethyl-DPP with various aryl substituents have been synthesized.^{2,69,70}

N-alkylated DPP can also be used as a basis of new red emitting polymers. Studies confirm that their deep red colour, intense red fluorescence with unusually large Stokes shift of more than a hundred nanometer and irreversible oxidation and reduction behaviour render the polymers attractive for electronic applications.⁷¹

The high planarity of DPP, its electron deficient nature and ability to form hydrogen bonds result in semiconducting materials with strong π - π stacking interactions and large intramolecular charge transfer. These characteristics of DPP units present in organic semiconductors (OSCs) have been attracting much interest for their promising features in organic field-effect transistors (OFETs).⁷²⁻⁷⁴

Derivatives of DPP are also often used in the design of molecular donor–acceptor systems, e.g. as donor components in fullerene-based molecular dyads or triads and as bridging units for the covalent connection of boron-dipyrromethene (BODIPY) derivatives or phthalocyanines (Scheme 21).⁷⁵⁻⁸²

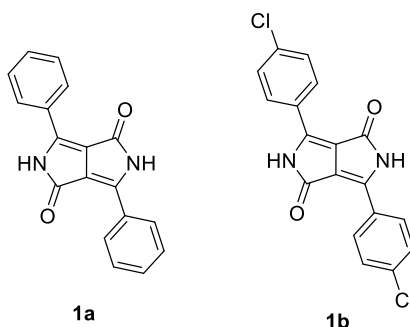


Scheme 21. (ZnPc)₂-DPP.⁸²

3. Results and discussion

Results and discussion

Diphenyl-DPP (**1a**) and bis(*p*-chlorophenyl)-DPP (**1b**), which are commercially available compounds, were used as the starting materials for the preparation of new DPP derivatives. Compound **1b** was selected to proceed with palladium-catalysed reactions on the chlorophenyl groups and compound **1a** was used to carry out the chlorosulfonation of the phenyl groups. Both compounds were substituted at the NH groups by alkyl or aryl groups.



Scheme 22. Starting materials.

3.1. Synthesis and characterization of DPP derivatives

3.1.1. *N*-alkylation of DPP

The principal method for alkylation of DPP uses alkyl halides as alkylating agents, because it is simple and gives much more satisfactory yields.^{18,83} In our work we reproduced some reported alkylation reactions but new or modified procedures were also used to prepare several mono- and di-alkylated DPP.

The alkylation reaction proceeds via several steps. Firstly, DPP goes from crystalline state to solution, where it gets deprotonated to DPP⁻ or DPP²⁻, depending on the strength of the base used, and then either of those anions reacts with the alkyl halide producing mono-alkylated DPP. A subsequent reaction with a second equivalent of alkyl halide produces di-alkylated DPP. In some cases, we used a strong base (KO^tBu) to obtain an almost complete deprotonation of the dissolved DPP, thus allowing the use of lower reaction temperatures (in the range of 60–120 °C).

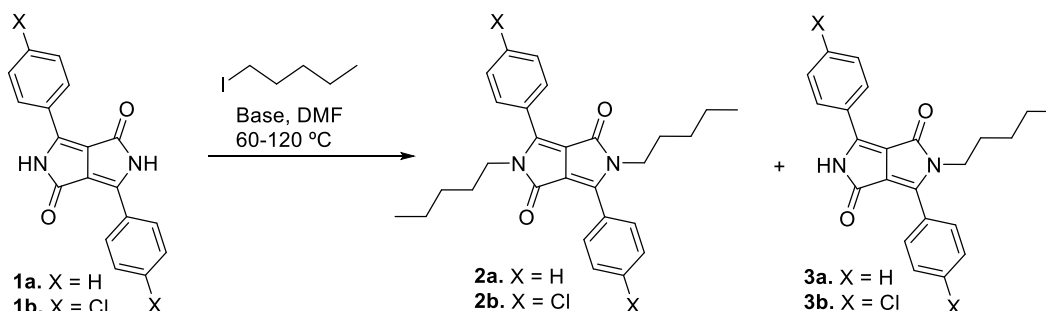
In order to investigate the effect of the reaction temperature on the alkylation yield, the reactions were carried out at different temperatures under similar reaction conditions. However, under high temperatures (>120 °C) lower yields were obtained. This is likely due to *O*-alkylation, which has been reported to occur.^{20,84,85} Aprotic polar solvents generally favour substitution at the hard centre (*O*-alkylation) and it can be

minimized by choosing a protic solvent or an apolar solvent. However, because of DPP insolubility in apolar or protic solvents, they cannot be used in the *N*-alkylation reactions. Typically the solvent used is DMSO or DMF (the most common in literature); organic or inorganic bases can be used.

The alkylation of **1a** and **1b** with 1-iodopentane was carried out in DMF in the presence of KO^tBu. A mixture of DPP with the base was stirred for 30 minutes at 80 °C to form the anionic compound (the colour of the mixture turned to violet) and then the alkyl halide was added slowly. After addition, the reaction carried out at the same temperature during 24 hours. The yield of the reaction was 22% for yellow compound **2a**. It was verified the formation of mono-*N*-alkylated DPP and probably *O*-alkylated DPP (Scheme 23). This last fact was not proven in this work, but the thin layer chromatography (TLC) of the reaction mixture showed the formation of various products, which can be explained by the distribution of the negative charge between the oxygen and nitrogen atoms of the amide group and reinforces the previously published results.⁸⁴

According to our interests, the same reaction was performed to obtain the mono-*N*-alkylated DPP **3a** as the major product, decreasing the number of equivalents of the alkylating agent and base. The mono-*N*-alkylated compound was obtained in 20% yield.

The reaction to obtain compounds **2b** and **3b** was carried out in similar conditions, with yields of 39% of di-alkylated-DPP **2b** and 14% of mono-*N*-alkylated DPP **3b** (Scheme 23).



Scheme 23. *N*-Alkylation of DPP with 1-iodopentane.

The ¹H-NMR spectrum of di-alkylated compound **2a** is shown in Figure 5. The multiplets signals of aromatic protons in *meta*-/para- and *ortho*- positions appear at 7.50–7.53 and 7.79–7.82, respectively. At 3.6 ppm (*J* = 7.7 Hz) appears the signal corresponding to the N-CH₂ protons while the remaining signals of the aliphatic chain appear between 0.79–1.64 ppm in ascending distance to the lactam unit.

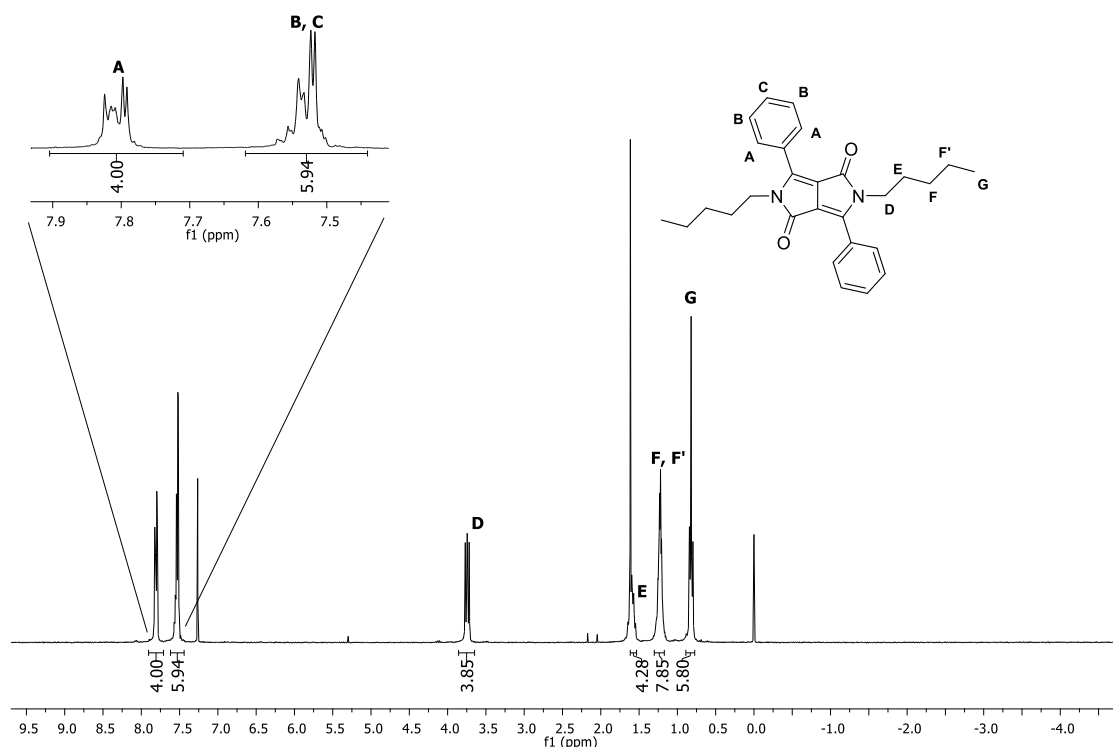


Figure 5. ^1H -NMR spectrum of di-alkylated DPP **2a** in CDCl_3 .

The Figure 6 shows the ^1H -NMR spectrum to mono-alkylated-DPP **3a**. The singlet at 9.56 ppm corresponding to the N-H proton confirms that it is a mono-alkylated compound. The multiplets corresponding to the aromatic protons A, A', B and B' appear at 8.33–8.36, 7.82–7.86, 7.51–7.53 and 7.55–7.58 ppm, respectively. At 3.83 ppm ($J = 7.6$ Hz) it is possible to find the triplet of the N-CH₂ protons. At *ca.* 1.60 ppm is observed the signal of protons E. Overlapped between 1.24 and 1.28 ppm appear the signals of protons F and F' and at 0.84 ppm ($J = 6.9$ Hz) is observed the signal of the terminal -CH₃.

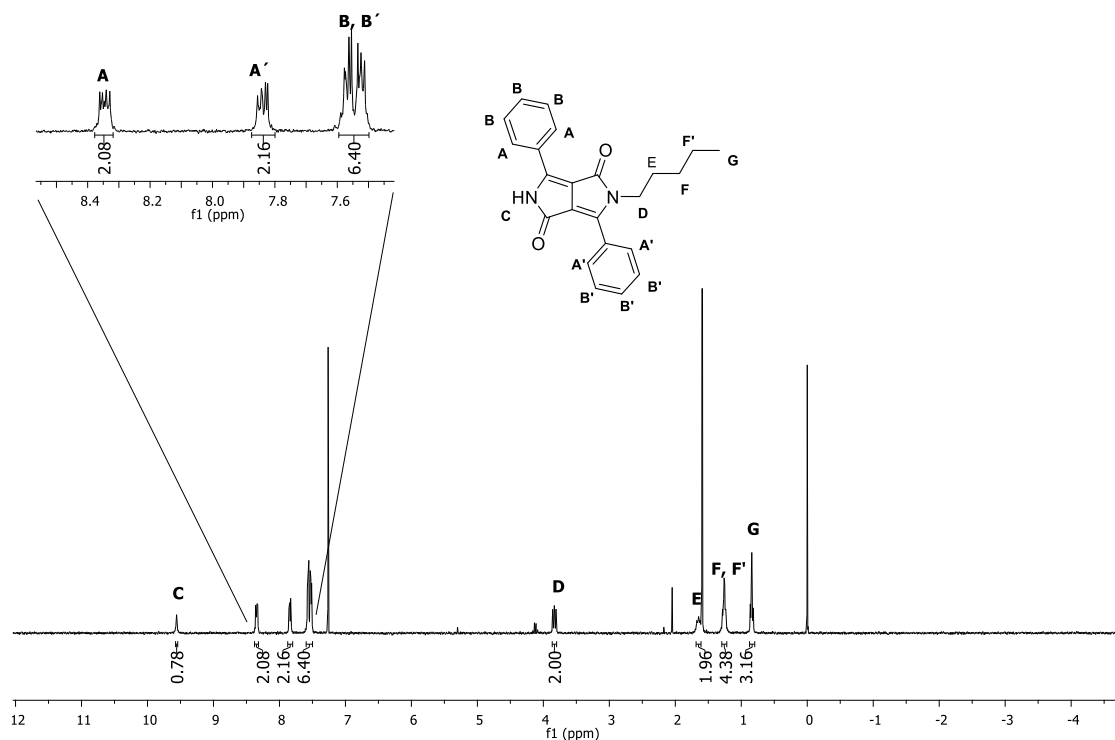


Figure 6. ^1H -NMR spectrum of mono-alkylated DPP **3a** in CDCl_3 .

The Figure 7 shows the ^1H NMR spectrum of compound **3b**. The signal of the *N-H* proton at 9.00 ppm confirms the mono-alkylation. Comparing with the spectrum of compound **3a**, the main difference is in aromatic region due to the presence of the $-\text{Cl}$ at the *para* position of the phenyl group. The same difference is observed when comparing the ^1H NMR spectra of compounds **2a** and **2b**.

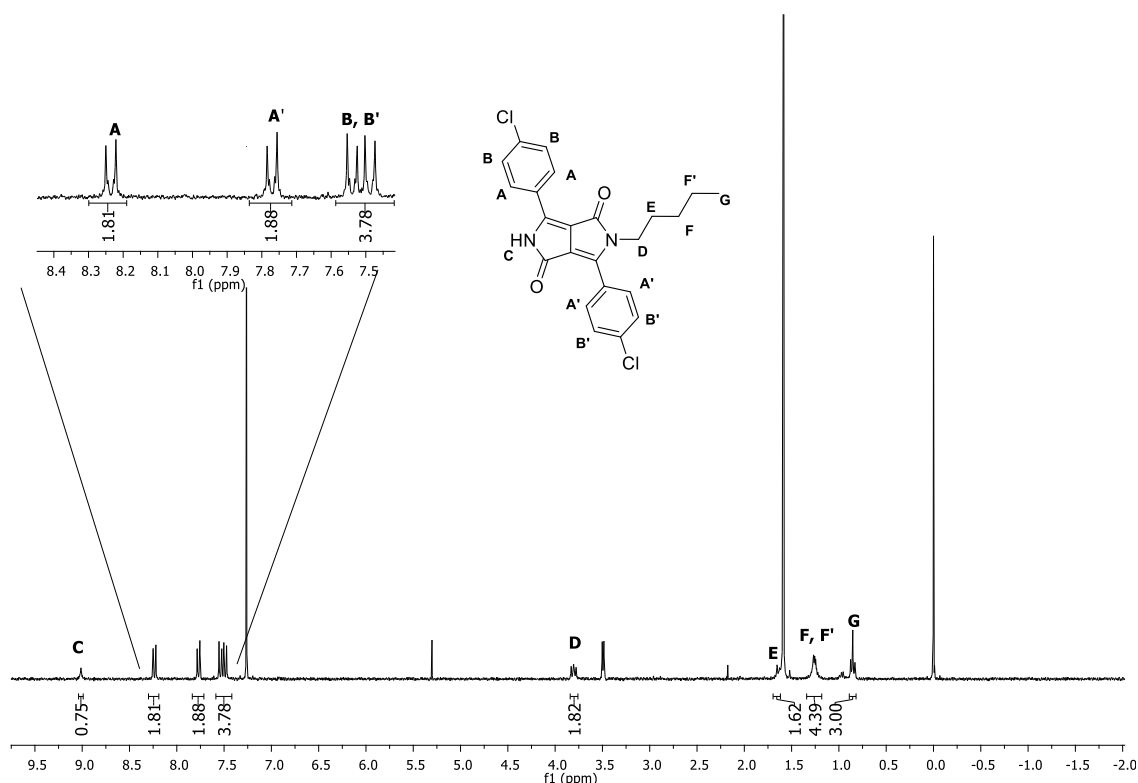
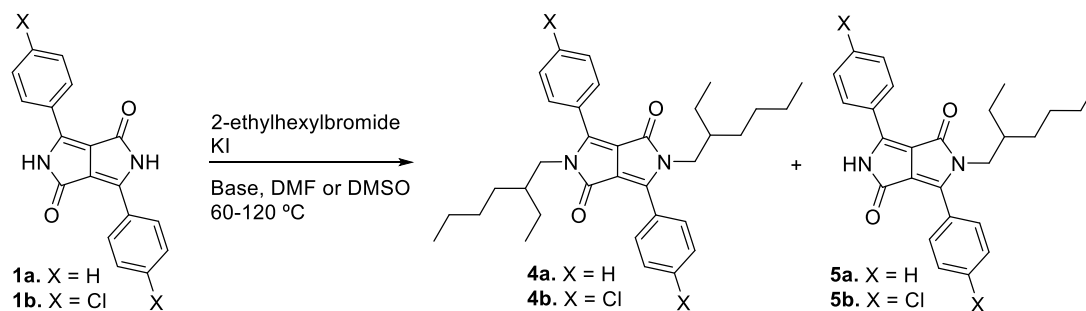


Figure 7. ^1H -NMR spectrum of mono-alkylated DPP **3b** in CDCl_3 .

The *N*-alkylation of DPP **1a** and **1b** with 2-ethylhexylbromide afforded the derivatives **4a**, **4b**, **5a** and **5b** (Scheme 24). Compounds **4a** and **4b** were obtained in 37% and 17% yield, respectively, in most common conditions present in literature, except the solvent which was DMSO in place of DMF. In addition to the formation of di-alkyl-DPP and mono-alkyl DPP, it has been observed that during the reaction there is competition between *O*-alkylation and *N*-alkylation. The mono-alkylated DPP **5a** and **5b** were not isolated. The derivatives were purified by column chromatography with DCM as the eluent. It has also been noted that the use of catalytic amounts of potassium iodide increases the reaction yields, which is due to the Br–I exchange.



Scheme 24. *N*-Alkylation of DPP with 2-ethylhexylbromide.

The Figure 8 shows the ^1H -NMR spectrum of compound **4b**. The multiplets of the aromatic protons are observed at 7.47–7.51 and 7.70–7.75 ppm. The signal of the N- CH_2 protons is observed at 3.7 ppm. The signal of protons D appears at 1.46 ppm as a multiplet and the signals of the other methylene units are overlapped between 1.01 and 1.60 ppm. The triplets corresponding to protons F and G appear at 0.69 ($J = 7.4$ Hz) and 0.79 ppm ($J = 6.8$ Hz).

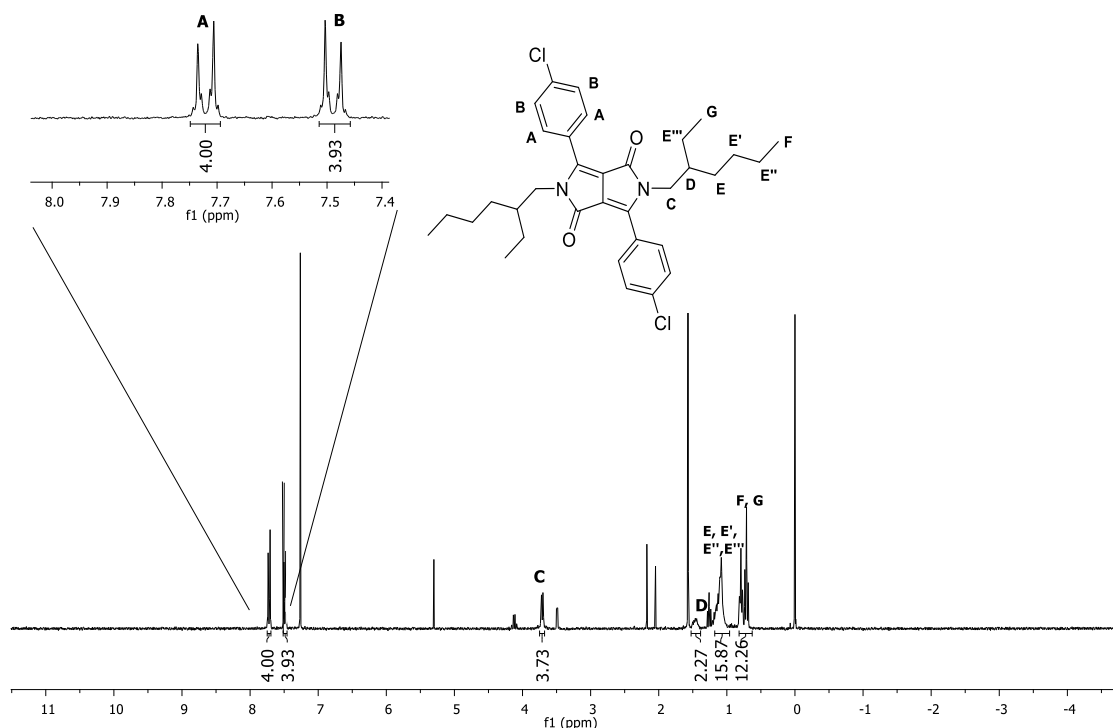


Figure 8. ^1H -NMR spectrum of di-alkylated DPP **4b** in CDCl_3 .

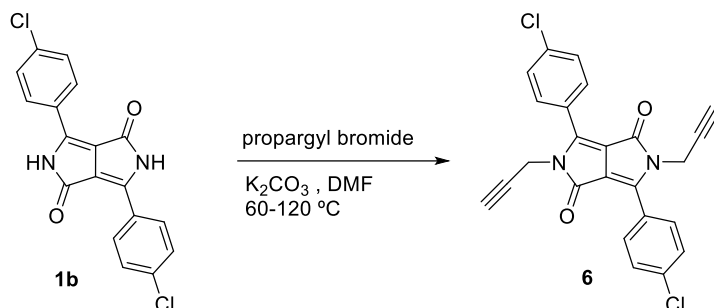
Comparing the ^1H NMR spectra of compounds **4a** and **4b**, the main differences are in the aromatic region, as previously described for compounds **2a** and **2b**.

The DPP derivatives described above are soluble in most common organic solvents, which give them greater chemical versatility. This is important for our purposes, because it will facilitate their transformation into other molecules.

The low yields of these reactions can be explained by the low solubility of the starting compounds, the formation of *N*-mono- and *N,N'*-dialkyl derivatives and also the probable formation of *O*-, *O,O'*- and *N,O*-alkylated compounds.

In the case of di-alkylated compounds our objective was to increase their solubility and to promote the reactions at the aromatic substituents. The mono-alkylated DPP were prepared mainly to increase the solubility of the compounds and, simultaneously, to leave an NH group for further modification, namely *N*-arylation.

Reaction of **1b** with propargyl bromide was performed in DMF with K_2CO_3 as a base. The purpose of this reaction was to obtain a compound with two terminal alkyne units that may be used in future reactions (e.g. “click” reactions). Compound **6** was obtained in 65% yield.



Scheme 25. Alkylation of DPP **1b** with propargyl bromide.

The Figure 9 shows the ^1H -NMR spectrum of compound **6**. The signals corresponding to the aromatic protons appear at 7.53–7.56 and 8.02–8.06 ppm while the signal of the N-CH_2 protons appears at 3.50 ppm. The signal corresponding to the two protons of the alkyne units appears at 2.36 ppm.

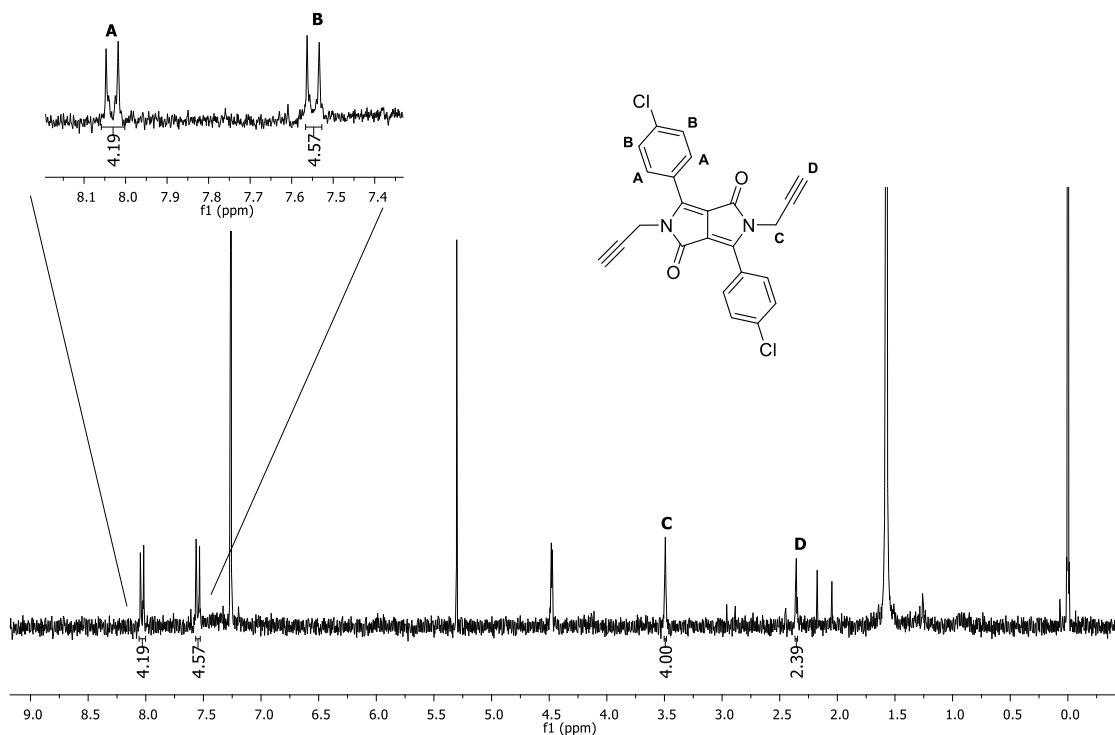
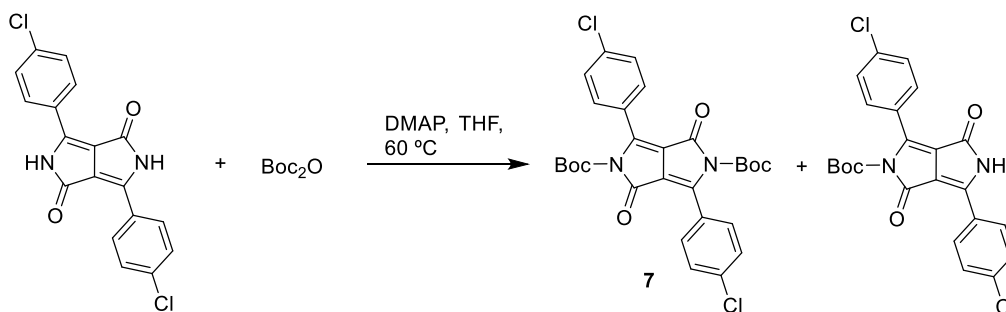


Figure 9. ^1H -NMR spectrum of the DPP **6** in CDCl_3 .

We have also attempted to increase the solubility of DPP using the Boc protecting group. Following a method reported in the literature,⁸⁶ the reaction with di-tert-butyl dicarbonate (Boc_2O) was carried out in THF at 60 °C with a catalytic amount of 4-dimethylaminopyridine (DMAP) (Scheme 26). The mixture was stirred overnight and then cooled to room temperature. The products were extracted with ethyl acetate and then separated by column chromatography using DCM as eluent. Compound **7** was obtained in 71% yield.



Scheme 26. Synthesis of DPP with *N*-*t*-butyloxycarbonyl protecting groups.

The Figure 10 shows the ^1H -NMR spectrum of compound **7**. At 7.45–7.49 ppm appears the signal of the aromatic protons at *meta* (B) positions and at 7.66–7.71 ppm appears the signal of aromatic protons at *ortho* (A) positions. The singlet at 1.40 ppm corresponds to the Boc methyl groups.

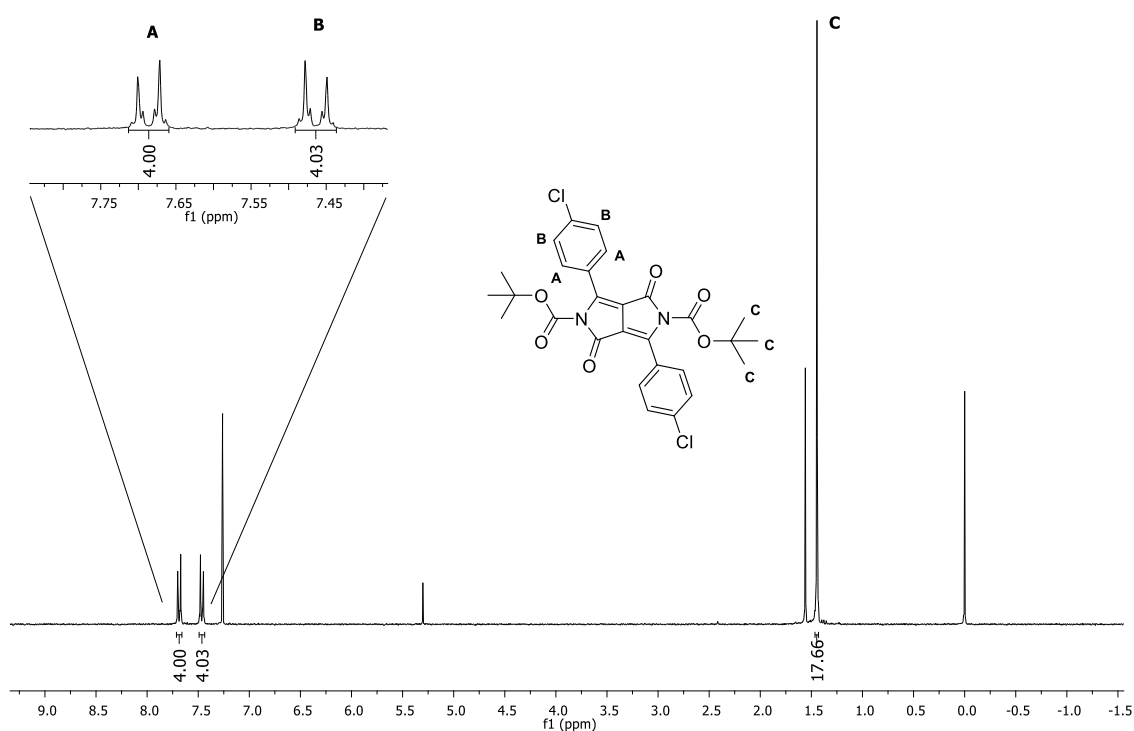
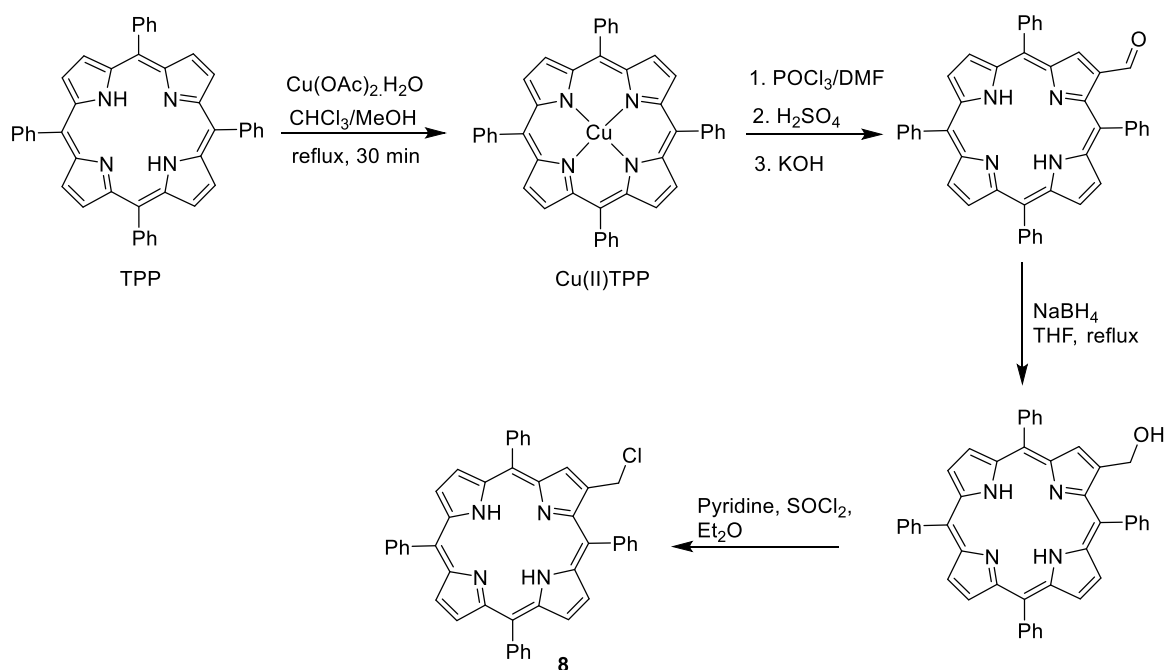


Figure 10. ^1H -NMR spectrum of di-BocDPP **7** in CDCl_3 .

One of the objectives of this work was to synthesize diketopyrrolopyrroles bearing other photosensitizing units (namely porphyrin or phthalocyanine units) covalently linked to the nitrogen atoms or at the aryl groups. Scheme 28 shows an example of such type of compound.

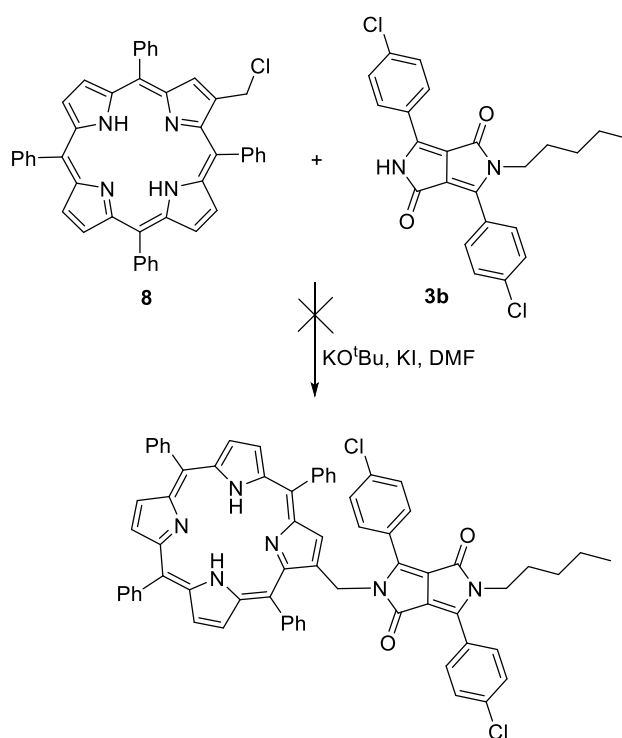
To carry out this reaction it was necessary to prepare the 2-chloromethyl-5,10,15,20-tetraphenylporphyrin (**8**) ($\text{ClCH}_2\text{-TPP}$) (Scheme 27). The first step was the metallation of 5,10,15,20-tetraphenylporphyrin (TPP) to obtain 5,10,15,20-tetraphenylporphyrinatocopper(II) (Cu(II)-TPP). The reaction proceeds in a mixture of $\text{CHCl}_3/\text{MeOH}$ at reflux for 30 minutes. The formylation requires the activation toward electrophilic attack by core metallation with metals such as Ni(II) or Cu(II) .⁸⁷ The acidic conditions of formylation preclude using Mg(II) or Zn(II) .

The next step was the formylation of Cu(II)-TPP . 500 mg of the complex were dissolved in 50 mL of dichloromethane with Vilsmeier reagent (a mixture of phosphoryl chloride and DMF) and reaction mixture was stirred overnight at 40 °C. After cooling to room temperature, 10 mL of sulfuric acid were added to the mixture and it was stirred for 30 minutes (this step was to demetallate the porphyrin). Then, the reactional mixture was added into saturated aqueous KOH solution in an ice bath until the colour of the solution changed from green to red. The 2-formyl-TPP was obtained in 56% yield. The next step was the reduction of 2-formyl-TPP. Reduction occurred with 2-formyl-TPP dissolved in THF with sodium borohydride as a reducing agent; the 2-hydroxymethyl-TPP was obtained in 92% yield. Finally, a mixture of pyridine/thionyl chloride converted the 2-hydroxymethyl-TPP, to the chloromethyl analogue, 2-chloromethyl-TPP (**8**) in 80% yield.⁸⁸



Scheme 27. Synthesis of ClCH₂-TPP.

Aiming to link covalently the porphyrin unit to the diketopyrrolopyrrole system we carried out the reaction described in Scheme 28. Unfortunately we did not obtain the expected compound and the starting material **3b** was recovered. It was noted the degradation of ClCH₂-TPP.

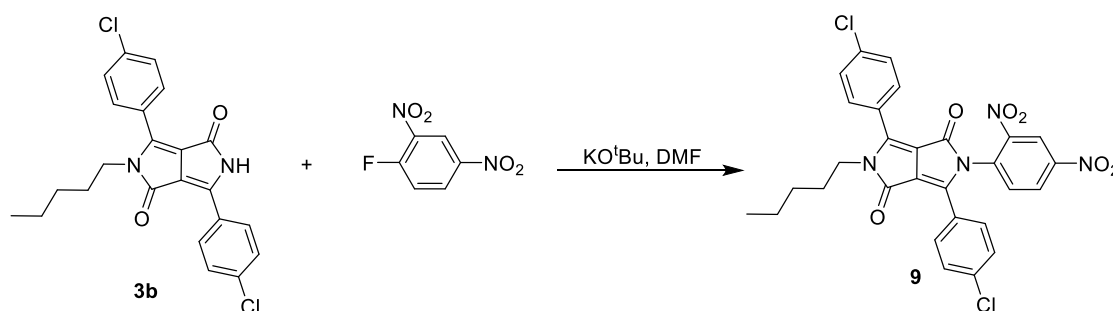


Scheme 28. Attempted synthesis of a diketopyrrolopyrrole covalently linked to a porphyrin unit.

3.1.2. *N*-Arylation of DPP

In contrast to the *N*-alkylation, direct *N*-arylation of amides is not readily accomplished without using highly electron deficient aryl electrophiles such as 1-fluoro-2,4-dinitrobenzene.^{21,22} In fact, the reaction of diphenyl-DPP with 1-fluoro-2,4-dinitrobenzene has been reported in the literature^{21,22} and occurs in DMF at room temperature, in the presence of potassium carbonate, to give the *N,N'*-bis-(2,4-dinitrophenyl)-DPP as an orange crystalline solid in good yield (Table 1). The four nitro groups strongly quench the fluorescence properties, rendering these compounds unsuitable for any fluorescence-based application.²¹

We also used this type of reaction but starting with the preformed mono-*N*-pentyl-ClC₆H₄DPP. It reacted with 1-fluoro-2,4-dinitrobenzene to give the corresponding *N*-aryl compound **9** in 82% yield (Scheme 29). This compound may be a useful intermediate to other DPP derivatives if we succeed to reduce the nitro groups to amino groups.



Scheme 29. Mono-arylation of DPP **3b**.

The Figure 11 shows the ¹H NMR spectrum of compound **9**. The signals of the aromatic protons appear between 7.25–8.90 ppm. The remaining signals, corresponding to the aliphatic protons, are identical to the already described for the ¹H NMR spectrum of compound **3b**.

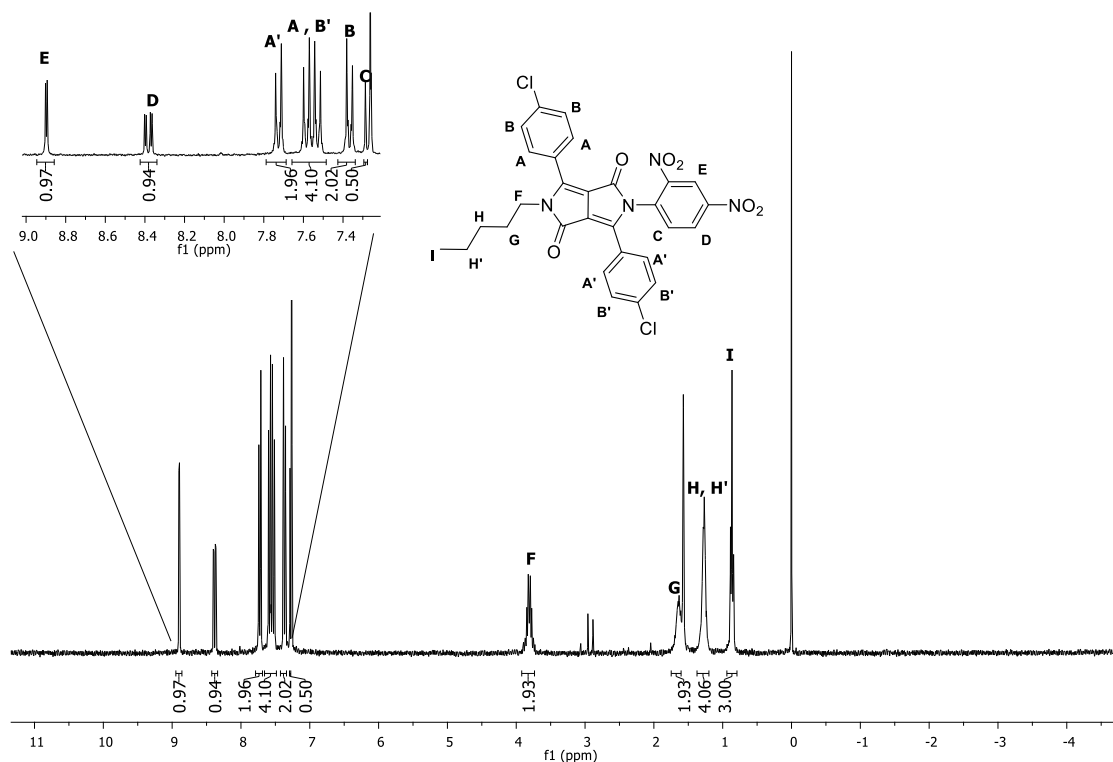
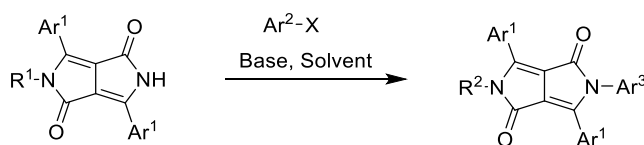


Figure 11. ^1H -NMR spectrum of compound **9** in CDCl_3 .

The reaction of DPP **1a** and **1b** and their mono-*N*-pentyl derivatives with other arylating agents was also tested using diverse types of bases (e.g. K_2CO_3 or NaH) and different temperatures. Unfortunately none of these reactions afforded the expected; only starting materials were recovered (Table 1), except for the reaction with 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (F_{20}TPP), which was degraded during the reaction.



Scheme 30. *N*-Arylation of DPP.

Table 1. Reaction of DPP derivatives with various *N*-aryllating agents.

R¹	Ar¹	Ar²-X	R²	Ar³	Solvent	Yield (%)
H	Ph	FC ₆ H ₃ (NO ₂) ₂	2,4-(NO ₂) ₂ C ₆ H ₃	2,4-(NO ₂) ₂ C ₆ H ₃	DMF	75
-pentyl	Ph	FC ₆ H ₃ (NO ₂) ₂	pentyl	2,4-(NO ₂) ₂ C ₆ H ₃	DMF	82
H	Ph	F ₂₀ TPP	F ₁₉ TPP	F ₁₉ TPP	DMF	- ^a
H	Ph	C ₆ F ₆	C ₆ F ₅	C ₆ F ₅	DMF	- ^a
-pentyl	Ph	C ₆ F ₆	pentyl	C ₆ F ₅	DMF	- ^a
-pentyl	4-ClC ₆ H ₄	cyanuric chloride	pentyl	C ₃ Cl ₂ N ₃	DMF	- ^a
H	4-ClC ₆ H ₄	4-nitrophthalonitrile	phthalonitrile	3,4-(CN) ₂ C ₆ H ₃	DMF	- ^a

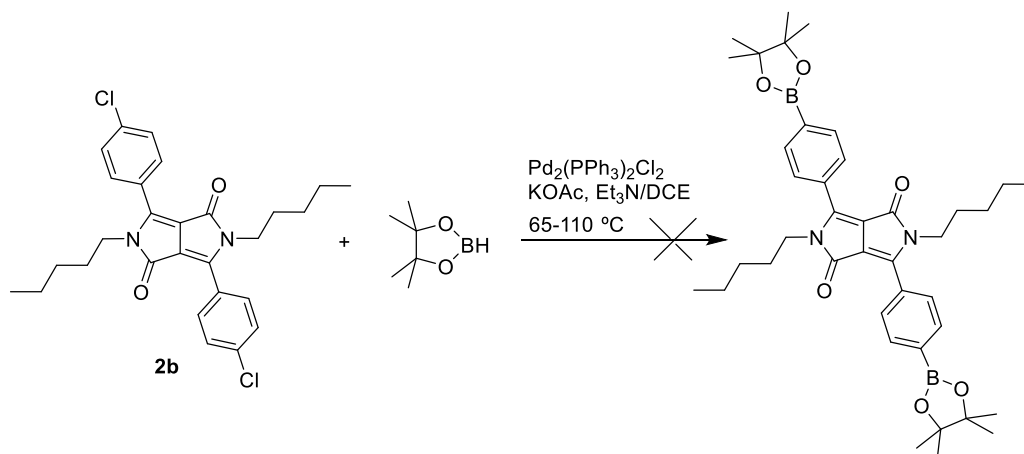
a. No reaction

3.1.3. Reactions at the aromatic groups of DPP

The Suzuki–Miyaura coupling reaction of organoboron compounds with aryl halides in the presence of a palladium catalyst is one of the most versatile methods for constructing carbon–carbon bonds.⁸⁹ The key advantages of the Suzuki–Miyaura cross-coupling are the mild conditions under which it is conducted, the high tolerance toward functional groups that is observed, the commercial availability and stability of boronic acids to heat, oxygen, and water and the ease of handling and separation of boron-containing byproducts from the reaction mixtures.^{89,90}

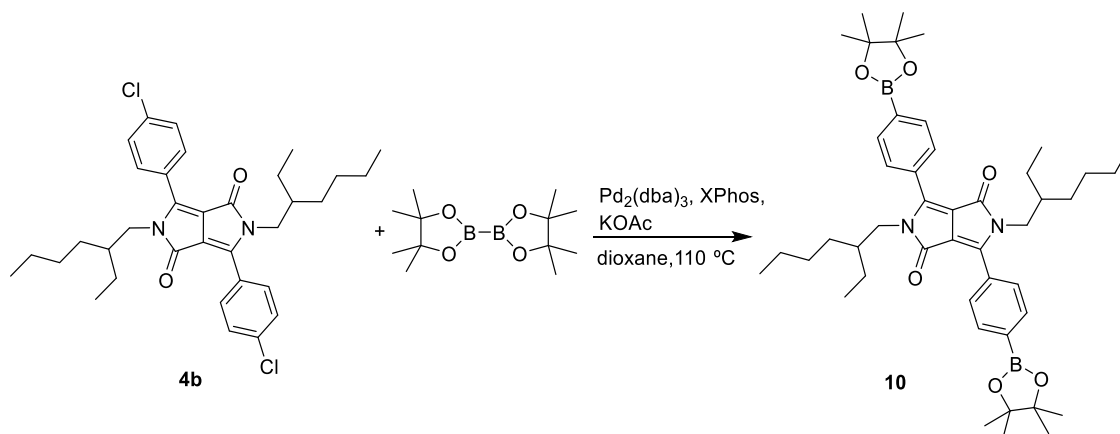
With this in mind, we decided to explore the versatility of the Suzuki–Miyaura coupling reaction in the preparation of new DPP derivatives. Considering that this reaction occurs under very mild conditions and can tolerate many functional groups, it can be an excellent approach to attach functional groups at the aryl substituents of DPP.

The first attempt was to try the reaction of compound **2b** with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane using a palladium catalyst. The reaction was carried out at 65 °C in a mixture of dichloroethane and triethylamine (Scheme 31) and it was monitored by TLC. After 23 hours without any sign of product formation the temperature was raised to 110 °C and KOAc was added. After 24 h no reaction products could be observed; the reaction was finished and compound **2b** was recovered.



Scheme 31. Attempted palladium-catalysed borylation of **2b** with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

The next approach involved the palladium-catalysed borylation of **4b** with bis(pinacolato)diboron in the presence of $\text{Pd}_2(\text{dba})_2$ with 2-dicyclohexylphosphanyl-2,4,6-triisopropyl biphenyl (XPhos). The reaction was carried out in dioxane at 110 °C for 4 h. In this case, the expected compound **10** was obtained in 73% yield. Compound **10** is an important intermediate to introduce other functional groups at the phenyl groups in 3 and 6 positions of DPP.



Scheme 32. Palladium-catalysed borylation of **4b**.

The ^1H -NMR spectrum of compound **10** is shown in Figure 12. The signals of the aromatic protons are found at 7.74 ($J = 8.3$ Hz) ppm and 7.95 ($J = 8.3$ Hz) ppm. The signal corresponding to the methyl groups of the pinacolato boron ester units appears at 1.34 ppm as a singlet. The remaining signals corresponding to the protons of the *N*-alkyl chains are identical to those observed in the ^1H -NMR spectrum of compound **4b**.

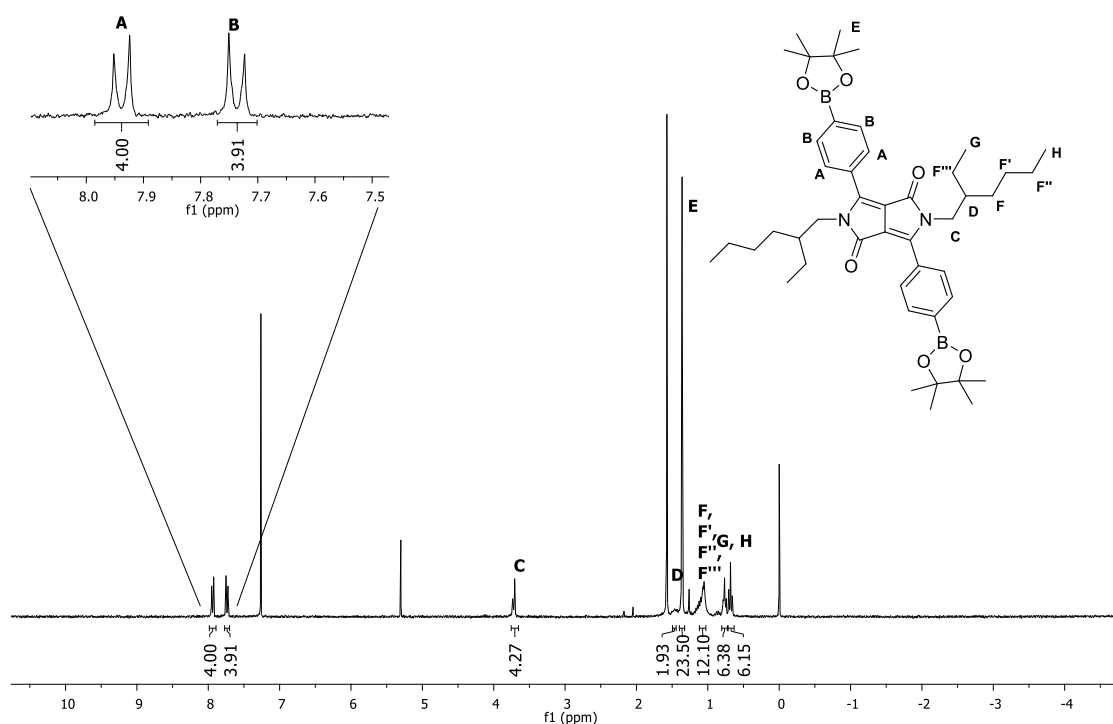
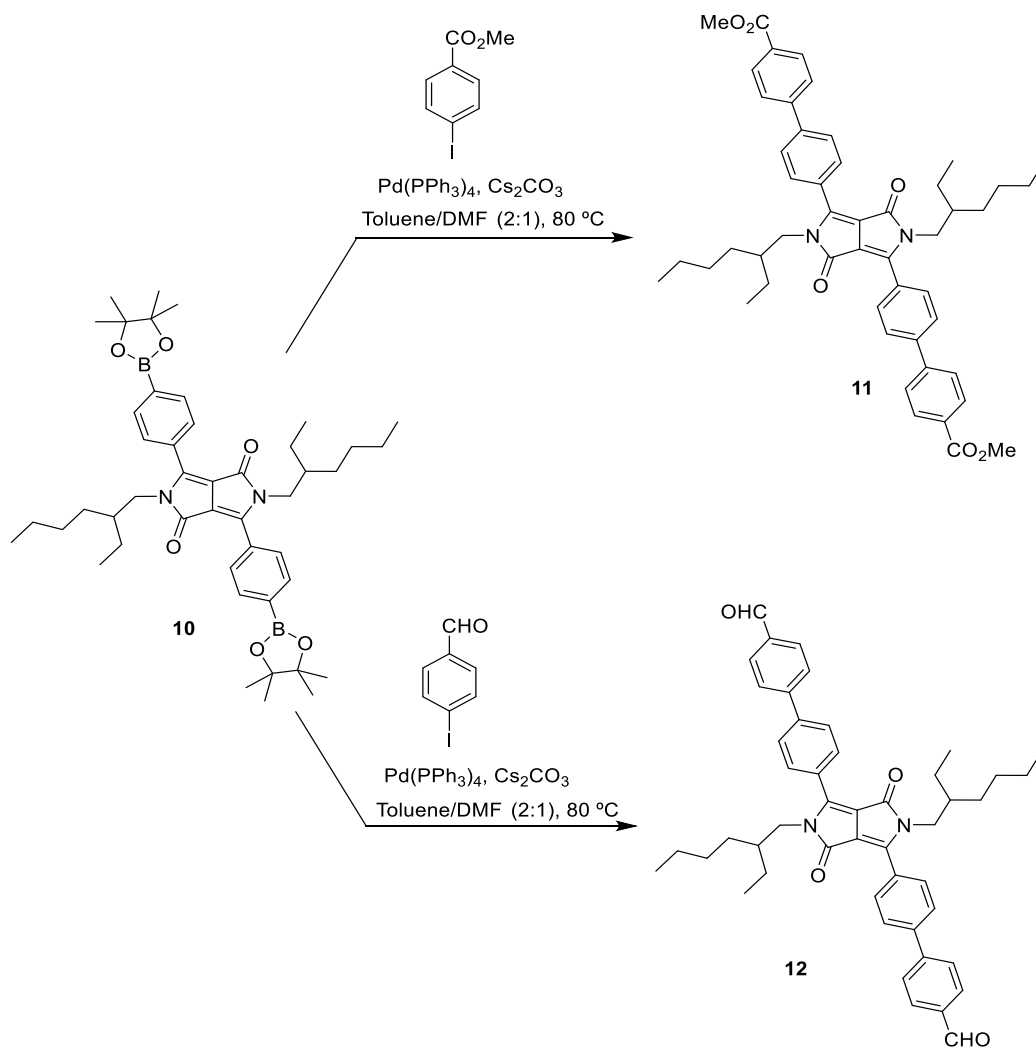


Figure 12. ^1H -NMR spectrum of compound **10** in CDCl_3 .

Compound **10** was used in Suzuki–Miyaura coupling reactions with iodoaryl compounds in the presence of $\text{Pd}(\text{PPh}_2)_3$ and Cs_2CO_3 (Scheme 33). The reactions proceed in a 2:1 toluene/DMF mixture at 80 °C for 4 hours. This allowed inserting methyl benzoate and benzaldehyde units, giving compounds **11** and **12** in 87% and 78% yield, respectively.

The dialdehyde **12** is potentially useful for a range of transformations. For instance, it may undergo Knoevenagel condensation with cyanoacetic acid to form a DPP derivative with anchoring cyanoacrylic acid groups.⁵⁶ In the case of compound **11**, basic hydrolysis can be carried out to convert the methylcarboxylate groups to anchoring carboxy groups.



Scheme 33. Functionalization of boronate **10**.

The Figure 13 shows the ^1H -NMR spectrum of compound **11**. In aromatic zone appear the signals of the new aromatic groups at 7.70–7.73 (D) and 7.90–7.93 (B) ppm and the signals of remaining aromatic protons at 7.77–7.80 (C) and 8.13–8.16 (A) ppm. The signal of the methyl ester group appears at 3.80 ppm. The remaining signals corresponding to the aliphatic zone have already been described.

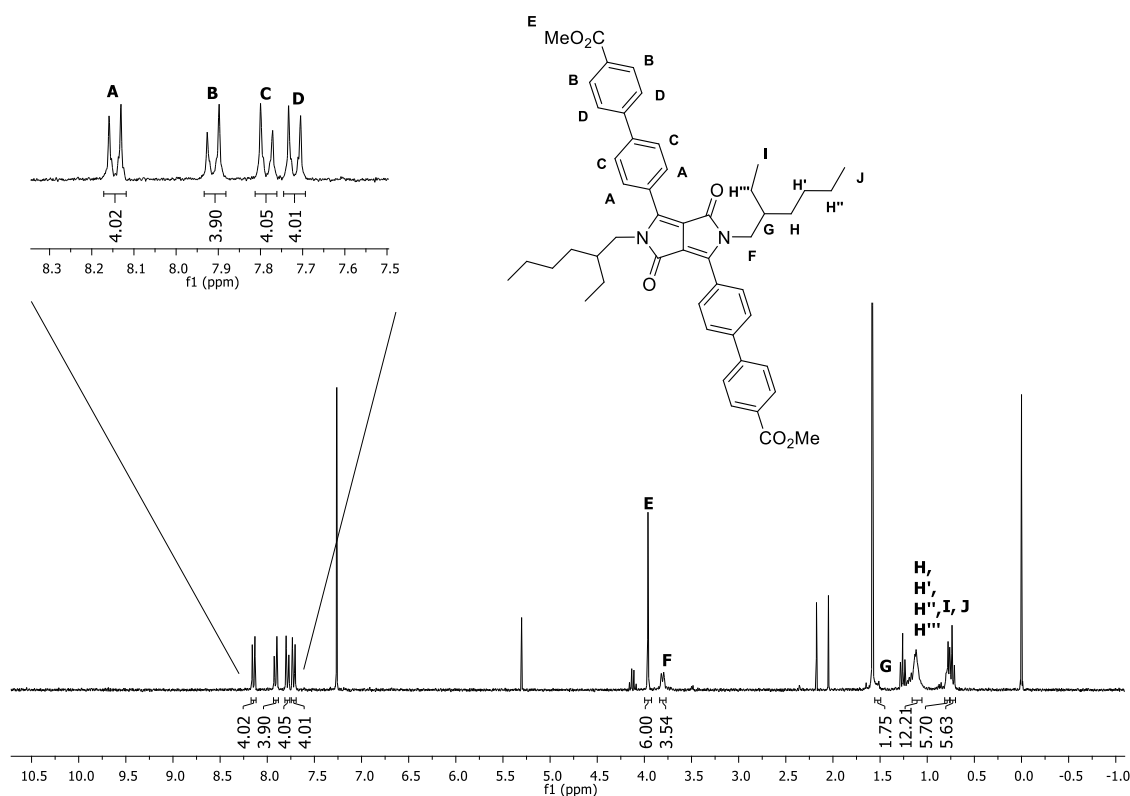


Figure 13. ^1H -NMR spectrum of compound **11** in CDCl_3 .

The Figure 14 shows the ^1H -NMR spectrum of compound **12**. The characteristic signal of the aldehyde proton occurs at 10.09 ppm. In aromatic zone of the spectrum appear the signals of the new aromatic groups at 7.78–7.80 (D) and 7.92–7.95 (B) ppm and the signals of remaining aromatic protons between 7.81–7.83 (C) and 7.98–8.02 (A) ppm. The remaining peaks correspond to the aliphatic zone, already described.

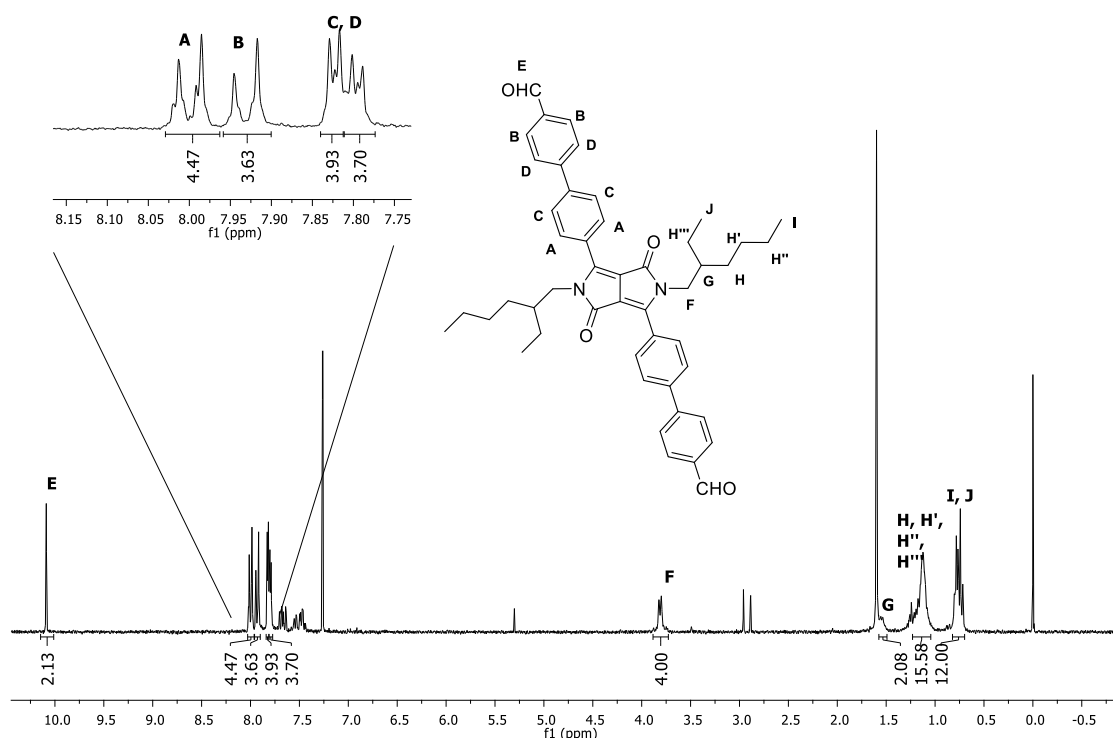
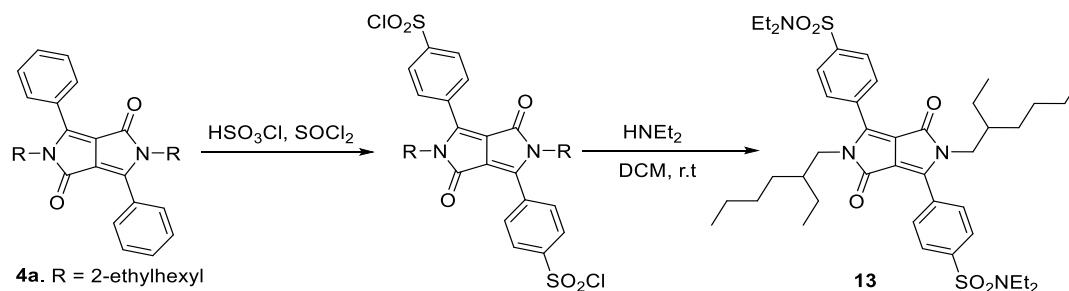


Figure 14. ^1H -NMR spectrum of compound **12** in CDCl_3 .

3.1.4. Synthesis of DPP-sulfonamide

Another approach to functionalise DPP at the aryl groups corresponds to the chlorosulfonation and conversion into sulfonamides. Compounds of this type of behave as fluorescent pH indicators.²⁵

In this experiment, compound **4a** was reacted with chlorosulfonic acid during 1 hour. Thionyl chloride was then added and allowed to react for 1 hour at room temperature and then 1 hour at 50 °C. After cooling to room temperature, the reaction mixture was added onto ice and the resulting solid was filtered and washed with cold water. Without purification, the product was dissolved with CH_2Cl_2 and immediately dropped in a solution of diethylamine in CH_2Cl_2 . The mixture was stirred during 2 days at room temperature. The product was purified by TLC using dichloromethane as eluent. It was noted that several products were formed in small quantities. These products strongly bind to the stationary phase and it is difficult to elute them completely. It was only possible to characterize compound **13**.



Scheme 34. Synthesis of DPP-sulfonamide.

The Figure 15 shows the ^1H NMR spectrum of compound **13**. The signals at 7.95–7.98 and 7.88–7.92 ppm correspond to the *meta* (A) and *ortho* (B) protons of aromatic ring, respectively. The doublet at 3.73 ($J = 7.4$ Hz) ppm corresponds to the $-\text{CH}_2$ adjacent to the lactam unit and at 3.29 ppm appears the signal of the $-\text{CH}_2$ of the sulfonamide group. The multiplet at 1.43 ppm corresponds to the E protons. The triplet at 1.18 ppm is due to the $-\text{CH}_3$ protons of the sulfonamide units. The signals of the other methylene units appeared overlapped between 1.0 and 1.6 ppm. The triplets of protons I and J appear between 0.69 and 0.79 ppm.

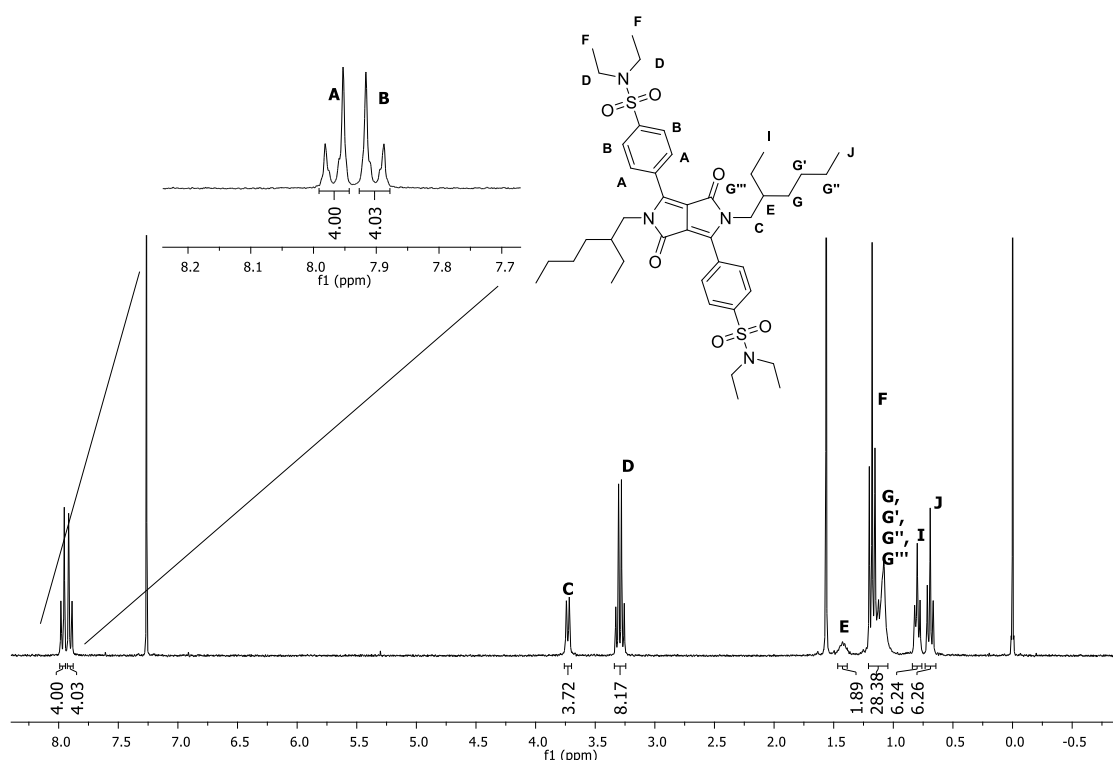


Figure 15. ^1H -NMR spectrum of compound **13** in CDCl_3 .

4. Photophysical properties

The photophysical properties are of extreme importance in the evaluation of a potential photosensitizer. Thus, the photophysical properties (absorption and emission spectra, molar absorption coefficient and the Stokes shift) of some of the new synthesized DPP derivatives were evaluated and the results of these studies are discussed in this chapter.

The Jablonski diagram is convenient for visualizing in a simple way the possible processes: photon absorption, internal conversion, fluorescence, intersystem crossing, phosphorescence, delayed fluorescence and triplet–triplet transitions (Figure 16).⁹¹

When a molecule absorbs a photon of appropriate energy, a valence electron is promoted from the ground state to some vibrational level in the excited singlet manifold (Figure 16). The process of light absorption is extremely rapid, in the order of one femtosecond ($1 \text{ fs} = 10^{-15} \text{ s}$).^{92,93}

In 1852, the British scientist Sir George G. Stokes fixed the term "fluorescence" after observing blue luminescence in the mineral fluorite. Stokes also discovered the redshift in band maximum of the fluorescence spectrum relative to the band maximum of absorption. The difference between the two band maximums is designed as Stokes shift.⁹²

Emission of photons accompanying the S_1 – S_0 relaxation is called fluorescence. The lowest vibrational level of S_1 is the starting point for fluorescence emission to the ground state S_0 and also transition to the lowest triplet state (intersystem crossing) (Figure 16). Within an excited state, an electron can decay *via* vibrational relaxation (VR) to the lowest vibrational level of that state, with dissipation of energy as heat (internal conversion). This relaxation pathway also allows for the decay from a higher energy state to the first excited singlet state S_1 . Fluorescence takes place on the nanosecond timescale ($1 \text{ ns} = 10^{-9} \text{ s}$) and depending on the molecular species, its duration amounts to 1–100 nanoseconds. It is clear from the Jablonski diagram that fluorescence always originates from the same level, irrespective of which electronic energy level is excited. The emitting state is the zeroth vibrational level of the first excited state $S_{1,0}$. It is for this reason that the fluorescence spectrum is shifted to lower energy than the corresponding absorption spectrum (Stokes shift). The Stokes shift can be enhanced by solvent interactions. We can also conclude from the sketched spectra in Figure 16 that vibronic bands in an absorption spectrum provide information on

vibrations in higher electronic excited states while vibrational fine structure in a fluorescence spectrum reports about vibrations in the ground state.⁹¹⁻⁹³

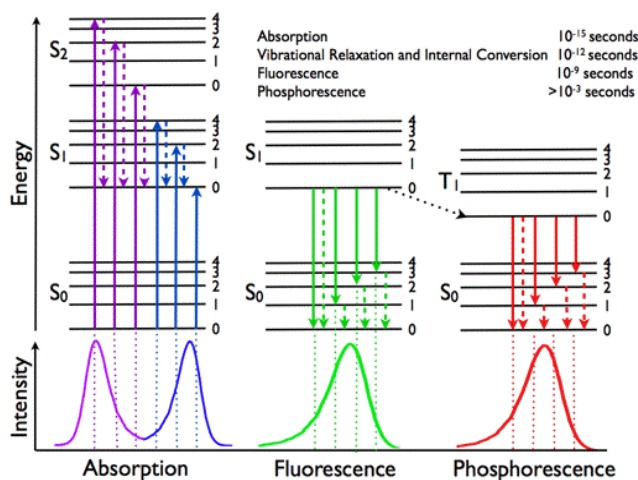


Figure 16. Jablonski diagram representing energy levels and spectra. Solid arrows indicate radiative transitions as occurring by absorption (violet, blue) or emission (green for fluorescence; red for phosphorescence) of a photon. Dashed arrows represent non-radiative transitions (violet, blue, green, red).⁹²

The UV/vis absorption spectra and fluorescence spectra of compounds **4b**, **11** and **12** were measured in DMF. Their UV/vis absorption spectra are shown in Figure 17 and the fluorescence spectra in Figure 19.

The measurement of an absorption spectrum is based on the Lambert-Beer law, and shows the ability of the investigated sample to absorb light at different wavelengths. As light absorption occurs almost always from the lowest vibrational level of the electronic ground state, the absorption spectrum characterizes the energetic structures of the electronic excited states of a molecule.^{91,92}

In our case, the introduction of alkyl substituents at the nitrogen atoms causes a loss of the vibronic structure, broadening and red shifting the absorption bands in the UV spectra. The “conversion” of the phenyl substituents of DPP into biphenyl groups leads to a red shift of the maximum absorption band in the visible region (472, 488 and 490 nm, respectively, for compounds **4b**, **11** and **12**. Comparing the compound **4b** with compounds **11** and **12**, is noted a bathochromic shift of due to the extension of the π -conjugated system.

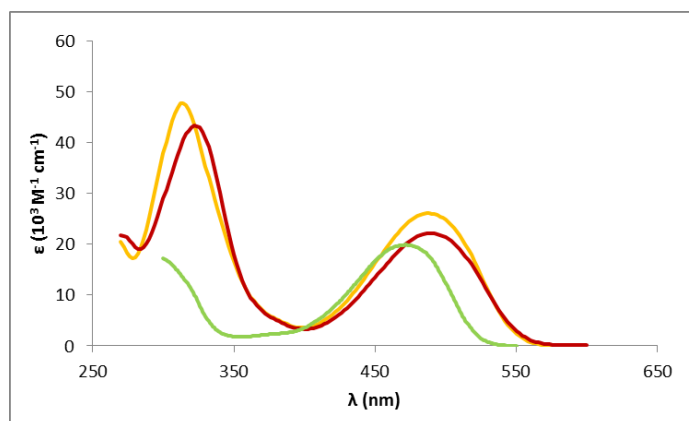


Figure 17. Absorption spectra of **4b** (green), **11** (yellow), and **12** (red) in DMF.

The Figure 18 shows compounds **4b**, **11** and **12** in solid state and in solution (DMF) under natural light and UV light.

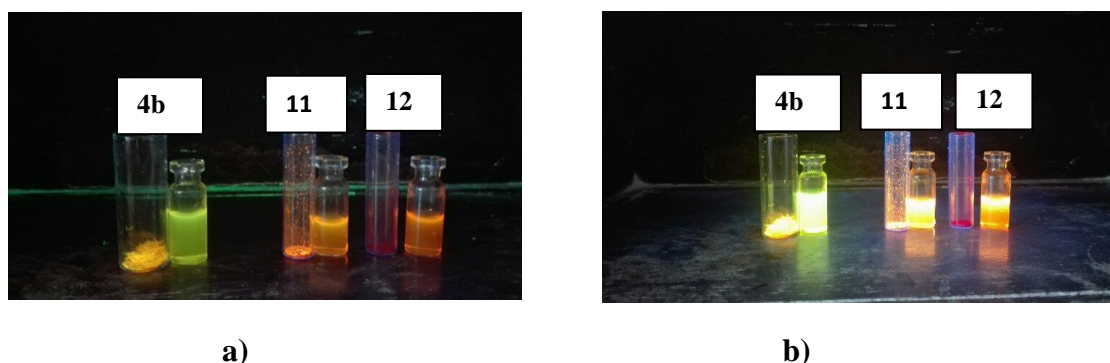


Figure 18. Compounds **4b**, **11** and **12** in the solid state and in solution (DMF): a) under natural light; b) under UV light.

A fluorescence spectrum represents the intensity of the fluorescence light emitted by the sample as a function of emission wavelength (Figure 19). As fluorescence transitions start from the lowest vibrational level of the first electronic excited state, fluorescence spectrum characterises the energetic structure of the electronic ground state.^{91,92}

The maximum emission wavelengths of DPP derivatives **4b**, **11** and **12** are 536, 566 and 570 nm, respectively. Emission spectra of these compounds in DMF were obtained by exciting at 450 nm at 20 °C.

The Figure 19 shows the comparison of absorption (solid lines) and emission spectra (dashed lines) of these compounds.

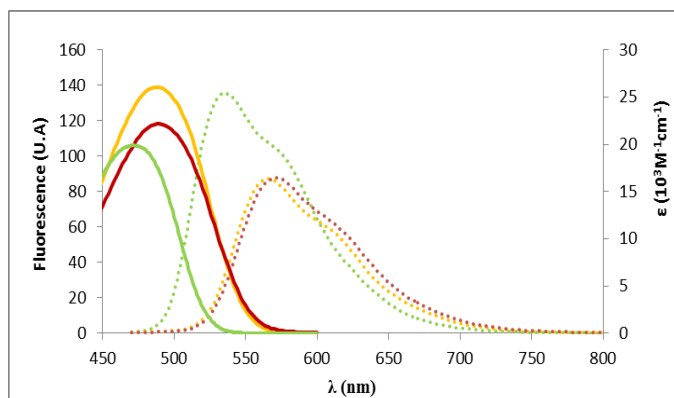


Figure 19. Absorption (solid lines) and emission spectra (dashed lines) of compounds **4b** (green), **11** (yellow) and **12** (red).

For compound **4b** a Stokes shift of 64 nm is observed, while for compounds **11** and **12** the shifts are 78 and 80 nm, respectively (Table 2). The Stokes shifts is the difference between the maximum emission and the maximum absorption and reflects the energy lost between the absorption and the emission of photons.⁹¹ Thus, it is concluded that compounds **11** and **12** lose more energy between the absorption and the photon emission process, comparatively with compound **4b**. Between compounds **11** and **12** the difference is small.

Table 2. Optical properties of DPP derivatives.

Compounds	λ_{max} [nm]	ϵ [$10^3 \text{ M}^{-1} \text{ cm}^{-1}$]	λ_{max} emission [nm]	Stokes shift [nm]
4b	300; 472	17.24; 19.88	536	64
11	312; 488	47.79; 26.07	566	78
12	322; 490	43.45; 22.16	570	80

5. Conclusions and future prospects

Conclusions and future prospects

We have prepared various mono- and di-*N*-alkylated DPP derivatives to increase the solubility of this type of compounds. Different experimental conditions were tested to increase the reactions yields. Those compounds were used to prepare a range of other DPP derivatives.

It was also tested the *N*-arylation of DPP with various arylating agents using procedures identical to those reported for related compounds. The results of those experiments were disappointing, since in most cases the starting DPP derivatives were recovered unchanged.

A particularly interesting result involved the synthesis of a DPP-diboronate and its use in Suzuki–Miyaura cross coupling reactions. That allowed the synthesis of new compounds incorporating carboxylic ester groups or formyl groups that can be easily modified to support the dye firmly at the surface of a semiconductor oxide in DSSCs. The photophysical properties of these compounds were evaluated. All dyes analysed showed a bathochromic shift compared to the original DPP core, regardless of the nature of the substituent.

In addition, experimental conditions to synthesize DPP containing sulfonamide groups were studied.

In near future our objective is to explore potential applications for the compounds synthesized and to use the most versatile ones in the synthesis of new dyes for solar cells. In particular, we will be focussed in the synthesis of dyads of the types diketopyrrolopyrrole–porphyrin and diketopyrrolopyrrole–phthalocyanine.

6. Experimental section

Experimental section

6.1. Materials and methods

The solvents used in the chemical transformations were mostly of analytical purity. Commercial solvents used in the purification processes were previously distilled.

The evolution of reactions was monitored by TLC performed on silica gel 60 (Merck) coated plastic sheets. Silica gel 60 (Merck) with particle size 0.063-0.200 mm was used for column separations. Purifications by preparative TLC were performed on glass plates (20 x 20 cm) precoated with a layer of silica gel 60 (Merck) with a thickness of 0.5 mm and activated in the oven at 100 °C for 12 hours.

¹H NMR spectra were mostly obtained in deuterated chloroform solution (CDCl₃), using TMS as internal reference, on a Bruker DRX 300 Advance operating at 300.13 MHz (for ¹H NMR spectra) or at 75.47 MHz (for ¹³C NMR spectra). Chemical shifts (δ) are expressed in parts per million (ppm). In the description of ¹H NMR, besides the chemical shift, the multiplicity of the signals and the corresponding coupling constants (J, Hz) are also indicated.

The mass spectra were obtained by ESI were performed on a Micromass Q-TOF-2TM spectrometer using chloroform or dichloromethane as the solvent and without matrix. The mass data are presented in terms of the *m/z* ratio.

Absorption spectra were recorded on a Shimadzu UV-2501-Pc spectrophotometer using 1 cm quartz cells and using DMF as the solvent.

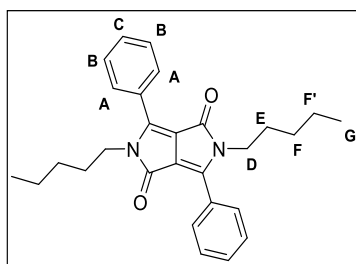
Fluorescence spectra were measured on 1 x 1 cm quartz cells on a Horiba Jobin Yvon FluoroMax-3 spectrofluorimeter with 3.0 nm slits.

Melting points were measured on a Büchi B-540 apparatus.

6.2 Synthesis and characterization

6.2.1. Synthesis of 2,5-dipentyl-3,6-diphenyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (2a)

A suspension of diphenyl-DPP (500 mg, 1.73 mmol) and KO^tBu (1.2 g, 10.38 mmol) in DMF (60 mL) was heated at 65 °C under nitrogen atmosphere during 30 min. At this temperature and under vigorous stirring, a solution of 1-iodopentane (2.055 g, 0.338 mL, 10.38 mmol) in DMF (8 mL) was added dropwise. The mixture was stirred for 24 h at 120 °C. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ and water. The organic layer was separated and washed with water and brine. The product was isolated by column chromatography on silica gel using CH₂Cl₂ as the eluent (163 mg, 22% yield).



¹H NMR (300 MHz, CDCl₃) δ (ppm) 0.82 (t, *J* = 6.9 Hz, 6H, G-H), 1.21–1.27 (m, 8H, F and F'-H), 1.55–1.64 (m, 4H, E-H), 3.74 (t, *J* = 7.6 Hz, 2H, D-H), 7.50–7.57 (m, 6H, B and C-H), 7.79–7.82 (m, 2H, A-H).

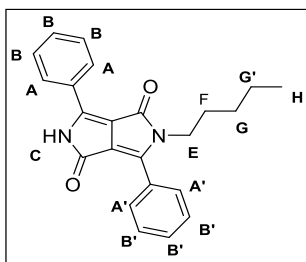
¹³C NMR (75 MHz, CDCl₃) δ (ppm) 13.90, 22.13, 28.85, 29.14, 41.88, 109.73, 128.27, 128.68, 128.90, 131.11, 148.52, 162.73;

MS (TOF): *m/z* 429.3 (M+H)⁺;

Melting point: 244–245.5 °C.

6.2.2. Synthesis of 2-pentyl-3,6-diphenyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (3a)

A suspension of diphenyl-DPP (500 mg, 1.73 mmol) and KO^tBu (572 mg, 5.1 mmol) in DMF (60 mL) was heated at 65 °C under nitrogen atmosphere during 30 min. At this temperature and under vigorous stirring, a solution of 1-iodopentane (514 mg, 0.4 mL, 2.6 mmol) in DMF (8 mL) was added dropwise. The mixture was stirred for 12 h at 120 °C. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ and water. The organic layer was separated and washed with water and brine. The product was isolated by column chromatography on silica gel using CH₂Cl₂ as the eluent (122 mg, 20% yield).



^1H NMR (300 MHz, CDCl_3) δ (ppm) 0.84 (t, $J = 6.9$ Hz, 3H, H-H), 1.22–1.29 (m, 4H, G,G'-H), 1.61–1.69 (m, 2H, F-H), 3.83 (t, $J = 7.6$ Hz, 2H, E-H), 7.51–7.58 (m, 6H, B and B'-H), 7.82–7.86 (m, 2H, A'-H), 8.33–8.36 (m, 2H, A-H), 9.56 (s, N-H);

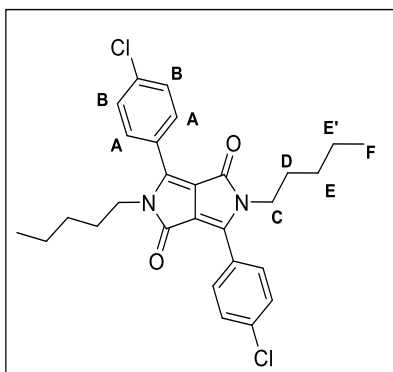
^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 13.92, 22.15, 28.86, 29.17, 42.16, 107.9, 127.68, 127.90, 128.81, 128.89, 129.17, 131.22, 132.06, 148.45, 163.23;

MS (TOF): m/z 359.2 ($\text{M}+\text{H}$) $^+$;

Melting point: 156–158 $^\circ\text{C}$.

6.5.3. Synthesis of 2,5-dipentyl-3,6-bis(4-chlorophenyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (2b)

A suspension of bis(*p*-chlorophenyl)-DPP (500 mg, 1.40 mmol) and K_2CO_3 (966.35 mg, 7 mmol) in DMF (60 mL) was heated at 65 $^\circ\text{C}$ under nitrogen atmosphere during 30 min. At this temperature and under vigorous stirring, a solution of 1-iodopentane (1.40 g, 0.883 mL, 7 mmol) in DMF (8 mL) was added dropwise. The mixture was stirred for 24 h at 120 $^\circ\text{C}$. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 and water. The organic layer was separated and washed with water and brine. The product was isolated by column chromatography on silica gel using CH_2Cl_2 as the eluent (270 mg, 39% yield).



^1H NMR (300 MHz, CDCl_3) δ (ppm) 0.83 (t, $J = 6.8$ Hz, 6H, F-H), 1.18–1.28 (m, 8H, E and E'-H), 1.51–1.59 (m, 4H, DH), 3.73 (t, $J = 7.7$ Hz, 4H, C-H), 7.47–7.51 (m, 4H, B-H), 7.72–7.77 (m, 4H, A-H);

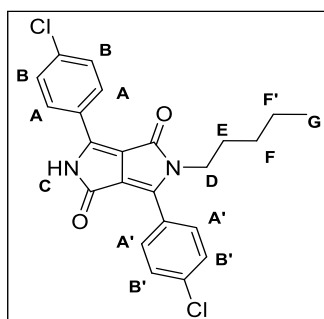
^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 13.89, 22.13, 28.82, 29.13, 41.87, 109.90, 126.50, 129.28, 129.98, 137.35, 147.38, 162.47;

MS (TOF): m/z 497.3 ($\text{M}+\text{H}$) $^+$;

Melting point: 205.8–206.8 $^\circ\text{C}$.

6.2.4. Synthesis of 2-pentyl-3,6-bis(4-chlorophenyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (3b)

A suspension of bis(*p*-chlorophenyl)-DPP (1g, 2.8 mmol) and KO^tBu (943 mg, 8.4 mmol) in DMF (60 mL) was heated at 65 °C under nitrogen atmosphere during 30 min. At this temperature and under vigorous stirring, a solution of 1-iodopentane (832 mg, 0.55 mL, 4.2 mmol) in DMF (8 mL) was added dropwise. The mixture was stirred for 24 h at 120 °C. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ and water. The organic layer was separated and washed with water and brine. The product was isolated by column chromatography on silica gel using CH₂Cl₂ as the eluent (167 mg, 14% yield).



¹H NMR (300 MHz, CDCl₃) δ (ppm) 0.85 (t, *J* = 6.8 Hz, 3H, G-H), 1.24–1.26 (m, 4H, F and F'-H), 1.58–1.66 (m, 2H, E-H), 3.80 (t, *J* = 7.8 Hz, 2H, D-H), 7.46–7.56 (m, 4H, B and B'-H), 7.74–7.79 (m, 2H, A'-H), 8.22–8.26 (m, 2H, A-H);

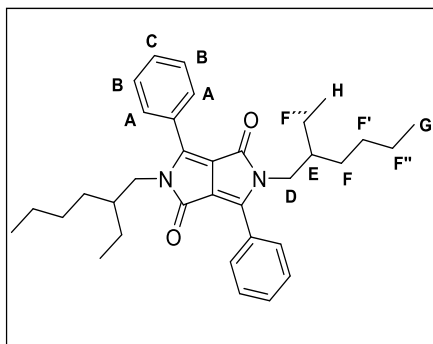
¹³C NMR (75 MHz, CDCl₃) δ (ppm) 13.93, 22.16, 28.85, 29.20, 42.22, 110.02, 126.35, 129.08, 130.07, 138.30, 143.63, 162.78;

MS (TOF): *m/z* 427.1 (M+H)⁺;

Melting point: 259.5–261.6 °C.

6.2.5. Synthesis of 2,5-bis(2-ethylhexyl)-3,6-diphenyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (4a)

A suspension of diphenyl-DPP (500 mg, 1.73 mmol) and K₂CO₃ (1.4 g, 10.4 mmol) in DMSO (60 mL) was heated at 65 °C under nitrogen atmosphere during 30 min. At this temperature and under vigorous stirring, a solution of 1-bromo-2-ethylhexane (1.8 mL, 10.38 mmol) in DMSO (8 mL) was added dropwise. Then 700 mg of KI were added. The mixture was stirred overnight at 80 °C. After cooling to room temperature, the mixture was diluted with ethyl acetate and water. The organic layer was separated and washed with water and brine. The product was isolated by column chromatography on silica gel using CH₂Cl₂ as the eluent (324 mg, 37% yield).



^1H NMR (300 MHz, CDCl_3) δ (ppm) 0.69 (t, J = 7.41 Hz, 6H, G-H), 0.77 (t, J = 6.7 Hz, 6H, H-H), 1.07–1.23 (m, 12H, F, F', F'' and F'''-H), 1.43–1.48 (m, 2H, E-H), 3.73 (m, 4H, D-H), 7.49–7.56 (m, 6H, B and C-H), 7.74–7.80 (m, 4H, A-H);

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 10.35, 13.94, 22.83, 23.70, 28.24, 30.29, 38.49, 44.88, 109.76,

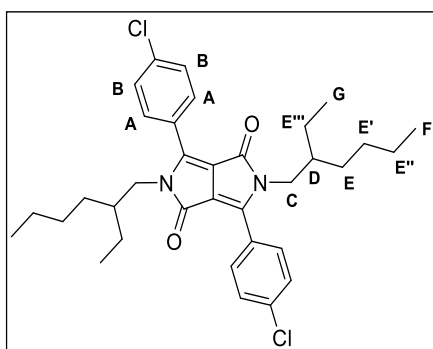
126.63, 128.82, 130.88, 148.74, 162.78;

MS (TOF): m/z 513.1 ($\text{M}+\text{H}$) $^+$;

Melting point: 169.8–170.7 $^\circ\text{C}$.

6.2.6. Synthesis of 2,5-bis(2-ethylhexyl)-3,6-bis(4-chlorophenyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (4b)

A suspension of bis(*p*-chlorophenyl)-DPP (1 g, 2.8 mmol) and K_2CO_3 (1.55 g, 11.2 mmol) in DMSO (60 mL) was heated at 120 $^\circ\text{C}$ under nitrogen atmosphere during 30 min. At this temperature and under vigorous stirring, a solution of 1-bromo-2-ethylhexane (2.4 mL, 14 mmol) in DMSO (8 mL) was added dropwise. Then 700 mg of KI were added. The mixture was stirred overnight at 120 $^\circ\text{C}$. After cooling to room temperature, the mixture was diluted with ethyl acetate and water. The organic layer was separated and washed with water and brine. The product was isolated by column chromatography on silica gel using CH_2Cl_2 as the eluent (127 mg, 12.6% yield).



^1H NMR (300 MHz, CDCl_3) δ (ppm) 0.71 (t, J = 7.4 Hz, 6H, F-H), 0.79 (t, J = 6.8 Hz, 6H, G-H), 1.03–1.19 (m, 12H, E, E', E''-H), 1.45 (m, 2H, D-H), 3.70 (m, 4H, C-H), 7.47–7.51 (m, 4H, B-H), 7.70–7.75 (m, 4H, A-H);

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 10.39, 13.94, 22.84, 23.70, 28.24, 30.27, 38.55, 44.98, 109.94,

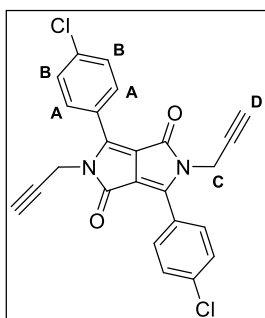
126.84, 129.23, 129.94, 137.36, 147.61;

MS (TOF): m/z 581.5 ($\text{M}+\text{H}$) $^+$;

Melting point: 259.5–261.6 $^\circ\text{C}$.

6.2.7. Synthesis of 2,5-bis(prop-2-yn-1-yl)-3,6-bis(4-chlorophenyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (6)

A suspension of bis(*p*-chlorophenyl)-DPP (150 mg, 0.42 mmol) and K₂CO₃ (174 mg, 1.26 mmol) in DMF (45 mL) was heated at 65 °C under nitrogen atmosphere during 30 min. Then, propargyl bromide 80% solution in toluene (150 mg, 1.26 mmol) was added. The mixture was stirred for 24 hours. After cooling to room temperature, the mixture was added to water and then filtered. The solid was subjected to column chromatography using dichloromethane as eluent and the main product crystallized in DCM/hexane (100 mg, 65%).



¹H NMR (300 MHz, CDCl₃): δ (ppm) 3.5 (s, 4H, C-H), 2.36 (s, 2H, D-H), 7.53–7.56 (m, 4H, B-H), 8.02–8.06 (m, 4H, A-H);

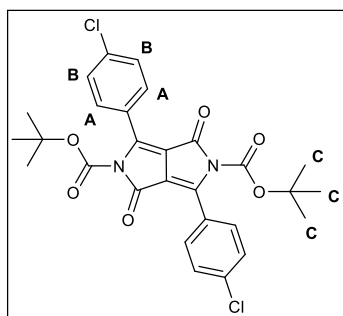
¹³C NMR (75 MHz, CDCl₃): δ (ppm) 31.95, 72.96, 78.48, 109.45, 125.75, 129.55, 130.39, 138.10, 146.95, 161.53.

MS (TOF): *m/z* 433.0 (M+H)⁺;

Melting point: 292.1–294.1 °C.

5.2.8. Synthesis of di-*tert*-butyl 3,6-bis(4-chlorophenyl)-1,4-dioxopyrrolo[3,4-*c*]pyrrole-2,5-dicarboxylate (7)

A solution of bis(*p*-chlorophenyl)-DPP (500 mg, 1.40 mmol) and a catalytic amount of DMAP in dry THF (120 mL) was stirred at room temperature under argon atmosphere. After 15 min, di-*tert*-butyldicarbonate (Boc₂O) (610 mg, 0.64 mL, 2.8 mmol) was added. The green yellow fluorescent solution was stirred at 50 °C overnight. After cooling to room temperature, the mixture was diluted with CH₂Cl₂ and water. The organic layer was separated and then washed with water and brine. The product was isolated by column chromatography on silica gel (CH₂Cl₂) to give the desired compound (563 mg, 71% yield).



¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.6 (s, 18H, C-H), 7.45–7.49 (m, 4 H, B-H), 7.66–7.71 (m, 4 H, A-H);

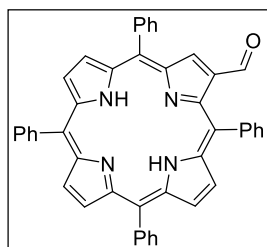
¹³C NMR (75 MHz, CDCl₃) δ (ppm) 27.58, 85.7, 126.53, 128.79, 129.79, 137.8, 145.22, 148.0, 159.14.

MS (TOF): *m/z* 557.5 (M+H)⁺;

Melting point: 185.5–186.6 °C

6.2.9. Synthesis of 2-formyl-5,10,15,20-tetraphenylporphyrin

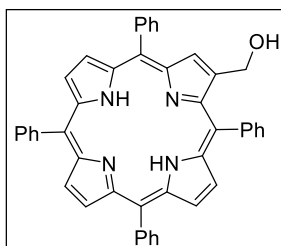
A solution of DMF (5 mL) and phosphoryl chloride (5 mL) was prepared. Then a solution of 5,10,15,20-tetraphenylporphyrinatocopper(II) (500 mg, 0.740 mmol) in 50 mL of 1,2-dichloroethane was added and the reaction mixture was refluxed overnight. The dark-green solution was then evaporated to dryness and the residue was treated, while cooling with an ice bath, with 10 mL of 96% H₂SO₄ to afford a green viscous solution, which was diluted with a saturated aqueous solution of KOH until the pH was basic. The reaction mixture was washed with water and the organic phase was extracted with dichloromethane, dried over anhydrous Na₂SO₄ and evaporated to dryness with the aid of the rotary evaporator. Purification by column chromatography (silica gel, toluene) afforded 268.4 mg (56% yield) as a purple solid after crystallization from a mixture of chloroform/hexane.



¹H NMR (300 MHz, CDCl₃): δ (ppm) -2.65 (s, 2H, NH), 7.70–7.84 (m, 12H, Ph-*m,p*-H), 8.16–8.05 (m, 8H, Ph-*o*-H), 8.75–8.80 (m, 2H, β -H), 8.84–8.94 (m, 4H, β -H), 9.23 (s, 1H, β -H), 9.41 (s, 1H, CHO).

6.2.10. Synthesis of 2-Hydroxymethyl-5,10,15,20-tetraphenylporphyrin

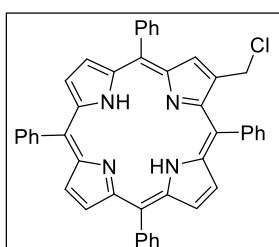
A sample of 2-formyl-5,10,15,20-tetraphenylporphyrin (250 mg, 0.389 mmol) was dissolved in 50 mL of refluxing dry tetrahydrofuran, then NaBH₄ (406 mg, 10 mmol) was added and the suspension was stirred for 15 min. The reaction mixture was cooled to room temperature, 100 mL of H₂O was added in order to eliminate the excess of NaBH₄, then the reaction mixture was transferred into a separating funnel and extracted with 100 mL of CHCl₃. The organic phase was separated, dried with Na₂SO₄ and evaporated under reduced pressure. The residue was purified by crystallisation from CH₂Cl₂/hexane to afford 229.8 mg (92% yield) as a purple solid.



¹H NMR (300 MHz, CDCl₃): δ (ppm) -2.79 (s, 2H, NH), 4.9 (s, 2H, CH₂O), 7.68–7.83 (m, 12H, Ph-*m,p*-H), 8.04–8.11 (m, 2H, Ph-*o*-H), 8.17–8.23 (m, 6H, Ph-*o*-H), 8.57–8.62 (m, 2H, β -H), 8.75–8.87 (m, 4H, β -H), 8.94 (s, 1H, β -H).

6.2.11. Synthesis of 2-(chloromethyl)-5,10,15,20-tetraphenylporphyrin (8).

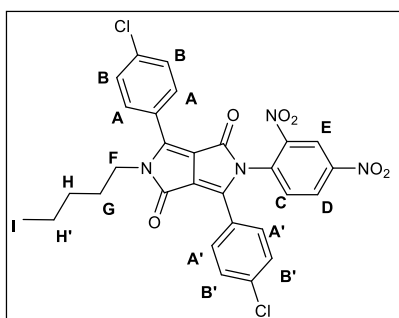
A solution of thionyl chloride (150 mg, 1.26 mmol) in 5 mL of Et₂O was slowly added, keeping the temperature in the range 0–5 °C, to a stirred solution of porphyrin (200 mg, 0.310 mmol) and pyridine (150 mg, 1.90 mmol) in 30 mL of Et₂O. Once the addition was complete, the temperature was raised to room temperature and the reaction mixture was stirred for 30 min. The mixture was then transferred into a separating funnel, diluted with 100 mL of CH₂Cl₂ and washed with water (70 mL) and aqueous 5% NaHCO₃ (60 mL). The organic phase was dried with Na₂SO₄ and the solvents evaporated in vacuo to afford a residue, which was purified by crystallisation from CH₂Cl₂/hexane to give 164.6 mg (80% yield) of a purple solid.



¹H NMR (300 MHz, CDCl₃): δ (ppm) – 2.70 (s, 2H, NH), 4.79 (s, 2H, CH₂Cl), 7.69–7.85 (m, 12H, Ph-*m,p*-H), 8.06–8.25 (m, 8H, Ph-*o*-H), 8.65 (d, J = 4.87 Hz, 2H, β -H), 8.76–8.86 (m, 4H, β -H), 8.96 (s, 1H, β -H).

6.2.12. Synthesis of 3,6-bis(4-chlorophenyl)-2-(2,4-dinitrophenyl)-5-pentyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (9)

A suspension of **3b** (100 mg, 0.24 mmol) and K₂CO₃ (100 mg, 0.72 mmol) in DMF (30 mL) was heated at 65 °C under nitrogen atmosphere during 30 min. Then, 1-fluoro-2,4-dinitrobenzene (90 mg, 0.48 mmol) was added. The mixture was stirred during 24 hours. After cooling to room temperature, the mixture was added to water and then filtered. The solid was subjected to column chromatography using dichloromethane as eluent. The main product was crystallized from CH₂Cl₂/hexane (108.4 mg, 75% yield).



¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.86 (t, J = 7 Hz, 3H, I-H), 1.24–1.28 (m, 4H, H,H'-H), 1.58–1.66 (m, 2H, G-H), 3.80 (m, 2H, F-H), 7.29 (d, J = 9 Hz, 1H, C-H), 7.34–7.39 (m, 2H, B-H), 7.51–7.60 (m, 4H, A, B'-H), 7.70–7.75 (m, 2H, A'-H), 8.36–8.40 (dd, J = 9 Hz, 1H, D-H), 8.90 (d, J = 3 Hz, 1H, E-H);

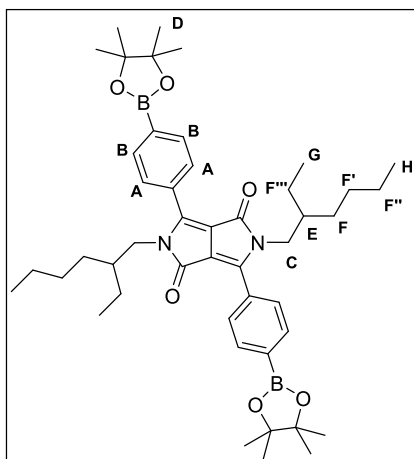
^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 13.89, 22.11, 28.81, 29.09, 42.40, 107.58, 113.95, 121.19, 124.90, 127.50, 129.5, 130.30, 131.3, 134.53, 142.67, 145.7, 146.18, 150.80, 162.37;

MS (TOF): m/z 593.2 ($\text{M}+\text{H}$) $^+$;

Melting point: 207.7–208.8 °C.

6.2.13. Synthesis of 2,5-bis(2-ethylhexyl)-3,6-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2 yl)phenyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**10**)

A mixture of **4b** (150 mg, 0.26 mmol), bis(pinacolato)diboron (525 mg, 2.1 mmol), KOAc (206 mg, 2.1 mmol), $\text{Pd}_2(\text{dba})_3$ (11.9 mg, 0.013 mmol), and XPhos (3.34 mg, 0.007 mmol) in dioxane (3.0 mL) was stirred under nitrogen at 110 °C for 4 h. After cooling to room temp., the mixture was diluted with CH_2Cl_2 and water. The organic layer was separated and then washed with water and brine. The product was isolated by column chromatography on silica gel (CH_2Cl_2) to give compound **10** (139 mg, 73% yield).



^1H NMR (300 MHz, CDCl_3): δ (ppm) 0.68 (t, J = 7.4 Hz, 6H, H-H), 0.76 (m, 6H, G-H), 1.06–1.12 (m, 12H, F, F', F'', F'''-H), 1.36 (s, 24 H, D-H), 1.45–1.50 (m, 2H, E-H), 3.71 (m, 4H, C-H), 7.74 (d, J = 8.3 Hz, 4H, B-H), 7.94 (d, J = 8.3 Hz, 4H, A-H)

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 10.41, 13.97, 22.85, 23.70, 24.86, 28.20, 30.26, 38.44, 44.98, 84.11, 110.13, 127.69, 130.99, 135.07, 148.71, 162.66;

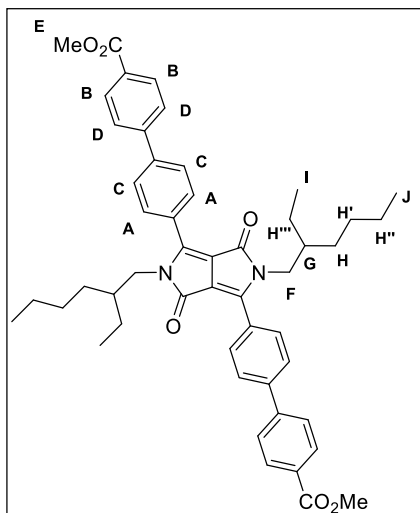
MS (TOF): m/z 764.8 ($\text{M}+\text{H}$) $^+$;

Melting point: 272.8–274.2 °C.

6.2.14. Synthesis of dimethyl 4',4'''-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis([1,1'-biphenyl]-4-carboxylate) (**11**)

A mixture of $\text{Pd}(\text{PPh}_3)_4$ (13.9 mg, 0.012 mmol), methyl iodobenzoate (42 mg, 0.16 mmol), Cs_2CO_3 (52 mg, 0.16 mmol) and **10** (30 mg, 0.04 mmol) in toluene/DMF (2:1) was stirred for 4 h at 80 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was diluted with ethyl acetate and water. The organic layer was

separated and washed with water and brine. The product was isolated by column chromatography on silica gel using CH_2Cl_2 as eluent (27.3 mg, 87% yield).



^1H NMR (300 Hz, CDCl_3) δ (ppm) 0.71–0.78 (m, 12H, I, J-H), 1.12–1.24 (m, 12H, H, H', H'', H'''), 1.5 (m, 2H, G-H), 3.80–3.82 (m, 4H, F-H), 3.96 (s, 6H, E-H), 7.70–7.73 (m, 4H, D-H), 7.77–7.80 (m, 4H, B-H), 7.90–7.93 (m, 4H, C-H), 8.13–8.16 (m, 4H, A-H);

^{13}C NMR (75 Hz, CDCl_3) δ (ppm) 10.46, 13.93, 22.86, 23.77, 28.26, 30.31, 38.57, 52.25, 110.0, 127.10, 127.63, 129.28, 129.59, 130.28, 142.37,

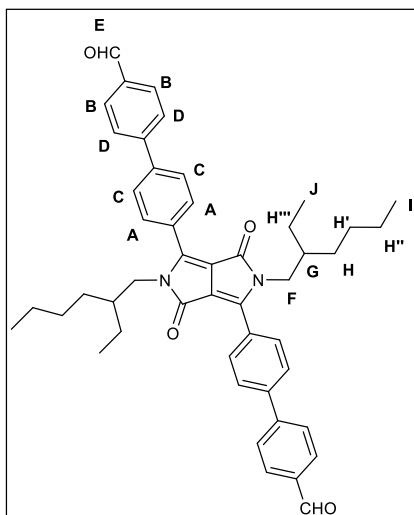
144.32, 148.18, 162.80, 166.86;

MS (TOF): m/z 781.7 ($\text{M}+\text{H}$) $^+$;

Melting point: 218.8–219.9 $^\circ\text{C}$.

6.2.15. Synthesis of 4',4'''-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis((1,1'-biphenyl)-4-carbaldehyde) (12)

A mixture of $\text{Pd}(\text{PPh}_3)_4$ (29.18 mg, 0.025 mmol), iodobenzaldehyde (93.7 mg, 0.404 mmol), Cs_2CO_3 (131.6 mg, 0.404 mmol) and **10** (80 mg, 0.101 mmol) in toluene/DMF (2:1) was stirred for 4 h at 80 $^\circ\text{C}$ under nitrogen atmosphere. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 and water. The organic layer was separated and washed with water and brine. The product was isolated by column chromatography on silica gel using CH_2Cl_2 eluent (57 mg, 78% yield).



^1H NMR (300 Hz, CDCl_3) δ (ppm) 0.70–0.79 (m, 12H, I, J-H), 1.12–1.21 (m, 12H, H, H', H'', H'''), 1.54–1.56 (m, 2H, G-H), 3.80–3.82 (d, 4H), 7.78–7.80 (m, 4H, D-H), 7.81–7.83 (m, 4H, C-H), 7.92–7.95 (m, 4H, B-H), 7.98–8.02 (m, 4H, A-H), 10.09 (s, 2H, E-H);

^{13}C NMR (75 Hz, CDCl_3) δ (ppm) 10.45, 13.99, 22.86, 23.77, 28.26, 30.31, 38.60, 45.10, 110.8, 127.75, 128.05, 129.35, 129.59, 135.82, 142.37,

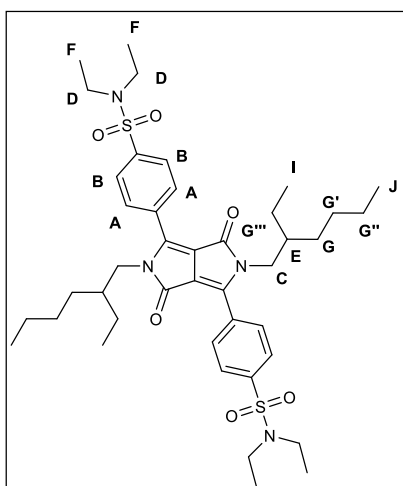
145.82, 148.13, 162.80, 191.82;

MS (TOF): m/z 721.6 ($M+H$)⁺;

Melting point: 130–132 °C.

6.2.16. Synthesis of 4,4'-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis(*N,N*-diethylbenzenesulfonamide) (13)

DPP **4a** (150 mg, 0.3 mmol) was added slowly to chlorosulfonic acid (0.24 mL, 3.5 mmol) at 0 °C. The mixture was stirred for 1 h at room temperature and then SOCl₂ (0.014 mL, 0.20 mmol) was added. The mixture was stirred for 1 h at room temperature and 1 h at 50 °C. The mixture was cooled to ambient temperature, and then poured onto ice. The product was extracted with dichloromethane and the solution was dropped slowly in a solution of diethylamine (0.250 mL, 2.1 mmol) and dichloromethane (30 mL). The mixture was stirred for 2 days at room temperature. Water was added to the reaction mixture and the product was extracted with dichloromethane. The organic phase was collected, dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure. The crude product was purified by preparative TLC with dichloromethane as the eluent. The product was dissolved in dichloromethane and precipitated with hexane to give a violet product (30 mg, 12.8% yield).



¹H NMR (300 MHz, CDCl₃) δ 0.69 (t, J = 7.43, 6H, J-H), 0.80 (t, J = 6.95, 6H, I-H), 1.04–1.22 (m, 28H, F, G, G', G'', G'''-H), 1.38–1.47 (m, 2H, E-H), 3.29 (q, 8H, D-H), 3.73 (d, J = 7.38 Hz, 4H, C-H), 7.88–7.92 (m, 4H, B-H), 7.95–7.98 (m, 4H, A-H);

¹³C NMR (75 MHz, CDCl₃): δ (ppm) 10.29, 13.92, 14.34, 22.83, 23.59, 28.23, 30.23, 38.67, 42.31, 45.15, 110.83, 127.46, 129.23, 131.85, 142.63, 147.46, 162.33;

MS (TOF): m/z 783.4 ($M+H$)⁺;

Melting point: 171–173 °C.

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