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# Helvetica Chimica Acta

## Unprecedented Nucleophilic Attack of Piperidine on the Electron Acceptor during the Synthesis of Push-Pull Dyes by a Knoevenagel Reaction

--Manuscript Draft--

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<b>Other Authors:</b>	Corentin Pigot Guillaume Noirbent Sébastien Peralta Sylvain Duval Malek Nechab Didier Gigmes Frédéric Dumur
<b>Keywords:</b>	Knoevenagel reaction; piperidine; push-pull; electron acceptor; electron donor
<b>Abstract:</b>	An unprecedented nucleophilic addition of piperidine on an electron acceptor, namely, 2-(3-oxo-2,3-dihydro-1 H -cyclopenta[ b ]naphthalen-1-ylidene)malononitrile is reported. This unexpected behavior was observed during the synthesis of push-pull dyes using the classical Knoevenagel reaction. To overcome this drawback, use of diisopropylethylamine (DIPEA) enabled to produce the expected dyes PP1 and PP2 . The optical and electrochemical properties of the different dyes were examined. Theoretical calculations were also carried out to support the experimental results. To evidence the higher electron-withdrawing ability of this electron acceptor, a comparison was established with two dyes ( PP3 and PP4 ) comprising its shorter analogue
<b>Response to Reviewers:</b>	<p>Dear Editor,</p> <p>Please find enclosed the revised version of our manuscript entitled: "Unprecedented Nucleophilic Attack of Piperidine on the Electron Acceptor during the Synthesis of Push-Pull Dyes by a Knoevenagel Reaction".</p> <p>We appreciate the thoughtful comments of the reviewer. We substantially revised the original version of our manuscript following the comments of the reviewer.</p> <p>We believe that this revised version should increase the quality and hence the impact of this manuscript. Please find below, our answers to the comments raised by the referee.</p> <p>Yours Sincerely,</p> <p>Dr. Frédéric Dumur</p>

References:

Please provide the title for the article of each reference in 'simple quotation marks'.

Titles of all articles have been added.

Composite references should be avoided. For each reference, a single number should be used. Please renumber the references.

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Graphical Abstract: A representative structural formula, scheme, or figure should be provided for the Table of Contents. The maximum available space for this graphical abstract is 7 × 11 cm.

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Files of the original graphics/artwork in easy-to-handle formats like ChemDraw, TIF or EPS or, alternatively, PDF files generated from all your vector graphics are highly welcome for print purposes.

Separated files are provided for all schemes and figures.

Reviewer #1:

Dumur et al described not only the addition of piperidine on electron acceptors giving the corresponding enamine, an improved synthesis of cyclopentanaphtaleylidene-malonitrile and the synthesis of push-pull dyes based on cyclopentanaphtaleylidene-malonitrile. The optoelectronic properties were compared with its smaller homologue as (dicyanomethylidene)indan-1-one.

The manuscript deserves publications, but some points have to be clarified.

1) In the following sentence, the word "aromaticity" should be changed to "core". "It has to be noticed that only few materials have been designed with Napht-EA, despite its extended aromaticity that makes it an ideal electron-withdrawing candidate for the design of materials for photovoltaic applications".

"Aromaticity" has been changed to "core".

	<p>2) The scheme 3 related to the formation of PP6 should be removed since the reaction is a simple enamine formation.</p> <p>Scheme 3 has been removed as suggested. Considering that the scheme was commented in the text, the corresponding paragraph has been removed.</p> <p>3) In section 3, the authors indicate that the LUMO is mainly centered on the electron acceptor. Looking at the LUMO orbitals, it appears that the LUMO is delocalized over the whole molecule. This should be changed in the main text.</p> <p>The paragraph has been modified as suggested.</p> <p>4) In table 2, the experimental HOMO-LUMO gaps have been determined by UV/Vis spectroscopy or cyclic voltammetry? In any case, the value seems to be wrong. Let's take PP1 as example. The HOMO-LUMO gap written in table 1 is 2.13 eV. In the UV/Visible spectrum, the lambda onset is around 640 nm that correspond to a band gap of 1.94 eV. By cyclic voltammetry, HOMO is at -5.36 eV and LUMO is at -3.61 eV consequently the HOMO-LUMO gap is of <math>-3.61 + 5.36 = 1.75</math> eV. The authors should clarify that in table 1.</p> <p>In fact, all optical HOMO-LUMO gaps have been determined by using the absorption maximum and not the onset of the intramolecular charge transfer band. Values in the Table 1 have been modified as suggested by the reviewer.</p> <p>Concerning the HOMO-LUMO gap determined by cyclic voltammetry, an additional column has been introduced in the Table 1. These values are consistent with those determined from the UV-visible absorption spectra. IN fact, a difference of 0.2 eV can be determined between the electrochemical and optical bandgap. This difference increases to 0.4 eV with the theoretical ones. The text has been corrected accordingly.</p> <p>5) In section 4, "At similar electron acceptor, reduction of PP2 was shifted at more cathodic potentials by ca. 200 mV compared to PP1. Thus, the irreversible reduction of PP2 was observed at - 1.18V contrarily to - 0.98V for PP1". ... As a result of this, Napht-EA is less acceptor in PP2 than in PP1 due to the electron donating effect of the extended donor. Cathodic shift of the reduction potential with elongation of the <math>\pi</math>-conjugated length was previously reported in the literature...</p> <p>According to the table 4, PP2 is reduced at -1.07V and PP1 at -1.19 V. Consequently, the insertion of an additional double bond between the A and D moieties leads to a shift of the reduction potential of 0.12 0 V to more cathodic potentials. Consequently, PP2 get reduced more easily than PP1 and therefor PP2 is a better acceptor than PP1. Actually, the authors find an opposite trend than in ref16. All the paragraph mentioned should be rewritten.</p> <p>We thank the reviewer for its comments. Indeed, in the present case, elongation of the conjugated spacer facilitates the reduction of the acceptor, what is the opposite trend classically reported in the literature. This is due to the fact that for these compounds, the LUMO extends over the whole molecule, including the electron donor. Consequently, when a spacer is introduced, the negative effect of the electron donor affects less the electron acceptor due to the distance between the two partners. As a result of this, the reduction is facilitated. The paragraph has been totally rewritten.</p> <p>6) The NMR spectra are missing in the supporting info.</p> <p>NMR spectra have been included.</p>
<b>Additional Information:</b>	
<b>Question</b>	<b>Response</b>
Submitted solely to this journal?	Yes
Has there been a previous version?	No
Dedication	
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# Unprecedented Nucleophilic Attack of Piperidine on the Electron Acceptor during the Synthesis of Push-Pull Dyes by a Knoevenagel Reaction

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and Frédéric Dumur<sup>\*,a</sup>

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An unprecedented nucleophilic addition of piperidine on an electron acceptor, namely, 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1-ylidene)malononitrile is reported. This unexpected behavior was observed during the synthesis of push-pull dyes using the classical Knoevenagel reaction. To overcome this drawback, use of diisopropylethylamine (DIPEA) enabled to produce the expected dyes **PP1** and **PP2**. The optical and electrochemical properties of the different dyes were examined. Theoretical calculations were also carried out to support the experimental results. To evidence the higher electron-withdrawing ability of this electron acceptor, a comparison was established with two dyes (**PP3** and **PP4**) comprising its shorter analogue.

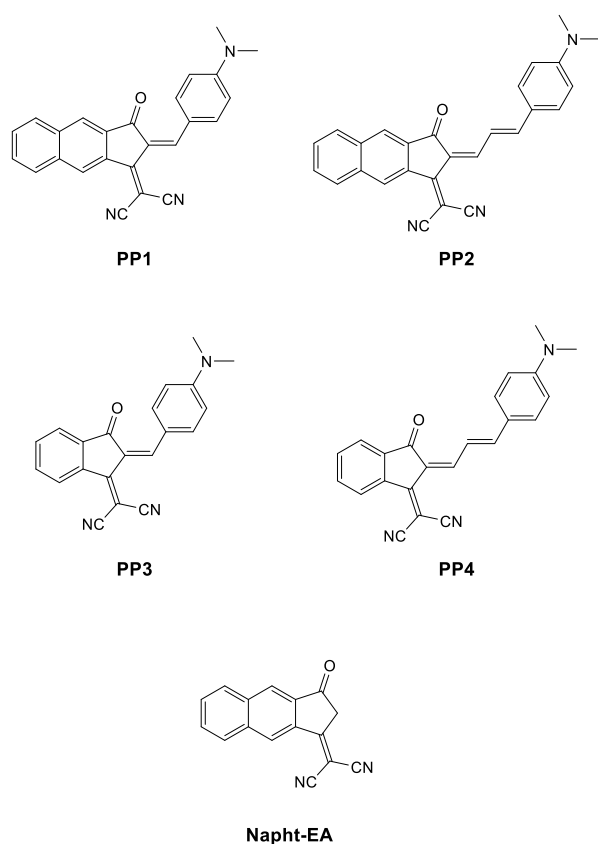
**Keywords:** Knoevenagel reaction • piperidine • push-pull • electron acceptor • electron donor

## Introduction

During the past decades, push-pull dyes have been extensively studied with regards to their numerous applications ranging from sensors,<sup>[1,2]</sup> energy conversion,<sup>[3,4]</sup> field effects transistors,<sup>[5,6]</sup> organic light-emitting diodes,<sup>[7,8]</sup> nonlinear optics<sup>[9,10]</sup> or photoinitiators of polymerization.<sup>[11-15]</sup> To access to these structures consisting in an electron donor connected to an electron acceptor by mean of a conjugated or none-conjugated spacer, the Knoevenagel reaction is undoubtedly the most popular reaction, opposing an aldehyde with an electron acceptor bearing an activated methylene group, in the presence of a catalytic amount of a base. Popularity of this reaction also arises from the facile availability of electron acceptors possessing activated methylene groups and malononitrile, indane-1,3-dione derivatives, (thio)barbituric derivatives, Meldrum derivatives, 1,1,3-tricyano-2-substituted propenes, isoxazolones, hydantions and rhodanines, and dicyanovinyl-thiophen-5-ylidenes can be cited as the most widely studied.<sup>[16,17]</sup> Interest for this reaction also originates from the easy work-up following the synthesis of the dyes. Indeed, the reaction is classically done by refluxing the reagents in ethanol and use of alcohols as solvents favors the precipitation of the dyes upon cooling. As a result, the expected products can be generally recovered in pure form by a simple filtration on a glass filtrate.

Among amines, piperidine is the most widely used.<sup>[18,19]</sup> In this field, the first condensation of benzaldehyde with ethyl acetoacetate in the presence of piperidine was reported as soon as 1896 by Knoevenagel providing the product in 95% yield.<sup>[20]</sup> In this work, an unprecedented nucleophilic attack of piperidine during a Knoevenagel reaction with 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*] naphthalen-1-ylidene)malononitrile **Napht-EA** was evidenced (See Figure 1). It has to be noticed that only few materials have been designed with **Napht-EA**, despite its extended **core** that makes it an ideal electron-withdrawing candidate for the design of materials for photovoltaic applications. In this field, the preliminary results revealed **Napht-EA** to be promising as a non-fullerene electron acceptor for the design of push-pull materials for energy conversion, justifying the development of new structures.<sup>[21-23]</sup> The low availability of **Napht-EA**-based push-pull dyes also originates from the difficult access to **Napht-EA** so that a careful optimization of the reaction conditions was required to prepare the different dyes. After optimization, **Napht-EA** could be prepared with reaction yield as high as 91% yield. To avoid the nucleophilic attack on **Napht-EA**, a non-nucleophilic base i.e. diisopropylethylamine (DIPEA) was used and the two targeted push-pull dyes **PP1** and **PP2** could be finally obtained in high yields. To evidence the benefits of the polyaromatic nature of **Napht-EA**, push-pull analogues **PP3** and **PP4** based on indane-1,2-dione derivatives were designed and synthesized for

comparison (See Figure 1). The optical and electrochemical properties of the different dyes were examined. To support the experimental results, theoretical calculations were carried out.



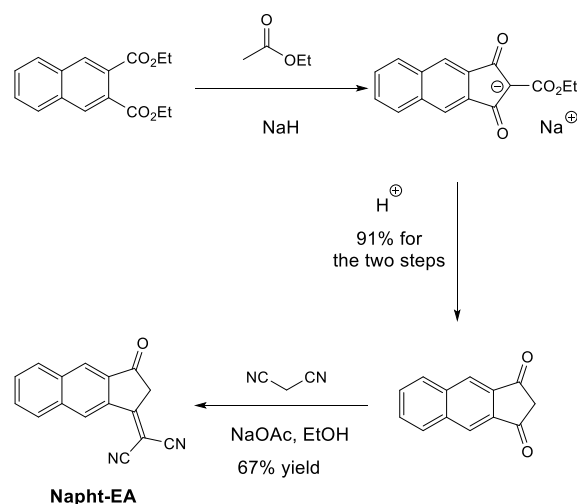
**Figure 1.** Chemical structures of **PP1-PP4** and the electron acceptor **Napht-EA**.

## Results and Discussion

### 1- Synthesis of **Napht-EA**.

The precursor of **Napht-EA** i.e. 1H-cyclopenta[b]naphthalene-1,3(2H)-dione was synthesized by introducing several modifications to the procedure previously reported in the literature, in 1973.<sup>[24]</sup> Typically, 1H-cyclopenta[b]naphthalene-1,3(2H)-dione can be prepared in a two-steps synthesis, by decarboxylation of the intermediate sodium salt under acidic conditions, this intermediate being obtained by a Claisen condensation of ethyl acetate with diethyl naphthalene-2,3-dicarboxylate (See Scheme 1). As the first improvement, an increased amount of sodium hydride was used for the first step (2.5 eq. vs. 1.45 eq. in the literature), this reaction being carried out without solvents. Indeed, the reagent i.e. ethyl acetate also acts as the solvent and this latter was introduced in a sufficient quantity (0.6 mL/mmol) to suspend diethyl naphthalene-2,3-dicarboxylate, producing rapidly a sticky paste upon heating. By

increasing the volume of ethyl acetate, a dramatic reduction of the reaction yield was observed.



**Scheme 1.** Synthetic scheme of **Napht-EA**.

Second, by increasing the decarboxylation time from 20 min. to 90 min., the reaction yield could be improved up to 91% for the two steps, significantly higher than that previously reported in the literature (65% yield). By condensation of malononitrile on 1H-cyclopenta[b]naphthalene-1,3(2H)-dione under basic conditions, **Napht-EA** could be obtained in 67% yield.

### 2- Synthesis of **PP1-PP4**.

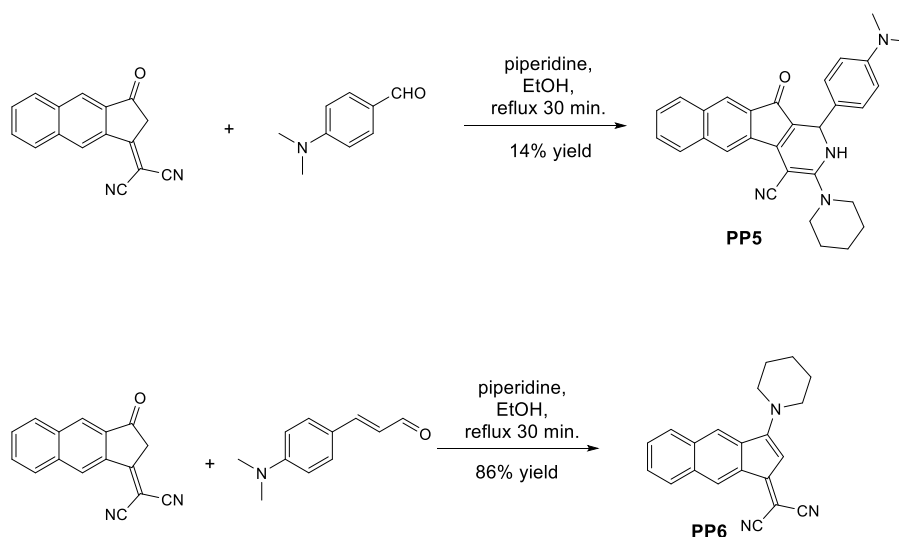
As already mentioned, the first attempts to prepare **PP1** and **PP2** consisted in refluxing for 30 min. an equimolar amount of 4-dimethylamino-benzaldehyde or 3-(4-(dimethylamino)phenyl)acrylaldehyde with **Napht-EA** in the presence of piperidine. Surprisingly, in the two cases, none of the expected dyes **PP1** or **PP2** were obtained (See Scheme 2). In the first case, a red solid **PP5** was formed, corresponding to the nucleophilic addition of piperidine onto **PP1** followed by a cyclization reaction. **PP5** was isolated after purification in 14% yield. The formation of 3-(dialkylamino)-1,2-dihydro-9-oxo-9H-indeno[2,1-c]pyridine-4-carbonitrile derivatives has been previously reported in the literature by Landmesser *et al.* on 3-(dicyanomethylidene)indan-1-one, using the same reaction conditions.<sup>[25]</sup> Conversely, while opposing 3-(4-(dimethylamino)phenyl)acrylaldehyde to **Napht-EA**, an unexpected product was formed (**PP6**) whose structure was determined by proton nuclear magnetic resonance ( $^1H$  NMR). As shown in the Figure 2, no presence of the dimethylaminophenyl group was found in the  $^1H$  NMR spectrum of **PP6**. On the opposite, two sets of signals at 1.85 and 3.86 ppm corresponding to a piperidine adduct and a singlet at 5.87

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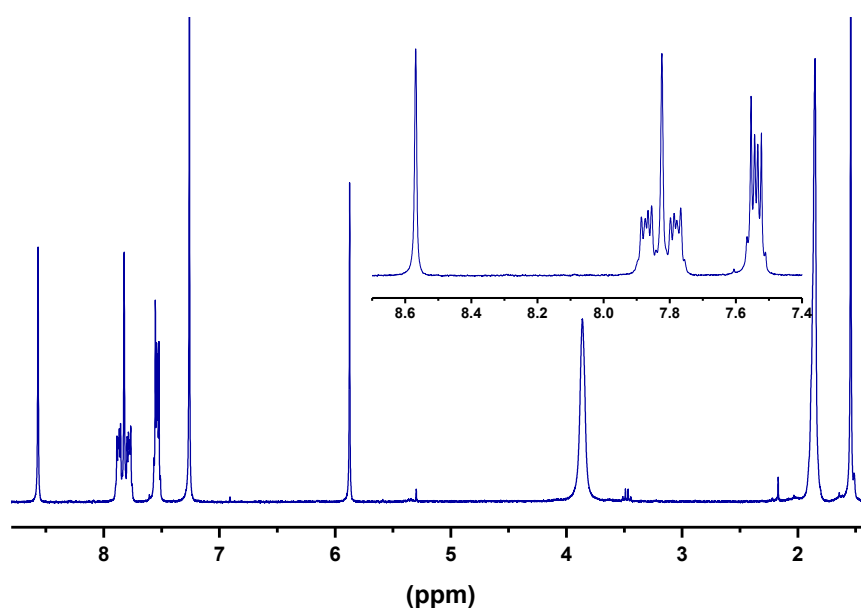
ppm integrating for one proton were detected. The exact chemical structure of **PP6** could be determined by X-Ray diffraction (XRD) analyses done on single crystals grown by slow evaporation of chloroform. As evidenced in the [Figure 3](#), an addition of piperidine onto the **Napht-EA** scaffold could be clearly evidenced. Face to these considerations and to avoid the addition of piperidine on **PP1** (resulting in the formation of **PP5**) or on **Napht-EA** (producing **PP6**), a non-nucleophilic base was used. Using DIPEA, **PP1** and **PP2** could be isolated in 68 and 44% yield respectively. For further comparison of the photophysical properties of **PP1** and **PP2**, **PP3** and **PP4** were synthesized starting from 3-(dicyanomethylidene)indan-1-one as the electron acceptor and isolated in pure form with reaction yields of 55 and 45% respectively ([See Scheme 3](#)).

### 3- UV-visible absorption and photoluminescence spectroscopy

The optical properties of the different dyes reported in this work were examined in chloroform. Due to the reduced solubility of **PP1** and **PP2** in most of the common organic solvents, no investigation of the solvatochromic properties could be carried out. Besides, a series of conclusions can nevertheless be established. A summary of the main absorption characteristics is provided in the Table 1. As evidenced in the Figure 4a, all dyes displayed a main transition centered in the visible range corresponding to the intramolecular charge transfer band (ICT) of the chromophore. A significant red-shift of the ICT bands upon elongation of the conjugated spacer between the electron donating and the electron-accepting groups could be demonstrated with **PP2** and **PP4** compared to **PP1** and **PP3** respectively.

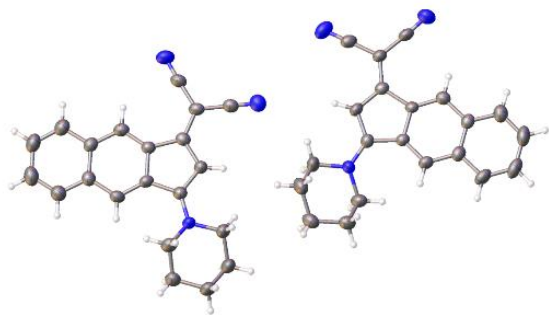
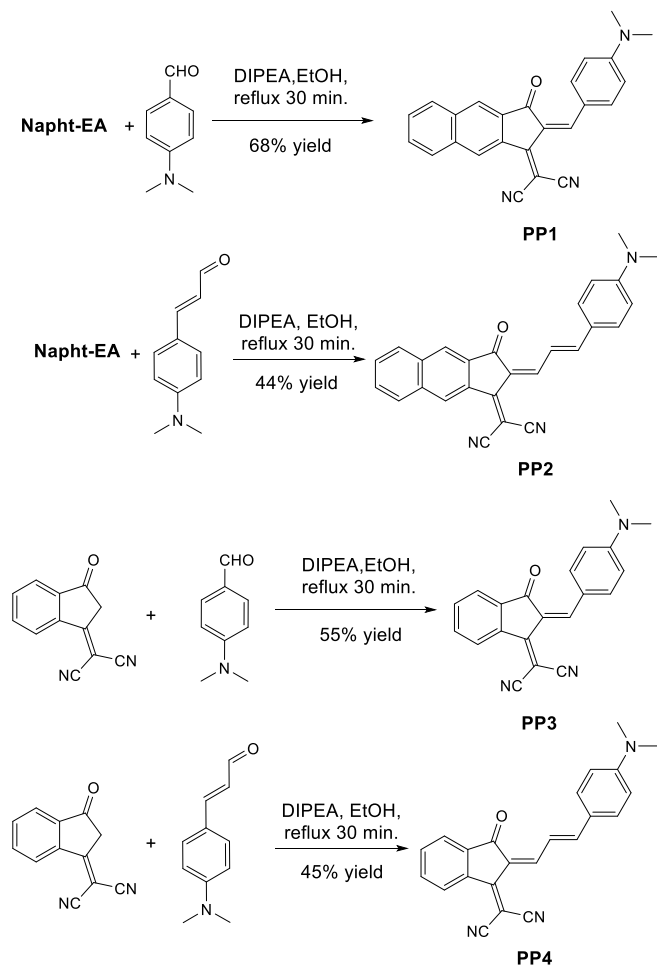


**Scheme 2.** Synthetic scheme of **PP5** and **PP6**.



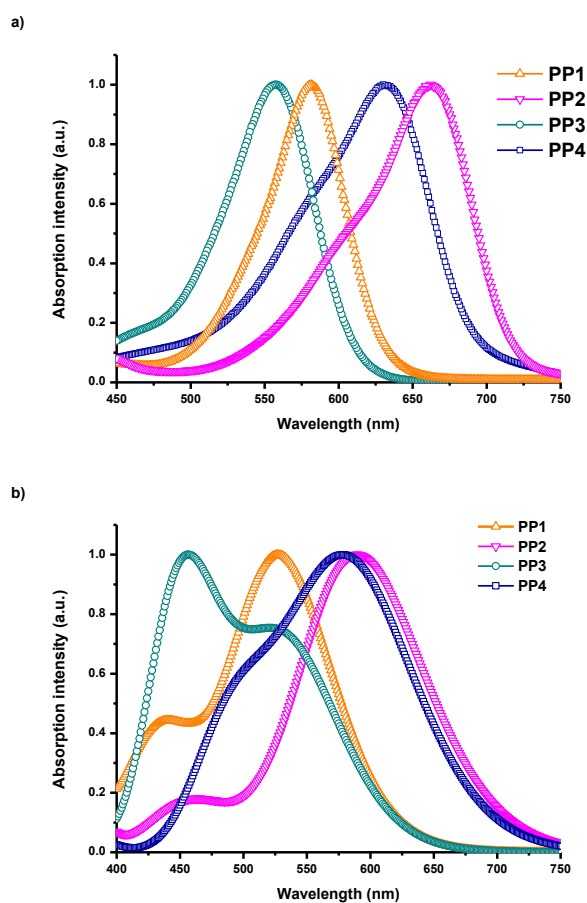
**Figure 2.** <sup>1</sup>H NMR spectrum of **PP6** in CDCl<sub>3</sub> (7.26 ppm) (left).




**Figure 3.** X-ray crystal structure of **PP6**

**Scheme 3.** Synthetic route to **PP1-PP4**.

Notably, a red-shift as high as 80 nm for **PP2** and 70 nm for **PP4** could be found, relative to **PP1** and **PP3** respectively. This is consistent with an improvement of the electron-donating ability of the electron donors by extending the  $\pi$ -conjugation.<sup>[26]</sup> As evidenced in the Figure 5, the highest occupied molecular orbital (HOMO) comprises both the dimethylaminobenzene group as well as the conjugated spacer. Conversely, the lowest unoccupied molecular orbital (LUMO) extends over the whole molecule. As a result of this, a destabilization of the HOMO energy levels is observed in **PP2** and **PP4**. Parallel to this, an improvement of the molar extinction

coefficient with the conjugation extension and therefore the oscillator strength was also demonstrated (See Table 1).<sup>[27]</sup> While comparing the dyes at constant electron donors, a red-shift of 30 nm was found for all dyes prepared with **Napht-EA** (**PP1** vs. **PP3**, **PP2** vs. **PP4**), consistent with an improved electron-withdrawing ability of **Napht-EA** relative to 3-(dicyanomethylidene)indan-1-one. Comparison of the theoretical UV-visible absorption spectra with the experimental ones revealed the order of the dyes to be the same even if a blue-shift by about 100 nm was found for all theoretical spectra relative to the experimental ones.


**Figure 4.** Experimental (a) and theoretical (b) UV-visible absorption spectra of **PP1-PP4**. Experimental spectra were recorded in chloroform.

This is attributable that the solvent effect which is incorrectly considered during the calculations. A summary of the main transitions involved in the ICT bands is provided in the table 2. As classical observed for push-pull dyes, the ICT bands of **PP1-PP4** mostly arise from a HOMO  $\rightarrow$  LUMO transition, even if a non-negligible contribution of the HOMO  $\rightarrow$  LUMO+1 transition is also found for **PP3**. Finally, comparison of the theoretical and experimental HOMO-LUMO gaps showed a good agreement (See Table 2).

**Table 1.** UV-visible absorption characteristics of the different dyes in chloroform ( $C = 5 \times 10^{-3}M$ )

dyes	PP1	PP2	PP3	PP4	PP5	PP6
$\lambda_1^a$	310 (16300)	330 (12350)	367 (4900)	304 (17100)	323 (25400)	332 (16500)
$\lambda_2$	330 (14500)	351 (sh) (7400)	559 (28150)	630 (37500)	333 (26700)	345 (18050)
$\lambda_3$	395 (6300)	421 (3450)			366 (4300)	363 (13100)
$\lambda_4$	421(sh) (5200)	663 (23200)			388 (5700)	396 (7600)
$\lambda_5$	580 (33350)				415 (6100)	422 (9150)
$\lambda_6$					595 (3850)	473 (sh) (13650)
$\lambda_7$						502 (17400)
$\lambda_8$						536 (sh) (11300)

<sup>a</sup> Wavelength are given in nm. Values in brackets correspond to the molar extinction coefficients at the corresponding wavelength.

**Table 2.** Simulated absorption characteristics of **PP1-PP4** in dichloromethane and comparison of the theoretical and experimental HOMO-LUMO gaps.

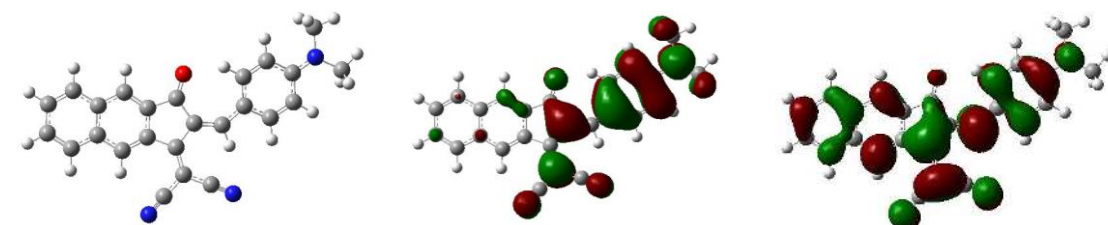
dyes	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	$\lambda_{max}$ (nm)	$\Delta E_{th}$ (eV)	$\Delta E_{opt}^a$ (eV)	$\Delta E_{CV}^b$ (eV)	Transitions
<b>PP1</b>	- 4.611	- 2.471	437 (sh), 526	2.36	1.94	1.75	HOMO->LUMO (100%)
<b>PP2</b>	- 4.450	- 2.542	591	2.09	1.70	1.44	HOMO->LUMO (100%)
<b>PP3</b>	- 4.636	- 2.432	456, 525 (sh)	2.36	2.00	1.86	HOMO->LUMO (91%) HOMO-> LUMO+1 (8%)
<b>PP4</b>	- 4.468	- 2.497	497 (sh), 577	2.15	1.74	1.52	HOMO->LUMO (95%) HOMO-> LUMO+1 (5%)

<sup>a</sup> determined from the onset of the absorption band in the UV-visible absorption spectrum. <sup>b</sup> determined by cyclic voltammetry

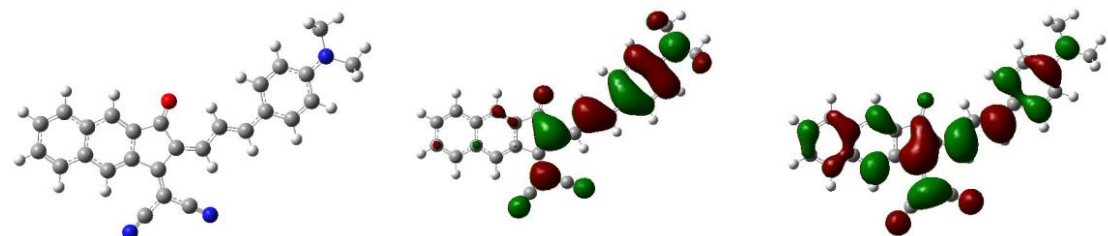
**Compounds**

**HOMO**

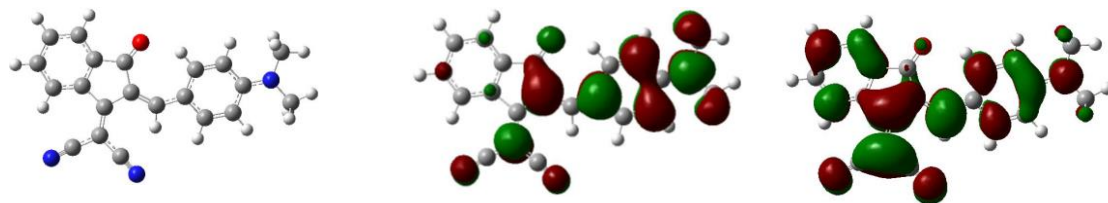
**LUMO**



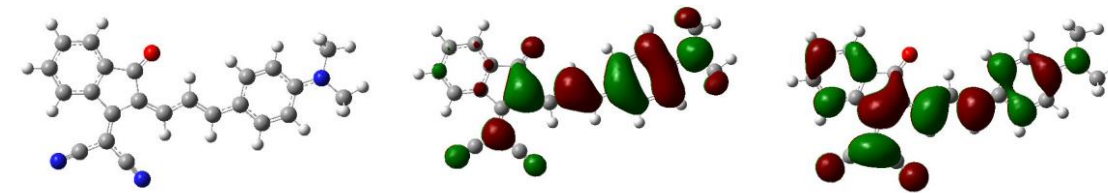
**PP1**

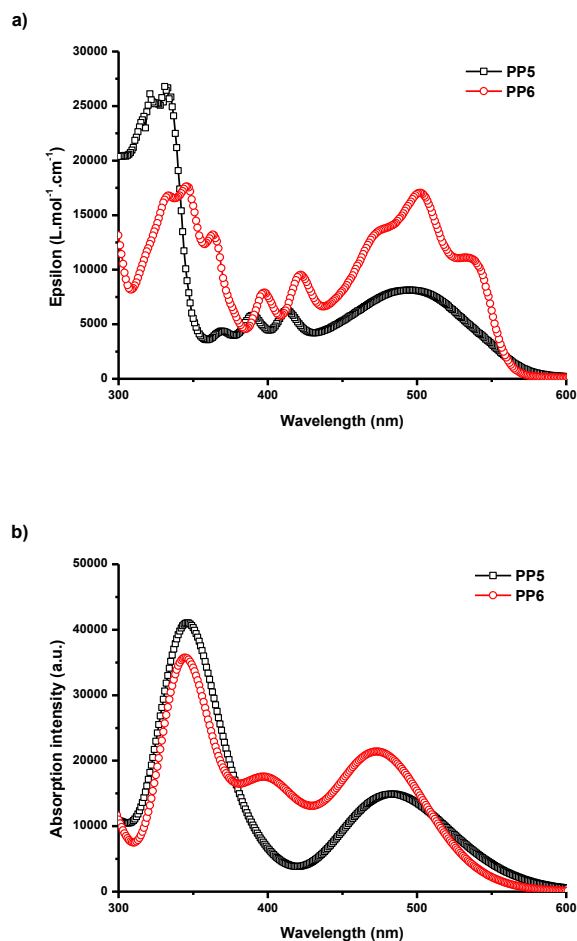


**PP2**



**PP3**



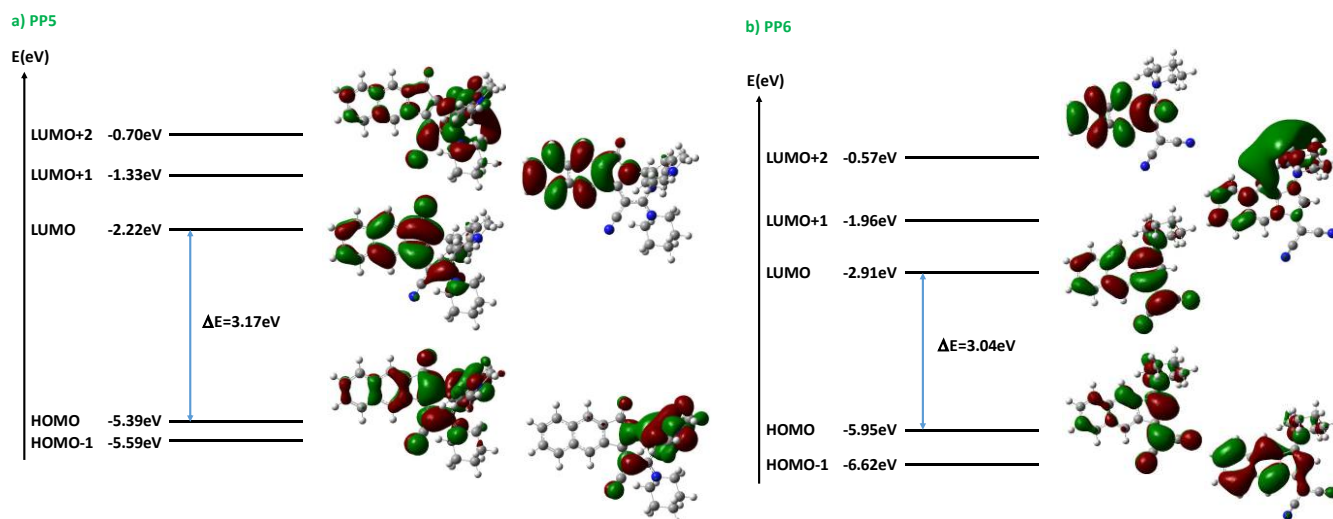
**Figure 5.** Optimized geometries and contour plots of the HOMO and LUMO energy levels for the push-pull dyes **PP1-PP4**.

**Figure 6.** UV-visible absorption spectra of **PP5** and **PP6** in chloroform (a) and the theoretical UV-visible absorption spectra (b).

More complex UV-visible absorption spectra were found for **PP5** and **PP6** in chloroform solutions. As shown in the Figure 6, numerous

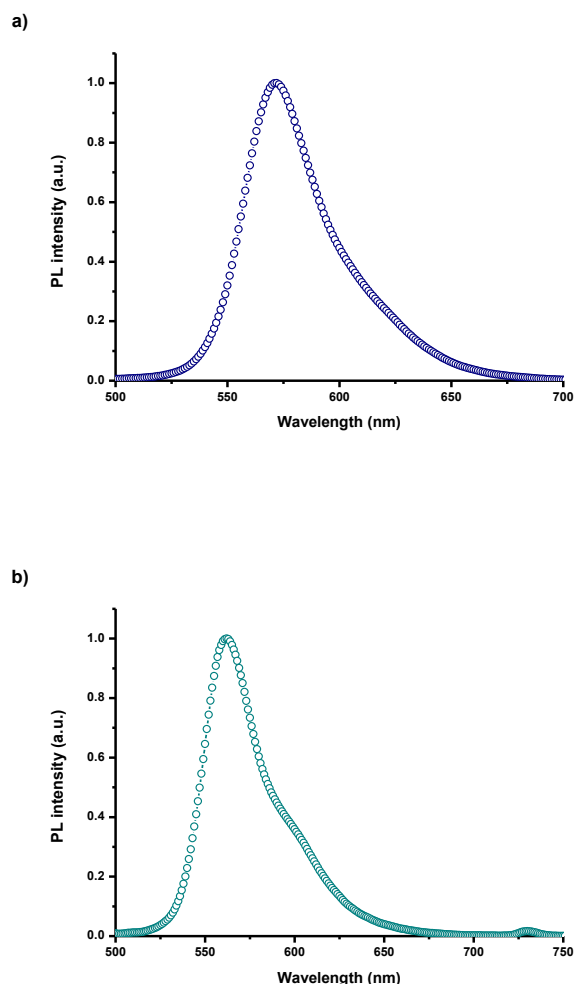
transitions can be found in the visible range, at 413 and 496 nm for **PP5**, 420, 472, 502 and 537 nm for **PP6** respectively. Theoretical calculations revealed these transitions to have numerous origins (see Table 3 and Figure 7). Besides the complexity of the transitions involved in the two spectra, a good accordance between the theoretical and the experimental spectra were found. Among the series of dyes investigated in this study, only **PP5** and **PP6** were photoluminescent and their emission spectra are presented in the Figure 8. The two spectra were obtained upon excitation of the molecules at 490 nm in chloroform. Despite the major difference of structures between **PP5** and **PP6**, similar emission wavelengths were found for the two compounds. A maximum emission at 571 and 561 nm were respectively determined for **PP5** and **PP6**.

**Table 3.** Simulated absorption characteristics of **PP5** and **PP6** in dilute dichloromethane.

dyes	Wavelength (nm)	Oscillator Strength	Major contributions	Minor contributions
<b>PP5</b>	505.97	0.0957	HOMO->LUMO (95%)	HOMO-1->LUMO (3%)
	472.10	0.1543	HOMO-1->LUMO (94%)	HOMO->LUMO (4%)
	387.22	0.0857	HOMO-2->LUMO (69%) HOMO-1->LUMO+1 (11%) HOMO->LUMO+1 (12%)	HOMO-3->LUMO (3%)
<b>PP6</b>	474.18	0.3133	HOMO->LUMO (92%)	HOMO-2->LUMO (7%)
	399.33	0.2441	HOMO-1->LUMO (88%)	HOMO->LUMO+1 (8%)



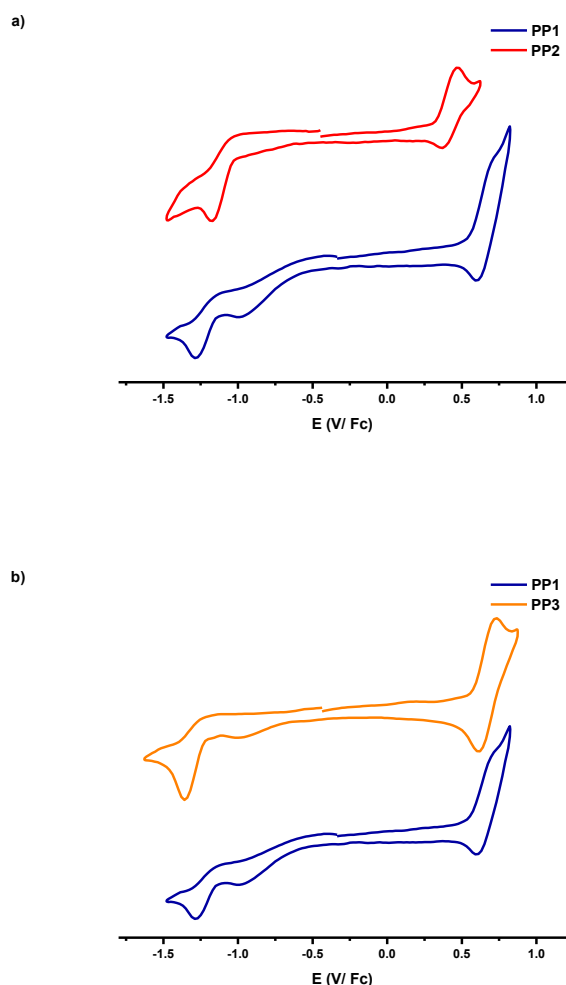
**Figure 7.** Optimized geometries and contour plots of the HOMO and LUMO energy levels for the push-pull dyes **PP5**, **PP6**. Energy diagrams for **PP5** and **PP6**.



**Figure 8.** Fluorescence spectra of **PP5** and **PP6** in chloroform recorded upon photoexcitation at 490 nm.

#### 4- Cyclic voltammetry

As mentioned in the introduction section, push-pull dyes can find applications in numerous research fields and their scope of applicability is greatly dominated by their electrochemical properties. Notably, in Organic Electronics, determination of the position of their respective HOMO and LUMO energy levels is of crucial importance to elaborate devices and select materials for the adjacent layers perfectly matching their energy levels. The electrochemical properties of **PP1-PP6** were investigated by cyclic voltammetry, in dichloromethane. The redox potentials were calibrated against Ferrocene/Ferrocenium as the internal reference and a summary of the electrochemical properties are given in the Table 4. Figure 9 depicts the voltammograms of **PP1**, **PP2** and **PP3** in dichloromethane solutions containing tetrabutylammonium perchlorate as the supporting electrolyte. As shown in Figure 9a, **PP1** and **PP2** exhibited a reversible single-electron oxidation process and irreversible reduction peaks. Reduction of the oxidation potential for **PP2** compared to **PP1** is consistent with an easier oxidation process facilitated by the elongation of the electron donor.<sup>[28-31]</sup> Similarly, the mono-electronic reduction processes in **PP1** and **PP2** were affected by the elongation of the spacer. At similar electron acceptor, the reduction of **PP2** was observed at a less cathodic potential by ca. 200 mV compared to that of **PP1**. Thus, the irreversible reduction of **PP2** was thus observed at  $-1.16\text{V}$  contrarily to  $-1.26\text{V}$  for **PP1**.



**Figure 9.** Cyclic voltammogram of **PP1**, **PP2** and **PP3** in dichloromethane solutions ( $10^{-3}$  M) with tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte. Scan rate: 100 mV/s.

**Table 4.** Summary of the electrochemical properties of **PP1-PP6**.

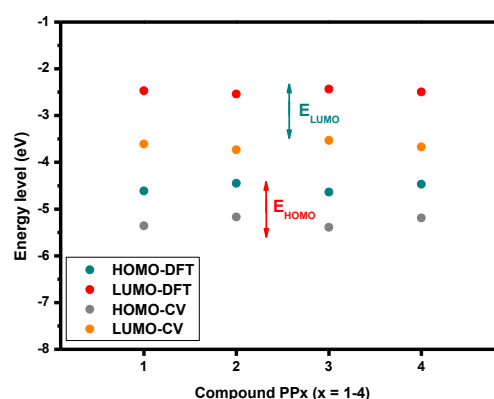
dyes	$E_{\text{red}}^a$	$E_{\text{Red(Onset)}}^a$	$E_{\text{ox}}^{a,c}$	$E_{\text{Ox(Onset)}}^{a,c}$	$E_{\text{HOMO}}^b$	$E_{\text{LUMO}}^b$
<b>PP1</b>	-1.264 <sup>irr</sup>	-1.19	0.664	0.56	-5.36	-3.61
<b>PP2</b>	-1.155 <sup>irr</sup>	-1.07	0.418	0.37	-5.17	-3.73
<b>PP3</b>	-1.341 <sup>irr</sup>	-1.27	0.667	0.59	-5.39	-3.53
<b>PP4</b>	-1.206 <sup>irr</sup>	-1.13	0.450	0.39	-5.19	-3.67
<b>PP5</b>	-1.409	-1.15	0.323 <sup>irr</sup>	0.23	-5.03	-3.65
<b>PP6</b>	-1.482	-1.43	0.598 <sup>irr</sup>	0.48	-5.52	-3.37
			0.832 <sup>irr</sup>	0.72		

<sup>a</sup> All potentials are given in V. <sup>b</sup>  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  are given in eV. <sup>c</sup> Onset oxidation and reduction potentials versus ferrocene ( $E_{\text{(onset)}}$  vs. Fc).  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  were determined from the formulas :  $E_{\text{HOMO}} = -4.8 - E_{\text{ox(onset)}}$  vs. Fc and  $E_{\text{LUMO}} = -4.8 - E_{\text{red(onset)}}$  vs. Fc

As evidenced in the Figure 5, the LUMO levels of **PP1** and **PP2** extend nonetheless over the electron-accepting part, but also on the whole molecule. As a result of this, **Napht-EA** is less acceptor in **PP1** than in **PP2** due to the closer proximity of the electron donating

group, adversely affecting its electron-withdrawing ability. Generally, the opposite trend consisting in a cathodic shift of the reduction potential with elongation of the  $\pi$ -conjugated length is reported in the literature.[32] Remarkable examples of this were notably reported with strong electron acceptors such as poly(nitrofluorene).[33] However, in these different works, the LUMO level doesn't extend over the whole molecule, and HOMO and LUMO levels respectively centered onto the electron donor and the electron acceptor are observed. The situation differs for **PP1** and **PP2**, for which the HOMO levels are localized onto the electron donor and the LUMO levels extend over the whole molecule. When a spacer is introduced, the distance isolates the electron acceptor from the donor so that a decrease of its reduction potential is observed.

While comparing **PP1** and **PP3** which differs by their electron acceptor (See Figure 9b), a decrease of the reduction potential by ca. 100 mV could be observed for **PP1** which comprises the most electron-withdrawing group. From the cyclic voltammograms and based on the oxidation and reduction potentials of **PP1-PP4**, an experimental determination of their HOMO and LUMO energy levels was possible.[34,35] As shown in the Figure 10 and in Table 4, a good agreement between the experimental and the theoretical values can be found. If a difference of 0.2 eV and 0.4 eV could be respectively found between the experimental and the theoretical values for the HOMO and the LUMO levels, variations of the theoretical HOMO and LUMO energy levels followed the same trend than that observed for the experimental ones.



**Figure 10.** Comparison of the theoretical and experimental HOMO and LUMO energy levels for **PP1-PP4**.

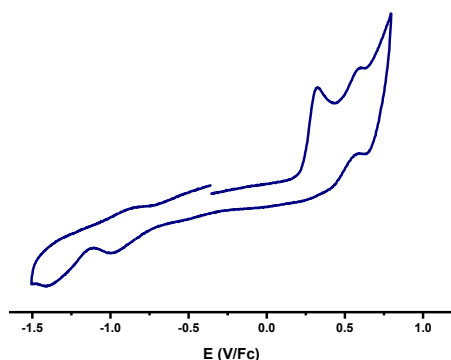
Finally, the electrochemical properties of **PP5** and **PP6** were also examined. Only irreversible oxidation and reduction processes could be detected for **PP5**. Concerning the oxidation, two monoelectronic processes were detected at 0.82V and 1.08 V whereas reduction

processes were detected at -0.49V and -0.92V (See Figure 11a).

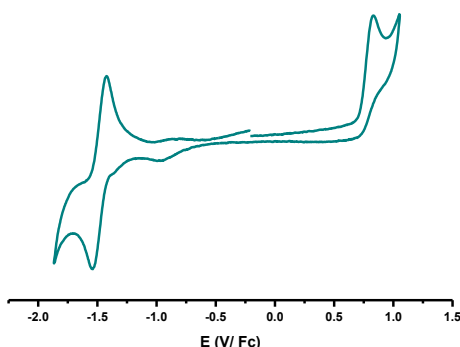
Conversely, for **PP6**, an irreversible oxidation process was detected at 0.82V, what is significantly higher than that observed for **PP1-PP4**.

This is consistent with an oxidation centered on the amine moiety, and the easier oxidation of the aromatic amines compared to the aliphatic ones. A reversible reduction process was also detected at -1.48V i.e. at a potential lower than that observed for **PP1-PP4** (See Figure 11b).

a)



b)



**Figure 11.** Cyclic voltammogram of **PP5** (a) and **PP6** (b) in dichloromethane solutions ( $10^{-3}$  M) with tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte. Scan rate: 100 mV/s.

## Conclusions

To conclude, a series of push-pull dyes differing by their electron donating and electron-withdrawing groups have been designed and synthesized. Surprisingly, choice of the amine was determined as being crucial in order to prepare the different dyes **PP1-PP4**. While using the standard piperidine as a base for the Knoevenagel reaction, none of the targeted dyes **PP1** and **PP2** could be obtained but products (**PP5** and **PP6**) resulting from the nucleophilic addition of piperidine on both the electron acceptor or the push-pull dye **PP1** formed intermediately. This issue could be addressed by replacing piperidine by diisopropylethylamine. With regards to the optical and

electrochemical properties of **PP1** and **PP2**, **Napht-EA** is a remarkable electron acceptor for future developments of dyes with applications ranging from energy conversion to nonlinear optical applications. The development of new dyes is currently under progress and will be presented in forthcoming publications.

## Experimental Section

### General informations

All reagents and solvents were purchased from Aldrich, Alfa Aesar or TCI Europe and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole:  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  (100 MHz). The  $^1\text{H}$  chemical shifts were referenced to the solvent peak  $\text{CDCl}_3$  (7.26 ppm) and the  $^{13}\text{C}$  chemical shifts were referenced to the solvent peak  $\text{CDCl}_3$  (77 ppm). 2-(3-Oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile [36] and 3-(4-(dimethylamino)phenyl)acrylaldehyde [37] were synthesized as previously reported in the literature, without modification and in similar yields. UV-visible absorption spectra were recorded on a Varian Cary 50 Scan UV Visible Spectrophotometer, with concentration of  $5 \times 10^{-3}$  M, corresponding to diluted solutions. Fluorescence spectra were recorded using a Jasco FP 6200 spectrometer. The electrochemical properties of the investigated compounds were measured in dichloromethane by cyclic voltammetry, scan rate 100 mV/s, with tetrabutylammonium perchlorate (0.1 M) as a supporting electrolyte in a standard one-compartment, three-electrode electrochemical cell under an argon stream using a VSP BioLogic potentiostat. The working, pseudo-reference and counter electrodes were platinum disk ( $\varnothing = 1$  mm), Ag wire, and Au wire gauze, respectively. Ferrocene was used as an internal standard, and the potentials are referred to the reversible formal potential of this compound. DFT calculations [38] employing the B3LYP functionals [39,40] and 6-311+G(d,p) basis set were performed with a Gaussian 09 program.[41] The geometry optimizations for all the molecules were carried out without symmetry constraints and were followed by frequency calculations. The spectroscopic properties of the molecules were calculated by mean of a time dependent density functional theory method

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(TDDFT).<sup>[42-46]</sup> Up to 10 excited states were calculated and the theoretical absorption bands were obtained by considering a band half-width at half-maximum of 0.2 eV.<sup>[47]</sup> The assignment of electronic transitions for  $\lambda_{\text{max}}$  has been determined with GaussSum 3.0 software.<sup>[48]</sup> [CCDC-1907964](https://www.ccdc.cam.ac.uk/data_request/cif) contains the supplementary crystallographic data for this work. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](https://www.ccdc.cam.ac.uk/data_request/cif).

### Synthesis of the electron acceptors and push-pull dyes

#### 2-(3-Oxo-2,3-dihydro-1H-cyclopenta[b]naphthalen-1-ylidene)

##### malononitrile Napht-EA

In a dried two-necked 100 mL flask, 1H-cyclopenta[b]naphthalene-1,3(2H)-dione (1.1 g, 5.6 mmol) and malononitrile (2.2 g, 33.3 mmol) were dissolved in ethanol (25 mL), and then anhydrous sodium acetate (1.84 g) was slowly added while stirring. After stirring for 2 h, the reaction mixture was poured into ice-water, and acidified to pH 1–2 by the addition of concentrated hydrochloric acid. The resulting precipitate was collected by filtration and washed with water giving the crude product. It was finally purified with a flash chromatography to afford 916 mg of product (eluent : DCM). Yield = 67%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.85 (s, 2H), 7.79 (dd, 2H, J = 6.2 Hz, J = 3.2 Hz), 8.07-8.19 (m, 2H), 8.49 (s, 1H), 9.19 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 44.6, 112.3, 112.6, 125.8, 128.1, 130.5, 130.6, 130.7, 130.9, 135.8, 136.3, 136.4, 166.5, 195.3; HRMS (ESI MS) m/z: theor: 244.0637 found: 244.0640 ([M]<sup>+</sup> detected)

##### 1H-Cyclopenta[b]naphthalene-1,3(2H)-dione

Diethyl naphthalene-2,3-dicarboxylate (10.5 g, 38.5 mmol) was suspended in dry EtOAc (24 mL) and NaH 95% in oil (2.44 g, 96.4 mmol, 2.5 eq) was added. The reaction mixture was refluxed at 105°C for 5h. After cooling, the yellow solid was filtered off and thoroughly washed with a mixture of EtOH-Et<sub>2</sub>O 50/50. Treatment of this solid with 200 mL of a 1M HCl solution under reflux for 1h30 furnished a new solid. After cooling, the solid was filtered off, washed with water and recrystallized in toluene (200 mL) overnight. The product was obtained as a brown solid (6.87 g). Yield = 91%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.38 (s, 2H), 7.66-7.75 (m, 2H), 8.10-8.13 (m, 2H), 8.52 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 46.7, 124.3, 129.7, 130.6, 136.4, 138.2, 197.6; HRMS (ESI MS) m/z: theor: 196.0524 found: 196.0526 ([M]<sup>+</sup> detected)

##### General procedure for the synthesis of the push-pull dyes PP1-PP4.

#### 2-(3-Oxo-2,3-dihydro-1H-cyclopenta[b]naphthalen-1-ylidene) malononitrile

**Napht-EA** (0.62 g, 2.55 mmol) or 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (0.50 g, 2.55 mmol) and the appropriate aldehyde (4-dimethylaminobenzaldehyde (0.38 g) or 3-(4-(dimethylamino)phenyl)acrylaldehyde (0.45 g, 2.55 mmol, 1. eq.) were dissolved in absolute ethanol (50 mL) and a few drops of DIPEA were added. The reaction mixture was refluxed and progress of the reaction was followed by thin layer chromatography (TLC). After cooling, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum.

#### 2-(2-(4-(Dimethylamino)benzylidene)-3-oxo-2,3-dihydro-1H-cyclopenta[b]naphthalen-1-ylidene)malononitrile PP1

Yield = 68%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.23 (s, 6H), 6.77 (d, 2H, J = 9.2 Hz), 7.65-7.67 (m, 2H), 8.01-8.03 (m, 1H), 8.06-8.08 (m, 1H), 8.32 (s, 1H), 8.44 (d, 2H, J = 9.2 Hz), 8.57 (s, 1H), 9.14 (s, 1H); HRMS (ESI MS) m/z: theor: 376.1444 found: 376.1442 ([M+H]<sup>+</sup> detected); Anal. Calc. for C<sub>25</sub>H<sub>17</sub>N<sub>3</sub>O: C, 80.0; H, 11.2; O, 4.3; Found: C, 79.8; H, 11.3; O, 4.5 %

#### 2-(2-(3-(4-(Dimethylamino)phenyl)allylidene)-3-oxo-2,3-dihydro-1H-cyclopenta[b]naphthalen-1-ylidene)malononitrile PP2

Yield = 44%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.15 (s, 6H), 6.72 (d, 2H, J = 9.0 Hz), 7.46 (d, 1H, J = 14.8 Hz), 7.66-7.68 (m, 3H), 8.02-8.08 (m, 2H), 8.32 (s, 1H), 8.61 (d, 1H, J = 11.9 Hz), 8.78 (dd, 1H, J = 12.0 Hz, J = 14.6 Hz), 9.15 (s, 1H); HRMS (ESI MS) m/z: theor: 402.1601 found: 402.1600 ([M+H]<sup>+</sup> detected); Anal. Calc. for C<sub>27</sub>H<sub>19</sub>N<sub>3</sub>O: C, 80.8; H, 4.8; O, 4.0; Found: C, 80.6; H, 4.6; O, 4.1 %

#### 2-(2-(4-(Dimethylamino)benzylidene)-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile PP3

Yield = 55%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.19 (s, 6H), 6.74 (d, 2H, J = 9.2 Hz), 7.65-7.72 (m, 2H), 7.84-7.86 (m, 1H), 8.37 (d, 2H, J = 9.2 Hz), 8.62 (s, 1H), 8.64 (d, 1H, J = 8.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 40.2, 67.3, 111.5, 115.2, 115.4, 121.9, 122.6, 123.4, 124.7, 133.9, 134.4, 137.3, 139.1, 139.6, 148.2, 154.7, 163.5, 187.4; HRMS (ESI MS) m/z: theor: 326.3785 found: 326.3788 ([M+H]<sup>+</sup> detected).

#### 2-(2-(3-(4-(Dimethylamino)phenyl)allylidene)-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile PP4 <sup>[49]</sup>

Yield = 45%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.13 (s, 6H), 6.70 (d, 2H, J = 8.9 Hz), 7.39 (d, 1H, J = 14.7 Hz), 7.62 (d, 2H, J = 8.9 Hz), 7.68-7.71 (m, 2H), 7.85-7.88 (m, 1H), 8.51 (d, 1H, J = 11.9 Hz), 8.61-8.70 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 40.2, 67.3, 112.1, 115.1, 115.2, 120.1, 122.4,

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123.3, 123.9, 125.0, 132.5, 133.9, 134.5, 137.3, 139.9, 149.0, 153.3, 156.2, 160.3, 189.8; HRMS (ESI MS) m/z: theor: 352.1444 found: 352.1441 ([M+H]<sup>+</sup> detected).

### 1-(4-(Dimethylamino)phenyl)-11-oxo-3-(piperidin-1-yl)-2,11-dihydro-1H-benzo[5,6]indeno[2,1-c]pyridine-4-carbonitrile PP5

3-(4-(Dimethylamino)phenyl)acrylaldehyde (287 mg, 1.64 mmol, 1 eq.) and **Napht-EA** (400 mg, 1.64 mmol, 1 eq.) were introduced in a preheated solution of ethanol (40 mL). The selected amine (0.5 mL) was added in the former solution while boiling. Monitoring of the reaction was done by TLC and the solution was approximately refluxed for 30 min. Depending of the amine, upon cooling, a precipitate formed in most of the time. This solid was filtered off and discarded. Addition of Et<sub>2</sub>O in the filtrate furnished a precipitate that was filtered off, washed with ether and dried under vacuum. Yield = 14%. <sup>1</sup>H NMR (400 MHz, Acetone-d<sub>6</sub>) δ: 1.68-1.80 (m, 6H), 2.90 (s, 6H), 3.58-3.87 (m, 4H), 5.59 (d, 2H, J = 4.8 Hz), 6.71 (d, 2H, J = 8.8 Hz), 7.23 (d, 2H, J = 8.8 Hz), 7.48-7.61 (m, 2H), 7.74 (s, 1H), 7.93 (dd, 2H, J = 13.7 Hz, J = 7.5 Hz), 8.20 (s, 1H); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.72-1.75 (m, 6H), 2.90 (s, 6H), 3.50-3.57 (m, 2H), 3.62-3.68 (m, 2H), 5.57-5.60 (m, 2H), 6.67 (d, 2H, J = 8.5 Hz), 7.25 (d, 2H, J = 8.5 Hz), 7.40-7.48 (m, 2H), 7.71 (s, 1H), 7.77 (d, 1H, J = 7.6 Hz), 7.82 (d, 1H, J = 7.6 Hz), 8.18 (s, 1H); HRMS (ESI MS) m/z: theor: 461.2336 found: 461.2333 ([M+H]<sup>+</sup> detected); Anal. Calc. for C<sub>30</sub>H<sub>28</sub>N<sub>4</sub>O: C, 78.3; H, 6.1; O, 3.5; Found: C, 78.6; H, 6.2; O, 3.3 %

### 2-(3-(Piperidin-1-yl)-1H-cyclopenta[b]naphthalen-1-ylidene)malononitrile PP6

4-Dimethylaminobenzaldehyde (0.77 g, 5.15 mmol) and 2-(3-oxo-2,3-dihydro-1H-cyclopenta[b]naphthalen-1-ylidene)malononitrile **Napht-EA** (1.25 g, 5.15 mmol) were suspended in absolute ethanol (20 mL) and a few drops of piperidine were added. Immediately, the solution turned deep red. The flask was introduced in an oil bath preheated at 90°C. After 15 min, the reaction was ended (TLC control). During that time, an extremely insoluble precipitate was formed. After cooling, the precipitate was filtered off, washed several times with ethanol and ether, and dried under vacuum. Yield = 86%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.85 (brs, 6H), 3.86 (brs, 4H), 5.87 (s, 1H), 7.52-7.57 (m, 2H), 7.77-7.89 (m, 3H), 8.57 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 23.8, 26.1, 51.5, 56.9, 103.1, 116.9, 117.0, 123.7, 124.3, 128.40, 128.41, 129.5, 129.8, 133.1, 133.3, 133.5, 134.3, 161.8, 162.6; HRMS (ESI MS) m/z: theor: 312.1495 found: 312.1492 ([M]<sup>+</sup> detected)

## Supplementary Material

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/MS-number.CCDC-1907964> contains the supplementary crystallographic data for this work. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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## Author Contribution Statement

C.P., G.N. and F.D. conceived this work. C.P. and F.D. designed and executed the experimental work, analyzed the data and discussed the results. C.P. and G.N. realized the chemical characterizations and the photophysical analysis of the compounds. S.D. solved the crystal structures. S.P. carried out the theoretical calculations. M.N. and D.G. did a critical review of the manuscript. C.P., G.N. and F.D. contributed to writing and editing the manuscript.

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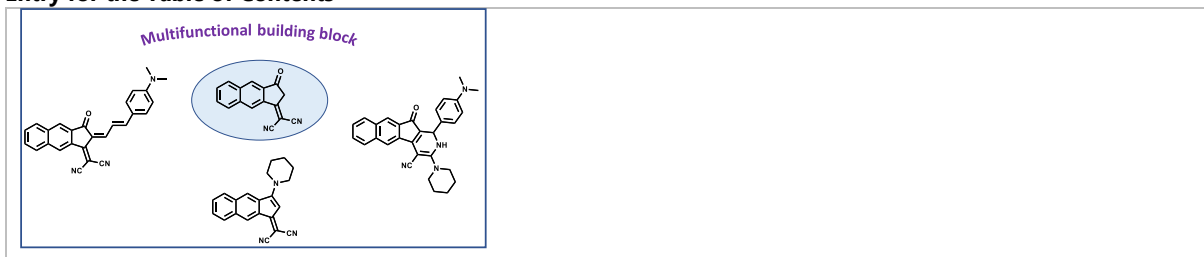
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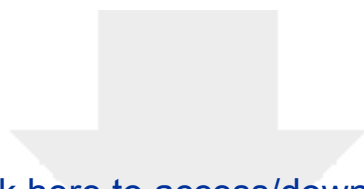


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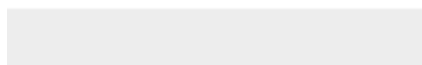
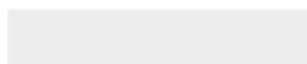




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