

Synthesis of a perylenediimide-fullerene C₆₀ dyad: A simple use of a nitro leaving group for a Suzuki-Miyaura coupling reaction

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Abstract

We describe herein a straightforward synthesis of a fullerene C₆₀ – perylenediimide (C₆₀-PDI) dyad. A simple and original cross-coupling Suzuki-Miyaura reaction was carried out using mononitro-bay substituted PDI as an electron-deficient aromatic system playing the role of electrophilic partner. Optical and electrochemical characterizations of this C₆₀-PDI dyad are also reported.

1. Introduction

Thanks to their exceptional high chemical, thermal and photochemical stability, perylenediimide (PDI) derivatives **1** are used as dyes and pigments [1,2]. With additional photophysical and photochemical properties characterized by high quantum yields of photoluminescence, PDI derivatives present potential applications as fluorescent dyes [3], near-IR dyes [4], molecular switches [5], dye lasers [6] and for water-soluble chromophores, the exploitation of their biocompatibility [7]. Moreover, their high electron affinity makes PDI derivatives strong electron acceptors with low lying LUMOs for utilization in organic electronics [8]. Additional interesting charge carrier mobilities [9] provide large prospects of these materials for investigations in organic solar cells [10–13]. Particularly, in order to take advantage of the solar spectrum coverage of the dye, intensive efforts have been devoted towards the synthesis of C₆₀-PDI dyads in the search of photoinduced electron and/or energy transfer processes. In most of the described examples, fullerene C₆₀ was attached at the imide position of the PDI [14–20] and these interesting super-absorbing fullerenes [21,22] could be used in organic solar cells [23]. Some other light-harvesting PDI-C₆₀ dyads were prepared as organic triplet photosensitizers with potential applications in photocatalysis, photooxidation and photodynamic therapy [24,25]. In a few examples, C₆₀ unit has been linked at the bay region of the PDI core [26–28]. Dyad systems **1a** [18] and **1b** [24] were synthesized starting from mono-bromoPDI derivative conveniently substituted at the imide position. The creation of a carbon–carbon bond is highly essential in organic chemistry for synthesizing more and more sophisticated molecules. Palladium-catalyzed coupling reactions are among the most popular and versatile carbon-carbon bond formation methods involving aromatic systems.

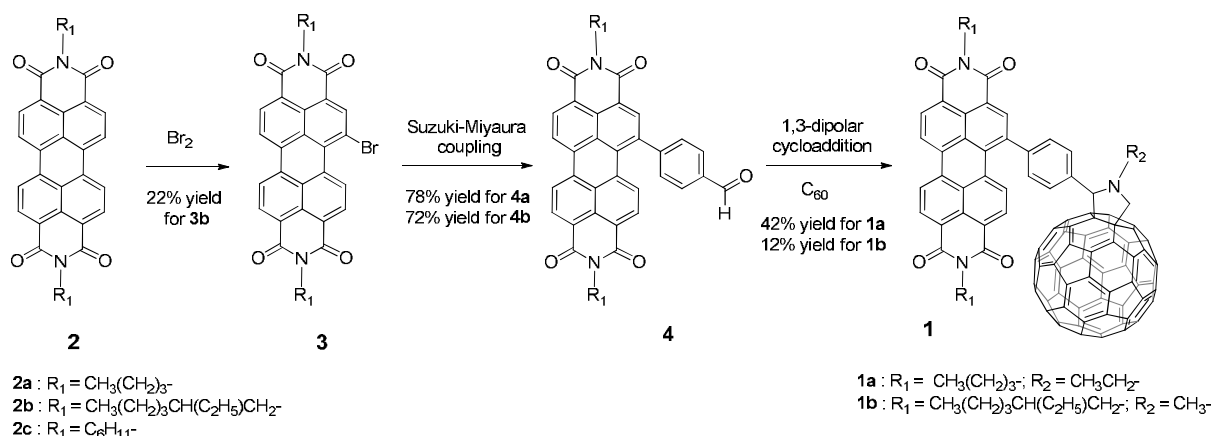
Usually, these reactions known as Heck, Suzuki-Miyaura, Negishi, Stille, Sonogashira reactions, depending on the hybridization of the carbon atom, are conventionally employing aryl halides as electrophilic coupling partners. Considering the Suzuki-Miyaura coupling (SMC), aromatic boron derivatives are playing the role of nucleophilic coupling partners. Very recently, the first Pd-catalyzed Suzuki-Miyaura reaction using nitroarene with the nitro group acting as the leaving group was reported [29]. Nevertheless, this new reaction was demonstrated using only nitrobenzene derivatives substituted with electron-donating groups. On the other hand, monohalogenation in the PDI series is considered as a difficult reaction to control because of the easy access to dibromo derivative. Moreover, the advantage of the nitro group results in an interesting better atom economy process. Consequently, we were interested in the investigation of the SMC applied in the PDI series using the nitro group as the electrophilic coupling partner. Herein we describe the synthesis of a PDI-C₆₀ dyad using as an intermediate reaction, an efficient and easy SMC from mono-nitroPDI as an electron poor aromatic starting material.

1. Results and discussion

1.1. Synthesis

N.R. Champness and coll. reported the synthesis and electrochemical studies of dyad **1a**. Starting from mono-bromoPDI **3a**, a SMC using 4-formylphenyl boronic acid in the presence of CsF, Ag₂O, Pd(PPh₃)₄ in THF yielded compound **4a** in 78% yield (Scheme 1). Further Prato reaction using C₆₀ and *N*-ethylglycine in refluxing toluene afforded dyad **1a** in 42% yield. J. Zhao and coll. described the synthesis of dyad **1b** and its detailed photophysical properties. Starting material **2b** was obtained in 77% yield by imidization reaction of perylene-3,4:9,10-tetracarboxylic acid dianhydride (PTCDA). Bromination of compound **2b** using Br₂ in CHCl₃ at room temperature gave corresponding PDI **3b** in 22% yield. The SMC was carried out using 4-formylphenyl boronic acid in the presence of Na₂CO₃, Pd(PPh₃)₄ in 2-methoxyethanol and water yielding compound **4b** in 72% yield. A modified Prato reaction using creatine and C₆₀ in refluxing toluene afforded dyad **1b** in lower 12% yield.

Concerning the bromination reaction, the low reactivity of PDI towards electrophiles was first demonstrated by H. Langhals and coll. Moreover, this bromination reaction suffers from its lack of selectivity with the concomitant introduction of a second bromine atom yielding to a mixture of 1,6- and 1,7-dibrominated PDI [31,32]. Compound **3c** with *N,N'*-dicyclohexyl groups was shown to be not accessible while upon reflux in CH₂Cl₂ for 4 days and only the mixture of 1,6- and 1,7-dibrominated regioisomers was obtained [32]. Very recently, PDI derivative **3c** was used as a starting material but its preparation was not described [33].

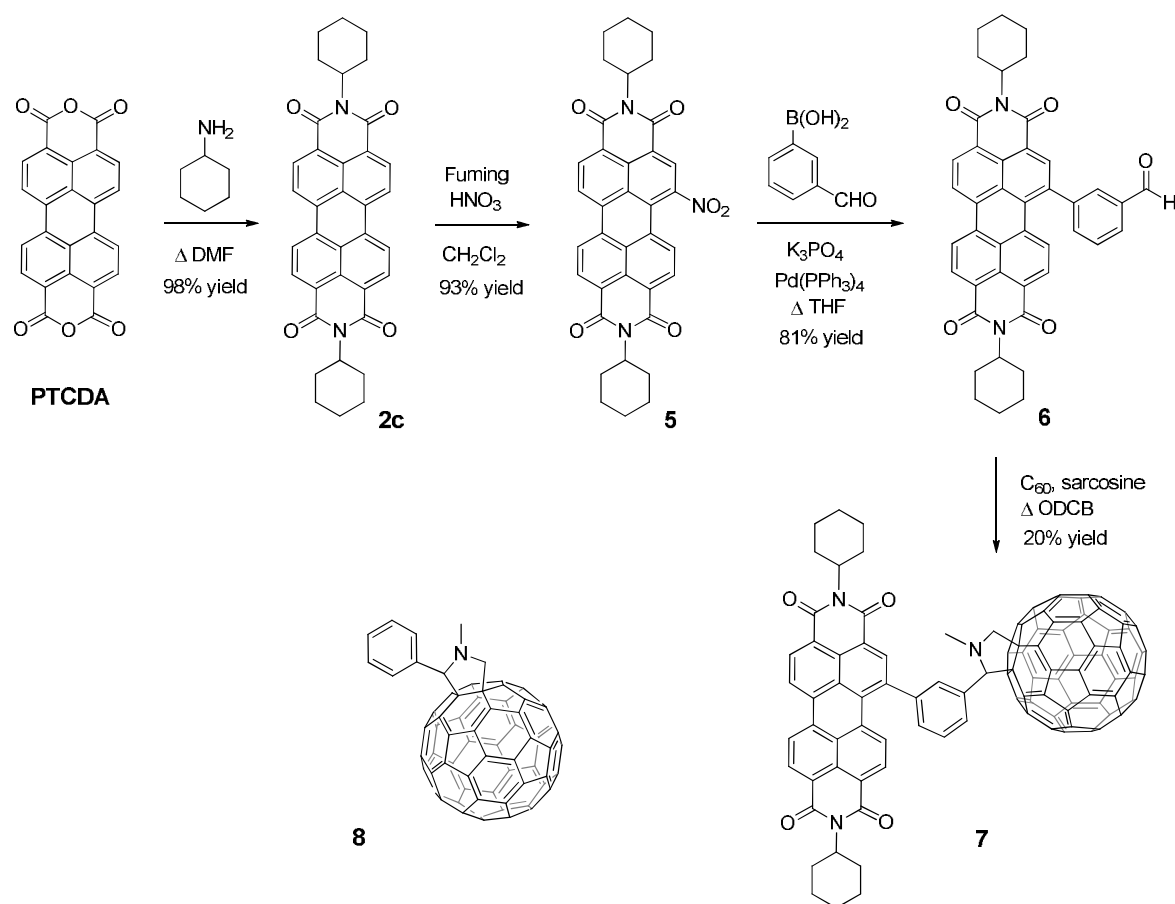


Scheme 1. Reported synthesis of dyads **1a-b**.

From all these considerations, we were interested in the access to mononitrated PDI derivative **5** and its potential use in the SMC reaction to reach target dyad **7** (Scheme 2). The mononitration reaction was effectively expected to be easier to control rather than monobromination, thanks to the inductive and mesomeric electron-withdrawing effects of the nitro group which sufficiently deactivates the PDI core towards the second electrophilic substitution. First, starting material PTCDA was transformed in 98% yield into compound **2c** by an imidization reaction using cyclohexylamine in refluxing DMF as a simplified and modified procedure than those reported [34–36]. Concerning the nitration reaction, we were not able to realize the nitration of compound **2c** by using HNO_3 0.1M in the presence of cerium ammonium nitrate (CAN) as described [37]. On the contrary, we have shown that the nitration reaction could be done using fuming nitric acid where the addition of CAN was not improving the yield or favoring the kinetic of the reaction [38]. We have succeeded in preparing mono-nitroPDI **5** in 93% yield (at room temperature and in short time) in a multigram scale without the need of purification using chromatographic techniques as a new simplified procedure [39].

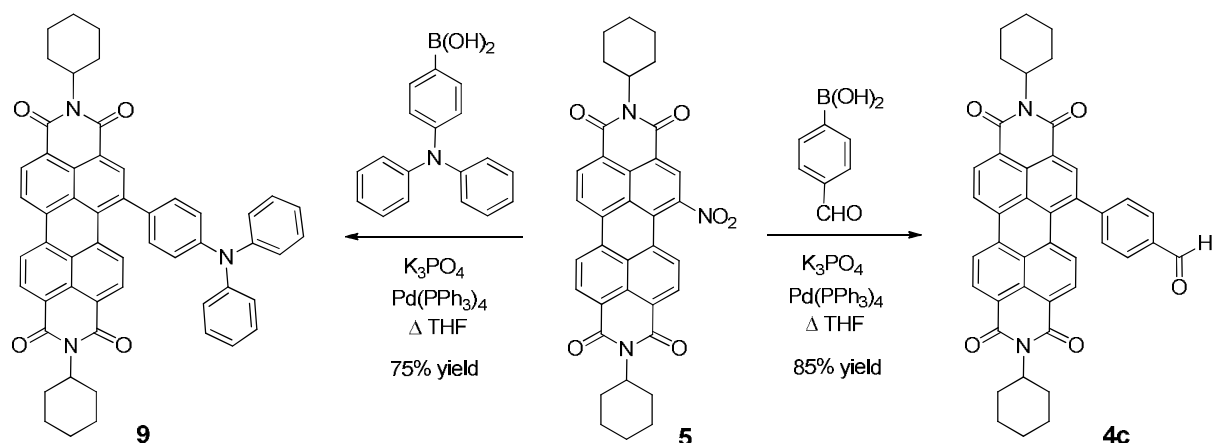
The SMC was investigated using 3-formylphenylboronic acid instead of the reported synthesis of dyad **1** realized with 4-formylphenylboronic acid. We have previously shown on PMI- C_{60} dyads that the shortest distance between the perylene core and C_{60} was in agreement with the ortho, meta, or para substitution of the phenyl group [40]. The described and optimized conditions for the SMC of nitroarenes with arylboronic acids were using $\text{Pd}(\text{acac})_2$, BrettPhos, 18-crown-6 and $\text{K}_3\text{PO}_4 \cdot n\text{H}_2\text{O}$ in 1,4-dioxane at 130 °C for 24 h. The absence of 18-crown-6 in the reaction medium resulted in a slightly decreased yield, $\text{Pd}(\text{PPh}_3)_4$ was found to be not effective and using toluene or THF as a solvent resulted in a diminished yield. Concerning the impact of the base, while CsF afforded the targeted biaryl compound, Cs_2CO_3 and K_2CO_3 did not, and the water contamination in K_3PO_4 seemed important [29]. We present herein a straightforward and simplified procedure using 3-formylphenylboronic acid in the presence only of $\text{Pd}(\text{PPh}_3)_4$ and K_3PO_4 as a base in refluxing THF. Compound **6** was isolated in a satisfactory 81% yield after column chromatography and crystallization. This reaction corresponds to the first example of SMC reaction using an electron-deficient arene system such as PDI possessing a nitro group as the electrophilic coupling partner. To the best of our

knowledge, mononitrated PDI was only known to react by replacement reactions using different nucleophiles known as aromatic nucleophilic substitutions [41]. Single crystals were obtained by slow evaporation of a solution containing PDI **6** in a mixture of CHCl_3 and petroleum ether then analyzed by X-ray diffraction. The crystallographic analysis revealed that the central six-membered ring is slightly twisted with a torsion angle of $11.74(4)^\circ$ associated with bay carbons C7-C8-C13-C22 and C9-C10-C15-C14, respectively (Fig. 1). On the other hand, the deviation of the phenyl group with respect to the PDI core is equal to $61.03(9)^\circ$.



Scheme 2. Suzuki-Miyaura coupling reaction from nitroPDI and synthesis of dyad PDI- C_{60} **7**.

Considering that in compound **6** the formyl group in *meta* position presents only an electron-withdrawing inductive effect, we have investigated the extension of this SMC reaction using a phenyl boronic acid substituted in *para* position either by an electron-withdrawing group or -donating group by mesomeric effect. Reaction with (4-formylphenyl)boronic acid or [(4-diphenylamino)phenyl]boronic acid [42] led to compound **4c** and **9** in 85 % and 75% yield, respectively (Scheme 3). PDI derivative **9** was previously synthesized in 49% yield using SMC reaction from mono-bromoPDI **3c** [43]. This demonstrates the versatility of this original SMC reaction which could be used with varied substituted phenyl boronic acid derivatives.



Scheme 3. Suzuki-Miyaura coupling reaction from nitroPDI using phenyl boronic acid substituted by electron-withdrawing or -donating group in *para* position.

Starting from compound **6**, the subsequent 1,3-dipolar cycloaddition [44] was carried out using C_{60} and *N*-methylglycine (sarcosine) in *o*-dichlorobenzene (*o*-DCB) at 180 °C affording, after purification by silica gel column chromatography, dyad **7** in 20% yield. The structure of PDI- C_{60} dyad **7** has been fully characterized through ^1H and ^{13}C NMR, mass spectrometry (MALDI-TOF and HRMS), and HPLC chromatography. From this technique, the purity of dyad **7** could be estimated to be higher to 99.8 %. As a further reference for electrochemical and optical studies, fulleropyrrolidine **8** was prepared using benzaldehyde as the starting material to generate the azomethine ylide.

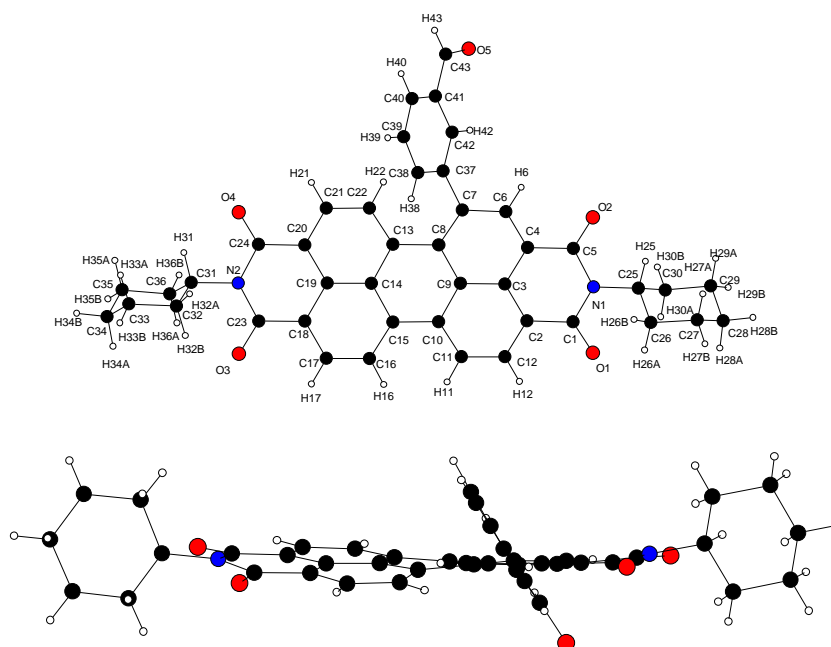


Fig. 1. View of the crystal structure of PDI derivative **6** (top) for determining the twist and distortion angles (down).

1.2. Electrochemical and optical properties

The electrochemical properties of PDI derivatives **5** and **6**, dyad **7** were investigated by cyclic voltammetry in CH_2Cl_2 in the presence of Bu_4NPF_6 as supporting electrolyte. While PDI derivatives show the expected two reversible one-electron reduction waves, we could detect four reversible reduction processes for dyad **7** (Fig. 2). Thanks to the deconvoluted cyclic voltammogram (CV) of dyad **7** and comparison with voltammograms of PDI **6** and reference C_{60} derivative **8**, we could assign the first wave to a two-electron process at $E_{\text{red}}^1 = -1.05$ V vs Fc/Fc^+ , suggesting that the first reduction process of C_{60} and the first reduction process of PDI are overlapping. Consequently this process was assigned to a simultaneous reduction of C_{60} and PDI leading to dianion-diradical $\text{C}_{60}^{2-}\text{-PDI}^{\cdot-}$ species. The second ($E_{\text{red}}^2 = -1.23$ V), third ($E_{\text{red}}^3 = -1.46$ V) and fourth ($E_{\text{red}}^4 = -1.99$ V) waves were assigned to one-electron processes corresponding to the successive formation of $\text{C}_{60}^{\cdot-}\text{-PDI}^{2-}$, then $\text{C}_{60}^{2-}\text{-PDI}^{2-}$, and at the end $\text{C}_{60}^{3-}\text{-PDI}^{2-}$ species (Table 1). Moreover, comparison of these different values for dyad **7** with reference compounds **6** and **8** suggests that there is no significant interaction taking place between both electroactive moieties in the ground state.

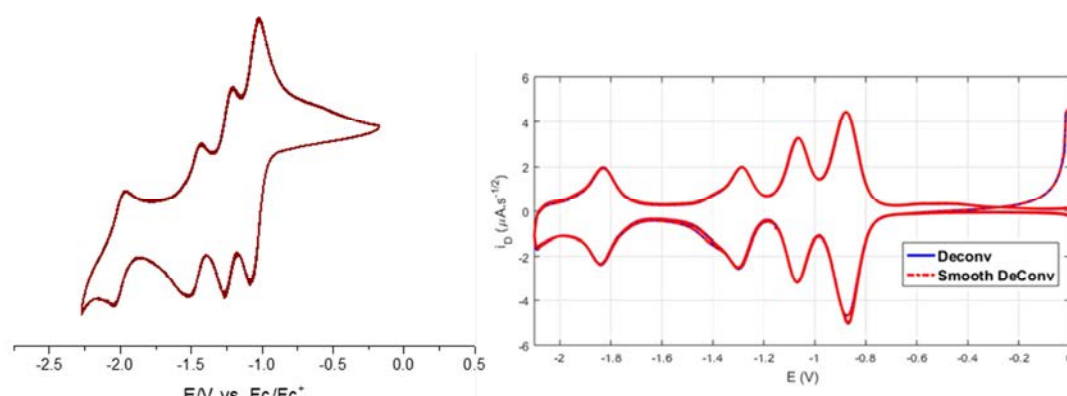


Fig. 2. Cyclic voltammogram (CV) and deconvoluted CV of PDI- C_{60} dyad **7**.

Table 1. Redox potential values (V vs Fc^+/Fc) of PDI- C_{60} dyad **7** and reference compounds **5**, **6** and **8**. Values recorded in a CH_2Cl_2 solution (0.5 mM) for **5**, **6** and **7** and *o*-DCB/ CH_2Cl_2 (1:1.2) for **8**, using Bu_4NPF_6 0.1M as the supporting electrolyte, platinum wires as counter and working electrodes. Scan rate: 100 mV/s.

| Compound | E_{red}^1 | E_{red}^2 | E_{red}^3 | E_{red}^4 |
|----------|--------------------|--------------------|--------------------|--------------------|
| 5 | - 0.77 | - 0.98 | | |
| 6 | - 0.98 | - 1.17 | | |
| 7 | - 1.05 | - 1.23 | - 1.46 | - 1.99 |
| 8 | - 1.07 | - 1.44 | - 1.97 | |

The optical properties of dyad **7** and PDI derivatives **5** and **6** have been analyzed in diluted CH₂Cl₂ solutions by UV-vis absorption (*ca.* 10⁻⁵ M) and photoluminescence emission (*ca.* 10⁻⁶ M) spectroscopy (Fig. 3). Absorption and steady-state fluorescence emissions of PDI derivatives **5** and **6**, dyad **7** in CH₂Cl₂ are collected in table 2. The UV-vis spectrum of these three compounds is characterized by two main absorption bands with a first peak with a maximum (λ_{max}) at 520-530 nm and a shoulder (490-500 nm) which corresponds to S₀→S₁ transition of PDI oriented along the long axis. A second peak (440–450 nm) is attributed to the S₀→S₂ transition oriented perpendicular to the long axis [45]. To summarize, the UV-vis spectrum of PDI-C₆₀ dyad **7** corresponds to the superimposition of the optical signature of PDI with that of C₆₀ derivative suggesting the absence of electronic coupling in the ground state between the acceptor PDI and the fullerene moiety.

These results are in agreement with the electrochemical studies of dyad **1a** reported by N.R. Champness and coll.[18] In the case of dyad **1a**, an overlap of the first reduction potentials and PDI moieties was observed confirming that the initial reduction step was leading to the simultaneous formation of the C₆₀⁻ - PDI⁻ species. It was also demonstrated by complementary spectroelectrochemical studies that this two-electron step was followed by two one-electron processes leading to the successive formation of C₆₀⁻ - PDI²⁻, then C₆₀²⁻ - PDI²⁻ species.

Table 2. UV-vis absorption (10⁻⁵ M in CH₂Cl₂) and emission data (10⁻⁶ M in CH₂Cl₂) of PDI derivatives **5**, **6** and dyad **7**.

| Compound | λ_1 (nm) | ϵ_1 (M ⁻¹ cm ⁻¹) | λ_2 (nm) | ϵ_2 (M ⁻¹ cm ⁻¹) | Φ^a | E_g^b | E^{LUMO} (eV) ^c | E^{HOMO} (eV) ^d |
|----------|---------------------|---|---------------------|---|-------------------|---------|--|--|
| 5 | 488 | 30 900 | 521 | 46 100 | 0 | 2.19 | - 4.33 | - 6.52 |
| 6 | 496 | 31 400 | 530 | 45 400 | 0.66 ^e | 2.27 | - 4.11 | - 6.38 |
| 7 | 497 | 28 900 | 533 | 41 200 | 0.01 | 2.16 | - 4.05 | - 6.21 |

^a *N,N'*-diphenylperylene-3,4,9,10-tetracarboxylic diimide ($\Phi_f = 0.96$ in CH₃CN) was used as standard for fluorescence quantum yield measurements [46]. The excitation wavelength was set at 530 nm.

^b Determined at the intersection of the absorption and emission spectra normalized with respect to the lowest energy absorption and from the onset of absorption.

^c Energy of the Lowest Unoccupied Molecular Orbital E^{LUMO} in eV determined from $E^{\text{LUMO}} = -(E_{\text{red}}^1 + 5.1)$.

^d Energy of the Highest Occupied Molecular Orbital determined from $E^{\text{HOMO}} = [E^{\text{LUMO}} - E_g]$. Values of - 4.25 and - 6.64 for LUMO and HOMO, respectively, have been previously reported [37].

^e $\lambda_{\text{em}} = 566$ nm

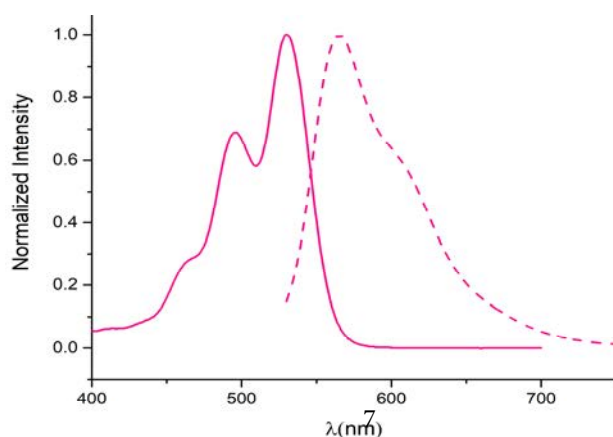


Fig. 3. Normalized steady-state absorption (full line) and emission spectra (dotted line; $\lambda_{\text{ex}} = 530$ nm) of compound **6** in CH_2Cl_2 .

In agreement with reported data [41], mono-nitroPDI derivative **5** does not exhibit any emission. On the other hand, in comparison with fluorescence spectrum of PDI **6**, a quasi-quantitative quenching (*ca.* 98.5 %) of the PDI fluorescence emission was observed in dyad **7** (Table 2). This fluorescence quantum yield decrease suggested the occurrence of either a photo-induced electron transfer or an energy transfer in solution from the photo-excited PDI chromophore to the electron-accepting fullerene unit.

Such photophysical properties were studied in detail by J. Zhao and coll. for dyad **1b**. [24] In the case of dyad **1b**, an estimated 98% quenching of fluorescence was observed. This was attributed to an intramolecular energy transfer and nanosecond time-resolved transient absorption and spin density analyses confirmed that the triplet state of dyad **1b** is localized on the PDI unit. Moreover, dyad **1b** was used as a singlet oxygen photosensitizer for photo-oxidation of 1,5-dihydroxynaphthalene and such C_{60} -PDI dyads present potential models to be used in photodynamic therapy. In another field of applications, considering their higher absorption in the visible range, light-harvesting fullerene derivatives could be used in organic solar cells by replacing advantageously PCBM [47] or in ternary blends [48].

Conclusion

In conclusion, we have developed a straightforward methodology to realize a Suzuki-Miyaura coupling (SMC) reaction using an electron-deficient arene system possessing a nitro group as the electrophilic coupling partner. We adopted this reaction to construct a PDI- C_{60} dyad for which C_{60} is connected at the bay region of the PDI core. Applications as singlet-oxygen photosensitizers and incorporation in organic solar cells of this visible light-harvesting PDI- C_{60} dyad are currently underway. We believe that this SMC reaction from nitro arene could provide guidance to be applied for the design and synthesis of new aromatic systems useful for organic electronics.

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