Synthesis of Alternative Electron Acceptor Compounds

Luigino Troisi,[1,*] Cinzia Citti[1], Catia Granito[1], Serena Perrone[1], Antonella Ciccarese[1], Simona Bettini[1], Gabriele Giancane[2] and Alessandro Troisi[3]

[1]*Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, University of Salento, Via Prov.le Lecce-Monteroni, I-73100 Lecce, Italy*

[2]*Department of Cultural Heritage, University of Salento, Via Birago 64, I-73100 Lecce, Italy*

[3]*Chemistry Department and Centre for Scientific Computing, University of Warwick, Coventry CV4 7AL, United Kingdom*

Abstract: New perylene monoimides, diimides and bis-diimides have been designed and synthetized. A detailed investigation of the synthesis of these compounds has also been performed in order to highlight the crucial factors for obtaining a specific class of molecules. Specifically, the attention has been focused on the synthesis of the intermediate perylene monoimides which are very useful precursors for many molecules difficult to obtain. Furthemore, two synthetic pathways have been developed for obtaining the bis-diimides variously substituted. These final compounds are predicted to mimic the excellent electron acceptor properties of fullerene derivatives and they can be used as building blocks to form 3D semiconducting materials.

INTRODUCTION

The synthesis of new classes of semiconducting materials or classes of materials is an essential components in the development of organic photovoltaics (OPV) [1-3], a technology that may be able to provide a clean, sustainable and low-cost source of energy [4]. A major synthetic effort is devoted to the design of electron acceptor materials to be used in organic solar cells instead of fullerene derivatives, which are considered not ideal because their electronic properties are not easily tunable and they do not absorb much solar radiation [5, 6].

Attempts to build solar cells where the fullerene derivatives are substituted by molecules with similar electron affinity (LUMO energy) invariably yield solar cells with lower efficiency [7], confirming that the correct position of the LUMO energy level is not the only parameter affecting the quality of an electron acceptor. It was recently proposed [8] that what makes fullerene derivatives special as electron acceptor is their ability to accept the electron in different excited states, a property that increase the rate of charge separation at the interface with an electron donor. According to this model, a molecule containing LUMO and LUMO+1 separated by a fraction of an eV has greater chance to mimic the excellent electron acceptor properties of fullerene derivatives.

The aim of the present study was to build a class of molecules with a "designed" vicinity of the LUMO and LUMO+1 levels. A strategy to generate electron acceptor with quasi degenerate LUMOs may consist of connecting identical conjugated electron acceptors through non-conjugated alkyl linkers. Changing the acceptor and the linker it is possible to modulate the energy levels and their separation. The new family of proposed acceptors is both easily synthetically accessible and virtually unrelated to any of the current attempts of matching the fullerene properties with different chemistries.

To realize our idea we have limited the synthetic work to a single class of compounds which bind one or more sp^3 carbon to two identical acceptors (P) showing a general formula $(CH_2)_nP_2$. A possible approach to the realization of this synthesis involves perylene (P) as the central core of the acceptor and a variety of alkyl chains as linkage units. The perylene derivatives are good fullerene mimic candidates as they exhibit the following strategic properties:

- large molar adsorption coefficients;

- good electron accepting properties [9];

- strength, thermal stability and low cost [10].

There are additional elements of interest for the synthesis of $(CH_2)_nP_2$ compounds that go beyond their potential application as electron acceptor. First of all, the synthesis requires the preparation of perylene monoimides, a so-far elusive intermediate that can be used to connect the very versatile perylene chromophore to other molecules with more complicated architecture (e.g. polymers, dendrimers). A second essential point is that a molecule with a structure

*Address correspondence to this author at the Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, University of Salento, *Via* Prov.le Lecce-Monteroni, 73100 Lecce, Italy; Tel/Fax: +39-832298701; E-mail: luigino.troisi@unisalento.it

like $(CH_2)_nP_2$ cannot easily pack in a 2-dimensional plane like the majority of planar conjugated molecules [11] and is more likely to form an amorphous solid or structure where the pi-pi interaction between molecules takes place in three dimensions. Fullerene derivatives are among the very few molecular solids where the pi-pi interaction develops in three dimensions and not just two and, also for this reason, the proposed class of molecules may find interesting applications in organic electronics.

EXPERIMENTAL

All used reagents were of commercial grade and used without any further purification. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 apparatus (400.13 and 100.62 MHz, for ^{1}H and ^{13}C, respectively) with CDCl$_3$ as solvent and TMS as internal standard ($\delta = 7.26$ ppm for ^{1}H spectra; $\delta = 77.0$ ppm for ^{13}C spectra). FT-IR spectra were acquired with a Jasco 4100 Fourier Transform Infrared Spectrometer and the analysis were performed on KBr. Elemental analyses were performed on a Carlo Erba C, H, N analyzer. Melting pointswere determined using an electrothermal melting point apparatus and are uncorrected. UV-Vis spectra were recorded with an Agilent Cary 5000 spectrophotometer using methylene chloride as solvent. Fluorescence emission spectra were acquired with a Horiba Jobin Yvon Fluorolog using chloroform as solvent and a polychromatic incident beam for excitation tool.

General experimental procedures for the synthesis of compounds 1a-1d, 2a-2d, and 3-6:

Route A: perylene-3,4,9,10-tetracarboxylic dianhydride (PDA, 2.0 mmol), and Zn(AcO)$_2$ (0.2 mmol) were dissolved in N-methylpyrrolidinone (NMP, 8.0 mL). The mixture was heated up to 100 °C and stirred for 20 min., then a solution of the primary amine (0.5 mmol) in NMP (1.0 mL) was added dropwise. The reaction mixture was further heated up to 200 °C until completion of the reaction (reactant amine decreasing, 5-6h). The mixture was then cooled to room temperature (r.t.) and filtered on a column of silica gel or

celite (h = 8.0 cm, ϕ = 3.0 cm) eluting with CH$_2$Cl$_2$ under pressure of N$_2$. The PDA excess does not elute and could be recovered from the column. The eluate (120-150 mL), instead, concentrated under vacuum, provided a solution of PMI **1a, 1b** and PDI **2a, 2b** (ratio 4:1) in N-methyl pyrrolidinone. This solution could be used without purification for the next synthesis of bis-diimides $(CH_2)_nP_2$ **3-6**. *Vice versa*, to obtain pure PMI **1a, 1b** and PDI **2a, 2b**, DMF (20 mL) and MeOH (5 mL) were added to the solution of NMP. A precipitate was obtained which was filtered, washed on the filter with MeOH and H$_2$O and dried in oven at 60 °C for few hours. Chromatography on silica gel column (h = 30.0 cm, ϕ = 3.0 cm, eluent CHCl$_3$/AcOH: 98/2) provided in the early fractions the PDI **2a, 2b** and then, in the subsequent fractions, the PMI **1a, 1b** with a total yields of 86 and 75 % showing a ratio PMI:PDI = 80:20 and 75:25 (Table **1**, entries 1 and 3).

For the synthesis of bis(alkylimidoperylene)alkanes **3-6**, to the solution of **1a**+**2a** (or **1d**+**2d** obtained from the synthesis in quinoline, see below), in a ratio of 80:20 in NMP, Zn(AcO)$_2$ (0.1 mmol) and R'(NH$_2$) (0.3 mmol) were added, the mixture was gradually heated up to 200 °C and stirred for 5-6h. After cooling to r.t., DMF (20 mL) and MeOH (5 mL) were added to the reaction mixture which was stirred for 20 min. and left to rest to allow the precipitation. The solid obtained was filtered and washed on the filter with MeOH and H$_2$O, then dried in oven at 60 °C for few hours. The purification was performed on a silica gel column (h = 30 cm, ϕ = 3.0 cm, eluent CHCl$_3$/AcOH: 98/2). In the early fractions the unreacted PDI **2a, 2d** and PMI **1a, 1d** were recovered, in the subsequent fractions, the bis (alkylimidoperylene)alkanes **3-6** were isolated with 55-75% yields (Table **2**, entries 1, 3, 5, 7).

The same protocol has been carried out using quinoline as solvent. The work-up of the cooled reaction mixtures was slightly different: in order to remove the quinoline a solution of 10% HCl (150 mL) was added to the mixture that was stirred for 20 min and left to rest to allow the precipitation. The solid obtained was filtered and washed on the filter with

Table 1. Synthesis of *N*-alkyl-3,4,9,10-perylenetetracarboxylic monoanhydride monoimides 1a-1d and *N*-alkyl-3,4,9,10-perylenetetracarboxylic diimides 2a-2d (*Route A*).

Entry	R	Solvent	Total yield (%)^c	Products distribution (%)^c	
1	Ph >—ξ Ph	NMP^a	86	1a (80)	2a (20)
2	-	Q^b	90	1a (80)	2a (20)
3	Ph >N−ξ Ph	NMP	75	1b (75)	2b (25)
4	-	Q	85	1b (75)	2b (25)
5	Ph Ph >—ξ Ph	Q	75	1c (77)	2c (23)
6	⌇⌇—ξ	Q	77	1d (85)	2d (15)

^{a}*N*-Methylpyrrolidinone. ^{b}Quinoline. ^{c}Isolated yield.

Table 2.   Synthesis of bis(alkylimidoperylene)alkanes 3-6 (*Route A*).

Entry	PMI	R'(NH$_2$)$_2$	Solvent	Total yield (%)[c]
1	1a	H$_2$N-(CH$_2$)$_2$-NH$_2$	NMP[a]	3 (58)
2	1a	-	Q[b]	3 (52)
3	1a	H$_2$N-(CH$_2$)$_3$-NH$_2$	NMP	4 (55)
4	1a	-	Q	4 (45)
5	1a	H$_2$N-(CH$_2$)$_4$-NH$_2$	NMP	5 (60)
6	1a	-	Q	5 (55)
7	1d	H$_2$N-(CH$_2$)$_2$-NH$_2$	NMP	6 (75)
8	1d	-	Q	6 (75)

[a]*N*-Methylpyrrolidinone; [b]Quinoline; [c]Isolated yield.

5% NaHCO$_3$, then dried in oven at 60 °C for few hours. The purification was performed as detailed for the synthesis in NMP. Specifically, on the first step of *Route A*, the chromatographic purification afforded the pure PDI **2a-2d,** initially, and then the pure PMI **1a-1d** were isolated with a total yields of 75-90%, showing a ratio of PMI:PDI up to 85:15 (Table **1**, entries 2 and 4-6). In the second step the chromatographic column yielded, in temporal order, unreacted PDI **2a, 2d** and PMI **1a, 1d** and then bis (alkylimidoperylene)alkanes **3-6** (yields 45-75%, Table **2**, entries 2, 4, 6, 8).

Route B: perylene-3,4,9,10-tetracarboxylic dianhydride (PDA, 2.0 mmol), and Zn(AcO)$_2$ (0.2 mmol) were dissolved in N-methylpyrrolidinone (NMP, 8.0 mL). The mixture was heated up to 100 °C and stirred for 20 min., then a solution of ethylenediamine (0.5 mmol) in NMP (1.0 mL) was added dropwise. The reaction mixture was further heated up to 200 °C for 5h. At this stage the intermediate compound

1,2-bis(anhydrideperyleneimido)ethane **3'** was formed, and the reaction temperature was lowered to 100 °C. Diphenylmethanamine (3.0 mmol) in NMP (1.0 mL) was added and the reaction mixture was heated up to 200 °C under magnetic stirring for further 5h. After cooling to r.t., DMF (20 mL) and MeOH (5 mL) were added to the reaction mixture which was stirred for 20 min. and left to rest to allow the precipitation. The solid obtained was filtered and washed on the filter in temporal order with MeOH, 10 % HCl to remove the unreacted diphenylmethanamine, and finally with 5 % NaHCO$_3$. The filtered solid was dried in oven at 60 °C for few hours and then purified by chromatography on a silica gel column (h = 30 cm, φ = 3.0 cm, eluent CHCl$_3$/AcOH: 98/2). Unreacted compounds **2a** and **1a**, were firstly isolated (arising from the reaction of PDA excess with diphenylmethanamine) finally, the pure product **3** was obtained with a yield of 65%.

Alternatively, after the formation of the intermediate **3'**, this latter could be purified before undergoing the reaction with diphenylmethanamine. Specifically, after cooling to r.t., DMF (20 mL) and MeOH (5 mL) were added to the NMP mixture which was stirred for 20 min. and left to rest to allow the precipitation. The solid was filtered and washed on the filter with MeOH and H$_2$O, and dried in oven at 60 °C

for few hours. The intermediate was finally purified by chromatography on silica gel column (h = 30 cm, φ = 3.0 cm, eluent CHCl$_3$/AcOH: 98/2). The pure 1,2-bis(anhydrideperyleneimido)ethane **3'** isolated was then suspended in NMP for the next reaction step consisting on the diphenylmethanamine addition following the same protocol described above.

The *Route B* has been carried out using quinoline as solvent. The work-up of the cooled reaction mixtures was the same as described at the end of *Route A* as well as the chromatographic purification. The pure product **3** was obtained with a yield almost similar to the one observed for the reaction in NMP. In Fig. (**2**) and Fig. (**3**) are reported the Uv-vis adsorption (from 450 to 550 nm) and the Fluorescence emission (from 550 to 650nm) spectra, respectively, of compounds **1a**, **2a** and **3** which are due to the perilenic system.

***N*-diphenylmethyl-3,4,9,10-perylenetetracarboxylic monoanhydride monoimide (1a):** red solid, yield 69%, 0.385g; M.p. >300 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.32-7.40 (6H, m, *meta* and *para* C**H**$_{arom}$), 7.54 (4H, d, $^3J_{HH}$ 7.6 Hz, *ortho* C**H**$_{arom}$), 7.67 (1H, s, N**CH**), 8.52-8.70 (8H, m, perylene C**H**$_{arom}$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 64.8 (N**CH**), 123.2, 123.4, 123.5, 123.6, 127.4, 128.3, 128.6, 128.9, 129.5, 131.8, 131.9, 134.6, 134.9, 135.0, 138.5 (**CH**$_{arom}$) 162.6 and 163.4 (**C**=O); FT-IR (KBr): ν 3118, 1772 and 1736 (anhydride groups), 1693 and 1663 (imido groups), 1593, 1406, 1359, 1301, 1017 cm^{-1}; Anal. calcd. for C$_{37}$H$_{19}$NO$_5$; C: 79.71, H: 3.43, N: 2.51. Found: C: 79.55, H: 3.58, N: 2.58 %.

***N*-diphenylamino-3,4,9,10-perylenetetracarboxylic monoanhydride monoimide (1b):** red solid, yield 56%, 0.313g; M.p. >300 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.06 (2H, t, $^3J_{HH}$ 7.0 Hz, *para* C**H**$_{arom}$), 7.27-7.33 (8H, m, *ortho* and *meta* C**H**$_{arom}$), 8.62-8.66 (4H, m, perylene C**H**$_{arom}$), 8.72-8.76 (4H, m, perylene C**H**$_{arom}$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 119.8, 123.3, 123.35, 123.4, 123.5, 123.6, 126.0, 129.2, 129.3, 131.8, 132.5, 135.5, 144.3 162.7 and 165.6 (**C**=O); FT-IR (KBr): ν 3120, 1770 and 1736 (anhydride groups), 1695 and 1665 (imido groups), 1595, 1405, 1300, 1015 cm^{-1}. Anal. calcd. for C$_{36}$H$_{18}$N$_2$O$_5$; C: 77.41, H: 3.25, N: 5.02. Found: C: 77.18, H: 3.31, N: 5.12 %.

N-triphenylmethyl-3,4,9,10-perylenetetracarboxylic monoanhydride monoimide (1c): red solid, yield 58%, 0.367g; M.p. >300 °C;. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.20-7.28 (15H, m, *ortho*, *meta* and *para* C**H**$_{arom}$), 8.68-8.72 (4H, m, perylene C**H**$_{arom}$), 8.75-8.79 (4H, m, perylene C**H**$_{arom}$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 53.4, 118.7, 123.3, 123.5, 127.2, 127.8, 127.9, 130.0, 131.9, 135.0, 148.6 162.6 and 165.0 (**C**=O); FT-IR (KBr): ν 3118, 1772 and 1736 (anhydride groups), 1693 and 1663 (imido groups), 1593, 1406, 1359, 1301, 1017 cm^{-1}. Anal. calcd. for C$_{43}$H$_{23}$NO$_5$; C: 81.51, H: 3.66, N: 2.21. Found: C: 81.73, H: 3.95, N: 2.03 %.

N-cyclohexyl-3,4,9,10-perylenetetracarboxylic monoanhydride monoimide (1d): red solid, yield 66%, 0.312g; M.p. >300 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.20-1.40 (6H, m, N-CHC**H$_2$CH$_2$CH$_2$**CH$_2$CH$_2$-), 1.80-1.83 (4H, m, N-CHCH$_2$CH$_2$CH$_2$C**H$_2$**CH$_2$-), 3.54 (1H, quintet, $^3J_{HH}$ 7.1 Hz, NC**H**), 8.50-8.70 (8H, m, perylene C**H**$_{arom}$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 24.1, 25.2, 32.1, 58.2, 123.1, 125.1, 128.3, 129.3, 129.4, 130.6, 137.0, 161.3 and 164.2 (**C**=O); FT-IR (KBr): ν 3118, 2930, 2850, 1772 and 1736 (anhydride groups), 1695 and 1665 (imido groups), 1593, 1405, 1359, 1300, 1020 cm^{-1}. Anal. calcd. for C$_{30}$H$_{19}$NO$_5$; C: 76.10, H: 4.04, N: 2.96. Found: C: 75.82, H: 4.16, N: 3.17 %.

N-diphenylmethyl-3,4,9,10-perylenetetracarboxylic diimide (2a): deep red solid, , yield 17%, 0.123g; M.p. >300 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.28-7.37 (12H, m, *meta* and *para* C**H**$_{arom}$), 7.49 (8H, d, $^3J_{HH}$ 7.4 Hz, *ortho* C**H**$_{arom}$), 7.68 (2H, s, NC**H**), 8.60 (4H, d, $^3J_{HH}$ 8.0 Hz, perylene C**H**$_{arom}$), 8.67 (4H, d, $^3J_{HH}$ 8.0 Hz, perylene C**H**$_{arom}$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 64.8 (N**C**H), 114.0, 123.3, 127.4, 128.3, 128,9, 131.9, 138.5, 139.3 (**C**H$_{arom}$), 163.5 (**C**=O); FT-IR (KBr): ν3118, 3060, 2921, 1699 and 1656 (imido groups), 1593, 1405, 1333, 1300, 1247, 1024 cm^{-1}. Anal. calcd. for C$_{50}$H$_{30}$N$_2$O$_4$; C: 83.09, H: 4.18, N: 3.88. Found: C: 83.33, H: 4.14, N: 3.75 %.

N-diphenylamino-3,4,9,10-perylenetetracarboxylic diimide (2b): deep red solid, yield 19%, 0.138g; M.p. >300 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.06 (4H, t, $^3J_{HH}$ 7.0 Hz, *para* C**H**$_{arom}$), 7.24-7.32 (16H, m, *ortho* and *meta* C**H**$_{arom}$), 8.69 (4H, d, $^3J_{HH}$ 7.9 Hz, perylene C**H**$_{arom}$), 8.77 (4H, d, $^3J_{HH}$ 7.9 Hz, perylene C**H**$_{arom}$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 119.8, 123.5, 123.6, 123.8, 126.9, 129.3, 129.7, 132.5, 135.2, 144.3, 162.6 (**C**=O); FT-IR (KBr): ν 3120, 3060, 1699 and 1656 (imido groups), 1592, 1405, 1302, 1024 cm^{-1}. Anal. calcd. for C$_{48}$H$_{28}$N$_4$O$_4$; C: 79.55, H: 3.89, N: 7.73. Found: C: 79.21, H: 3.96, N: 7.58 %.

N-triphenylmethyl-3,4,9,10-perylenetetracarboxylic diimide (2c): deep red solid, yield 17%, 0.149g; M.p. >300 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.05-7.25 (30H, m, *ortho*, *meta* and *para* C**H**$_{arom}$), 8.72 (4H, d, $^3J_{HH}$ 7.8 Hz, perylene C**H**$_{arom}$), 8.75 (4H, d, $^3J_{HH}$ 7.8 Hz, perylene C**H**$_{arom}$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 53.4, 123.3, 123.6, 126.6, 127.9, 128.1, 131.8, 134.9, 135.0, 135.1, 148.6. 165.2 (**C**=O); FT-IR (KBr): ν 3118, 3060, 2921, 1699 and 1656 (imido groups), 1593, 1405, 1333, 1300, 1247, 1024 cm^{-1}. Anal. calcd. for C$_{62}$H$_{38}$N$_2$O$_4$; C: 85.11, H: 4.38, N: 3.20. Found: C: 84.85, H: 4.18, N: 3.25 %.

N-cyclohexyl-3,4,9,10-perylenetetracarboxylic diimide (2d): deep red solid, yield 11%, 0.061g; M.p. >300 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.18-1.38 (12H, m, N-CHC**H$_2$CH$_2$CH$_2$**CH$_2$CH$_2$-), 1.78-1.80 (8H, m, N-CHCH$_2$CH$_2$CH$_2$C**H$_2$**CH$_2$-), 3.48 (2H, quintet, $^3J_{HH}$ 7.1 Hz, NC**H**), 8.58 (4H, d, $^3J_{HH}$ Hz, perylene C**H**$_{arom}$), 8.62 (4H, d, $^3J_{HH}$ 7.8 Hz, perylene C**H**$_{arom}$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 24.0, 25.2, 32.2, 58.4, 123.3, 125.0, 129.5, 128.9, 129.4, 130.1, 137.1, 162.4 (**C**=O); FT-IR (KBr): ν 3118, 3060, 2921, 1860, 1699 and 1656 (imido groups), 1593, 1405, 1333, 1300, 1247, 1024 cm^{-1}. Anal. calcd. for C$_{36}$H$_{30}$N$_2$O$_4$; C: 77.96, H: 5.45, N: 5.05. Found: C: 78.20, H: 5.32, N: 5.13 %.

1,2-bis(diphenylmethyldiimidoperylene)ethane (3); deep purple-violet solid, yield 58%, 0.660g; M.p. >300 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.31 (4H, m, *aa'bb'* system, C**H$_2$CH$_2$**), 7.31-7.38 (12H, m, *meta* and *para* C**H**$_{arom}$), 7.54 (8H, d, $^3J_{HH}$ 7.4 Hz, *ortho* C**H**$_{arom}$), 7.71 (2H, s, NC**H**), 8.59-8.72 (16H, m, perylene C**H**$_{arom}$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 32.0 (**C**H$_2$), 60.0 (N**C**H), 123.2, 123.6, 123.9, 126.0, 127.4, 128.3, 128.9. 130.9, 131.5, 131.9, 134.7, 138.4, 139.3 (aromatic **C**H), 163.4 and 163.5 (**C**=O); FT-IR (KBr): ν 3116, 2922, 2852, 1700 and 1659 (imido groups) 1593, 1455, 1340, 1278 cm^{-1}. Anal. calcd. for C$_{76}$H$_{42}$N$_4$O$_8$; C: 80.13, H: 3.72, N: 4.92. Found: C: 80.26, H: 3.54, N: 4.73 %.

1,2-bis(diphenylmethyldiimidoperylene)propane (4): deep purple-violet solid, yield 55%, 0.634g; M.p. >300 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.10 (2H, quintet, $^3J_{HH}$ 6.8 Hz, CH$_2$C**H$_2$**CH$_2$), 3.65 (4H, t, $^3J_{HH}$ 6.8 Hz, C**H$_2$**CH$_2$C**H$_2$**), 7.28-7.38 (12H, m, *meta* and *para* C**H**$_{arom}$), 7.51 (8H, d, $^3J_{HH}$ 7.4 Hz, *ortho* C**H**$_{arom}$), 7.70 (2H, s, NC**H**), 8.60-8.70 (16H, m, perylene C**H**$_{arom}$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 28.0, 36.1, 59.8, 123.1, 123.5, 126.0, 127.3, 128.3, 128.8, 130.9, 131.0, 131.8, 134.5, 138.4, 139.2, 163.2 and 163.6 (**C**=O); FT-IR (KBr): ν 3115, 2925, 2849, 1699 and 1659 (imido groups) 1590, 1454, 1340, 1278 cm^{-1}. Anal. calcd. for C$_{77}$H$_{44}$N$_4$O$_8$; C: 80.20, H: 3.85, N: 4.86. Found: C: 80.31, H: 3.96, N: 4.95 %.

1,2-bis(diphenylmethyldiimidoperylene)butane (5): deep purple-violet solid, yield 60%, 0.700g; M.p. >300 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.00 (4H, t, $^3J_{HH}$ 6.7 Hz, CH$_2$C**H$_2$CH$_2$**CH$_2$), 3.50 (4H, t, $^3J_{HH}$ 6.7 Hz, C**H$_2$**CH$_2$CH$_2$C**H$_2$**), 7.28-7.38 (12H, m, *meta* and *para* C**H**$_{arom}$), 7.50 (8H, d, $^3J_{HH}$ 7.4 Hz, *ortho* C**H**$_{arom}$), 7.71 (2H, s, NC**H**), 8.62-8.72 (16H, m, perylene C**H**$_{arom}$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 32.2, 49.2, 123.3, 123.4, 123.8, 126.0, 127.4, 128.1, 128.7. 129.4, 131.1, 132.0, 134.4, 138.0, 165.5 and 166.1 (**C**=O). FT-IR (KBr): ν 3112, 2922, 2851, 1698 and 1660 (imido groups) 1591, 1340 cm^{-1}. Anal. calcd. for C$_{78}$H$_{46}$N$_4$O$_8$; C: 80.26, H: 3.97, N: 4.80. Found: C: 80.07, H: 3.82, N: 4.83 %.

1,2-bis(cyclohexyldiimidoperylene)ethane (6): deep purple-violet solid, yield 75%, 0.728g; M.p. >300 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.20-1.38 (12H, m, N-CHC**H$_2$CH$_2$CH$_2$**CH$_2$CH$_2$-), 1.75-1.81 (8H, m, N-CHC**H$_2$**CH$_2$CH$_2$C**H$_2$**CH$_2$-), 3.50 (2H, quintet, $^3J_{HH}$ 7.1 Hz, NC**H**), 4.28 (4H, m, C**H$_2$CH$_2$**), 8.50 (8H, d, $^3J_{HH}$ 7.8 Hz, perylene C**H**$_{arom}$), 8.55 (8H, d, $^3J_{HH}$ 7.8 Hz, perylene C**H**$_{arom}$); ^{13}CNMR (100 MHz, CDCl$_3$): δ 23.8, 24.7, 29.6, 58.3, 123.3,

125.1, 129.1, 128.4, 128.9, 129.0, 130.2, 135.1, 162.3 (**C**=O); FT-IR (KBr): ν 3116, 2922, 2852, 1700 and 1659 (imido groups) 1593, 1455, 1340, 1278 cm^{-1}. Anal. calcd for $C_{62}H_{42}N_4O_8$; C: 76.69, H: 4.36, N: 5.77. Found: C: 76.86, H: 4.30, N: 5.64 %.
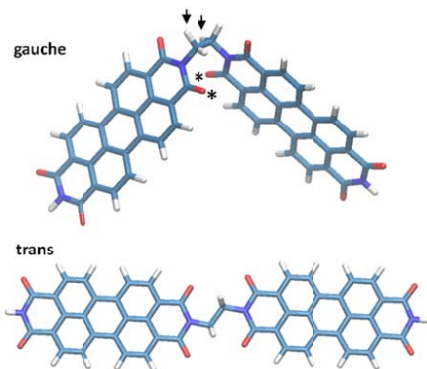

Fig. (1). Computed *gauche* and *trans* structure of a bis-diimide model. For the most stable (*gauche*) conformation the two C=O bonds strongly interacting at 3.34 Å are indicated with an asterisk. Arrows indicate two magnetically inequivalent hydrogens.
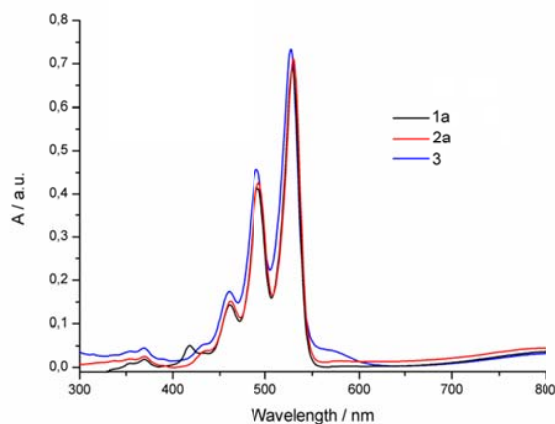
Fig. (2). UV-Vis adsorption spectra of **1a**, **2a** and **3** at the concentration of 1.25 μM in chloroform.

RESULTS AND DISCUSSION

The general synthetic pathways followed to prepare *N*-alkyl-3,4,9,10-perylenetetracarboxylic monoanhydride monoimides (PMI **1a-1d**), *N*-alkyl-3,4,9,10-perylenetetra-carboxylic diimides (PDI **2a-2d**) and bis(alkyldiimidopery-lene)alkanes (**3-6**) are outlined in Scheme **1** and Scheme **2**, respectively. The compounds were synthetized according to two methods settled on the basis of literature data [12-17]. Specifically, the new protocols proposed have allowed us to isolate the perylene monoimides easily and with good yields conversely to what we have obtained by following exclusively the literature synthetic pathways.
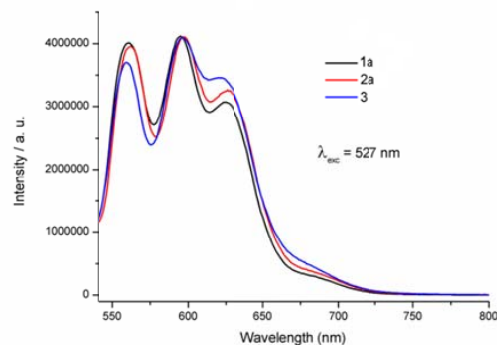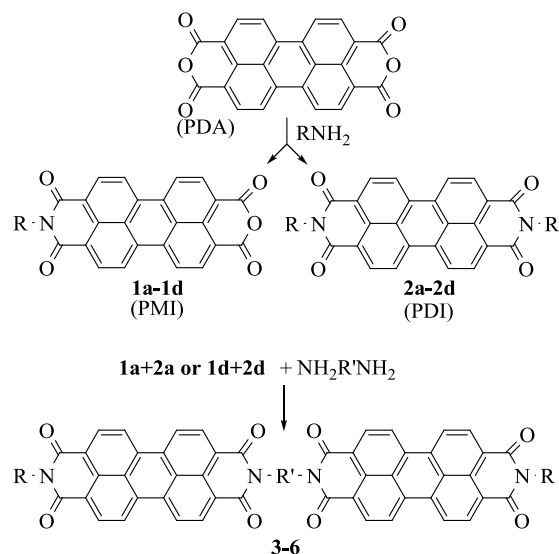

Fig. (3). Fluorescence emission spectra of **1a**, **2a** and **3** at the concentration of 0.1 μM in chloroform.

The first synthetic route (*Route A*, Scheme **1**) consists of a preliminary condensation of 3,4,9,10-perylenetetracar-boxylic dianhydride (PDA) with different alkylamines in *N*-methylpyrrolidinone (NMP) as solvent and in the presence of Zn(AcO)$_2$.

Scheme 1. General synthetic pathway: *Route A* for preparing perylene monoimides (PMI) **1a-1d**, diimides (PDI) **2a-2d** and bis-diimides **3-6**.

The reaction afforded a mixture of PMI **1a**, **1b** and PDI **2a**, **2b** in good yields (75%, 86%), and showing the PMI as the major product (Table **1**, entries 1 and 3).

The same synthetic protocol has been performed with the same reactants and with two more alkylamines in quinoline as solvent, instead of NMP, and the obtained results (**1a-1d**, **2a-2d**) are listed in Table **1** (entries 2, and 4-6): the measured yields are not significantly different changing the solvent. The mixture could be used without purification for the second step of the reaction or the PMI could be purified before undergoing the bis-diimide formation.

The unseparated mixture of **1a+2a** or **1d+2d** (ratio 80:20) has been reacted with various alkyl diamines in NMP and in the presence of Zn(AcO)$_2$, giving the bis(alkylimido-

perylene)alkanes **3-6** in moderate to good yields (55-75%, Table **2**, entries 1, 3, 5, 7).

The same reaction has been performed with the same reactants in quinoline as solvent, instead of NMP, and the obtained results are listed in Table **2** (entries 2, 4, 6, 8). The measured yields are not significantly different with both solvents denoting the importance of using a high boiling solvent.

The second synthetic route used (*Route B*, Scheme **2**) is based on the initial reaction of 3,4,9,10-perylenetetracarboxylic dianhydride (PDA) with ethylenediamine in NMP and in the presence of Zn(AcO)$_2$, affording the 1,2-bis(anhydrideperyleneimido)ethane **3'**.

Diphenylmethanamine has been directly added to the reaction mixture, without the intermediate step of purification, leading to the final perylene bis-diimide **3** in good yield (65%). Alternatively, the 1,2-bis(anhydrideperyleneimido)ethane **3'** could be purified and then suspended in NMP and added of diphenylmethanamine and Zn(AcO)$_2$ to give the final compound **3** in similar yield.
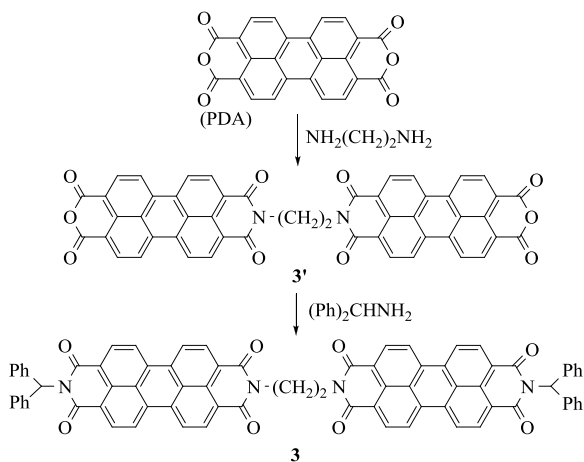
Scheme 2. General synthetic pathway: *Route B* for preparing bis-diimide **3**.

The same synthetic procedure has been carried out using quinoline as solvent: the bis-diimide **3** has been isolated with similar good yields.

The synthetic routes developed have been successfully applied to prepare variously substituted bis(alkylimido-perylene)alkanes in moderate to good yields (45-75%) denoting the versatility of the methodologies based on the use of high boiling solvents. Moreover, the work-up of the reaction mixtures, as more detailed on the experimental section, is a crucial step of the synthesis as the product could be isolated from the high boiling solvent in two different ways, depending on the solvent. Specifically, the product has been isolated from NMP with a precipitation process by adding a mixture of dimethylformamide (DMF) and methanol. Quinoline, instead, has been removed with a salification process by addition of methanol and aqueous 10% hydrochloric acid mixture.

Electronic structure calculations of the model compound in Fig. (**1**) have been carried out (i) to suggest the most likely conformation of the bis-diimide molecule and (ii) to estimate the degree of electronic coupling between the two chromophores in these compounds (their electron accepting properties have been discussed in ref. [8]). Optimizations at the B3LYP/6-31G* level of theory indicate, surprisingly, that the gauche conformation is more stable than the *trans* conformation by 16.3 Kcal/mol, i.e. that essentially all molecules are expected to be in the *gauche* conformation. This conformation seems to be stabilized by a strong electrostatic interaction between the chromophore and in particular between two C=O bonds in different chromophores that are found antiparallel and at a very close distance of 3.34 Å. In this (fairly rigid) conformation, possessing a C$_2$ symmetry axis, there are two pairs of magnetically inequivalent protons in the two methylene units connecting the chromophores; accordingly, the experimental NMR data for compound **3** show a *aa'bb'* system. The *trans* conformation instead possess a C$_{2h}$ symmetry that would make the 4 methylene protons magnetically equivalent, which is clearly inconsistent with the experimental NMR.

Like any system formed by weakly interacting pairs of chromophores also the bis-diimide molecule displays very close HOMO and HOMO-1 orbitals deriving from the plus and minus combination of the HOMO of the isolated chromophores. The energy separation between HOMO and HOMO-1 (and, equivalently, between LUMO and LUMO+1) provides a measure of the degree of electronic coupling or delocalization between the chromophores. The computed energy splitting is considerable in the most stable gauche conformation (9 meV for the HOMOs and 13 meV for the LUMOs) because of the vicinity of the C=O bonds belonging to different chromophores. The splitting is still appreciable in the *trans* conformation (2 meV for both HOMOs and LUMOs). This level of interaction, mediated by two sp^3 carbons, is comparable and even superior to that found between chromophores connected by fully conjugated fragments. If the two chromophores were to be connected by a thiophene unit, as found in many conjugated polymers [18] the HOMO and LUMO energy splittings would be 2 and 1 meV respectively, i.e. similar to the values found in the *trans* (less stable) bis-diimide conformation. (More strongly coupled bis-diimides have been reported but for very different structure containing a chemical bond between carbon atoms of two perylene units [19]).

These results demonstrate the potential importance of these derivatives in many applications of organic electronics. The fully saturated molecular bridge that still allows sufficient electronic interaction between the chromophores can be used to control their relative orientation and modulate the coupling. The orbital delocalization in these compounds is not limited to a single plane, just as in fullerene derivatives, suggesting that they can be used as building blocks to design molecular semiconductors with high mobility in three dimensions.

CONCLUSION

In summary, we have developed a robust and versatile methodology for a yielding synthesis of new materials that have been proposed as electron acceptors in organic electronics applications. Particular attention was devoted to the preparation of the intermediate perylene monoimides

which are very useful precursors for many molecules difficult to obtain. Two synthetic pathways were proposed for the synthesis of bis-diimides variously substituted. We have verified that there is an appreciable electronic coupling between the diimides notwithstanding the breaking of the pi-conjugation. These final products would be able to mimic the peculiar electron acceptor properties of fullerene derivatives, up to now the best candidates as accepting materials. Furthemore, the orbital delocalization across different planes make these molecules potentially interesting as building blocks for 3D molecular semiconductors.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

REFERENCES

[1]　Morel, D.L.; Ghosh, A.K.; Feng, T.; Stogryn, E.L.; Purwin, P.E.; Shaw, R.F.; Fishman, C. High-efficiency organic solar cells. *Appl. Phys. Lett.,* **1978**, *32*, 495-497.

[2]　Green, M.A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E.D. Solar cell efficiency tables (version 38). *Prog. Photovoltaic,* **2011**, *19*, 565-572.

[3]　Li, C.; Wonneberger, H. Perylene. Imides for organic photovoltaics: Yesterday, today, and tomorrow. *Adv. Mater.,* **2012**, *24*, 613-636 and ref. therein cited.

[4]　Kippelen, B.; Brédas, J.-L. Organic photovoltaics. *Energy Environ. Sci.,* **2009**, *2*, 251-261.

[5]　Anthony, J. E.; Facchetti A.; Heeney M.; Marder S.R.; Zhan X. n-Type organic semiconductor in organic electronics. *Adv. Mater.,* **2010**, *22*, 3876-3892.

[6]　Ahmed, E.; Ren, G.; Kim, F.S.; Hollenbeck, E.C.; Jenekhe, S.A. Design of new electron acceptor materials for organic photovoltaics: Synthesis, electron transport, photophysics, and photovoltaic properties of oligothiophene-functionalized naphthalene diimides. *Chem. Mater.,* **2011**, *23*, 4563-4577.

[7]　Sonar, P.; Lim, J.P.F.; Chan, K.L. Organic non-fullerene acceptors for organic photovoltaics. *Environ Sci,* **2011**, *4*, 1558-1574.

[8]　Liu, T.; Troisi, A. What makes fullerene acceptors special as electron acceptors in organic solar cells and how to replace them. *Adv. Mater.,* **2013**, *25*, 1038-1041.

[9]　Neuteboom, E.E.; Meskers, S.C.J.; Van Hal, P.A.; Van Duren, J.K.J.; Meijer, E.W.; Janssen, R.A.J.; Dupin, H.; Pourtois, G.; Cornil, J.; Lazzaroni, R.; Bredas, J.-L.; Beljonne, D. Alternating oligo(p-phenylene vinylene)-perylene bisimide copolymers: synthesis, photophysics, and photovoltaic properties of a new class of donor-acceptor materials. *J. Am. Chem. Soc.,* **2003**, *125*, 8625-8638.

[10]　Liu, S.G.; Sui, G.; Cormier, R.A.; Leblanc, R.M.; Gregg, B.A. Self-organizing liquid crystal perylene diimide thin films: spectroscopy, crystallinity, and molecular orientation *J. Phys. Chem. B,* **2002**, *106*, 1307-1315.

[11]　Mishra, A.; Bäuerle, P. Small molecule organic semiconductors on the move: Promises for future solar energy technology. *Angew. Chem. Int. Ed.,* **2012**, *51*, 2020–2067.

[12]　Dincalp, H.; Avcibasi, N.; Icli, S. Spectral properties and G-quadruplex DNA binding selectivities of a series of unsymmetrical perylene diimides. *J. Photochem. Photobiol. A Chem.,* **2007**, *185*, 1-12.

[13]　Zafer, C.; Kus, M.; Turkmen, G.; Dincalp, H.; Demic, S.; Kuban, B.; Teoman, Y.; Icli, S. New perylene derivative dyes for dye-sensitized solar cells. *Sol. Energ. Mater. Sol. Cells,* **2007**, *91*, 427-431.

[14]　Duff, J.M.; Hor, A.-M.; Allen, C.G.; Gaynor, R.E.; Hsiao, C.-K. Photoconductive imaging members. U.S. Patent 6,287,738 B1, September 11, 2001.

[15]　Gaynor, R.E.; Duff, J.M.; Allen, C.G.; Hamer, G.K.; Hor, A.-M. Perylene mixtures. U.S. Patent 6,464,902 B1, October 15, 2002.

[16]　Rodríguez-Llorente, S.; Aroca, R.; Duff, J. Infrared and raman spectra of thin solid films of 1,2-bis[(propylimido)perylene]ethane. *Spectrochim. Acta. A Mol. Biomol. Spectrosc.,* **1999**, *55 (5)*, 969-978.

[17]　Langhals, H; Saulich, S. Bichromophoric perylene derivatives: energy transfer from non-fluorescent chromophores. *Chem. Eur. J.,* **2002**, *8(24)*, 5630-5643.

[18]　Facchetti, A. π-Conjugated polymers for organic electronics and photovoltaic cell applications. *Chem. Mater.,* **2011**, *23*, 733-758.

[19]　Jiang, W.; Xiao, C.; Hao, L.; Wang, Z.; Ceymann, H.; Lambert, C.; Di Motta, S.; Negri, F. Localization/Delocalization of charges in bay-linked perylene bisimides. *Chem. Eur. J.,* **2012**, *18*, 6764-6775.