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Extended triphenylamine conjugated systems derivatized by perfluorophenyl groups

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ABSTRACT

Two triphenylamine derivatives bearing terminal perfluorophenyl groups have been synthesized. Their HOMO, LUMO levels and electronic band gap have been evaluated by spectroscopic and electrochemical measurements and rationalized with theoretical calculations. X-ray structure analysis of crystals allowed the observation of multiple intermolecular interactions due to the presence of the perfluorophenyl pendant groups. The multiplication of these interactions explains the differences between calculated (in gas phase) and observed (in solid states) structures.

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Organic semi-conducting materials based on triphenylamine¹ (TPA) are widely investigated as hole-transporting materials for OLEDs or as donor materials for organic solar cells. Indeed, TPA based materials combine processability, amorphous structure and isotropic optical and electronic properties.² As recently shown, increasing the crystallinity of these materials can lead to improved hole-mobility.³ In this regard, recent studies have shown that the grafting of moieties promoting intermolecular interactions such as dithiolethione⁴ or benzothiadiazole⁵ at the periphery of TPA, can lead to enhanced intermolecular interactions.

Perfluorophenyl groups (PFP) are known to promote intermolecular interactions via PFP–PFP, PFP–aryl aromatic interactions, or C–H…F contacts.⁶ In this work we report on the synthesis of two TPA systems **1–2** functionalized at their periphery with PFP groups (Scheme 1) and show the importance of these interactions on the supra-molecular organization in crystals.

Compounds **1** and **2** were obtained by Wittig reaction between ((perfluorophenyl)methylene)triphenylphosphorane⁷ **5** and trisaldehydes **3**⁸ and **4**⁹ in 35 and 25% yield.¹⁰ ¹H NMR spectra of compounds **1** and **2** (ESI, Figs. S1 and S2) show clearly *J*-coupling constants for the vinyl protons in the range of 16–17 Hz, thus indicating the formation of all trans-configurations.

The optical and electrochemical properties of compounds **1** and **2** have been analyzed by UV–vis absorption and fluorescence emission spectroscopies and cyclic voltammetry. The results are collected in Table 1.

* Corresponding author. *E-mail address:* philippe.leriche@univ-angers.fr (P. Leriche). The CV of compound **1** presents two reversible one-electron oxidation processes with anodic peak potential $E_{pa}1$ and $E_{pa}2$ at 0.85 and 1.29 V respectively leading to stable radical cation and dication (Fig. 1). Compound **2** also oxidizes in two steps at more positive potentials of 1.03 and 1.68 V, the second process being irreversible. The lower, more reversible and less separated oxidation potentials for compound **1** ($E_{pa}2 - E_{pa}1 = 0.65$ V for **2**, and 0.44 V for **1**) reflect the longer conjugated system which stabilizes the oxidized states and favors the access to dicationic state by decreasing the intramolecular coulombic repulsions between the positive charges.

The UV–vis absorption spectra of the two compounds in CH₂Cl₂ exhibit two absorption maxima at 342 and 431 nm for **1** and 292 and 405 nm for **2** (Table 1, Fig. 2). As expected compound **1** which presents the longest conjugated system, absorbs at longer wavelengths and shows energy transitions with higher molar absorption coefficients (λ_{00} , $\varepsilon(\mathbf{1}) = 115000 \text{ Lmol}^{-1} \text{ cm}^{-1}$, $\varepsilon(\mathbf{2}) = 81000 \text{ Lmol}^{-1} \text{ cm}^{-1}$).

Solvatochromic studies were performed on these compounds (ESI, Fig. 3) and showed that their absorption maxima are nearly independent on the nature of the solvent that shows a low degree of charge transfer in the absorption bands. This result contrasted with the others obtained with TPA systems derivatized with stronger acceptors¹¹ shows that the perfluorophenyl group is probably not electron-withdrawing enough to generate a significant polarity in these molecules.

The fluorescence emission spectra of 1 and 2 in CH_2Cl_2 (Table 1, Fig. 2) present emission maxima at 494 and 451 nm, respectively, and high emission quantum yields of 65 and 73%. Compound 1





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Scheme 1. Syntheses of compounds 1-2.

Table 1

Electrochemical and spectroscopic data for compounds ${\bf 1}$ and ${\bf 2}$

Compd	$E_{\rm pa}$ 1, $E_{\rm pa}$ 2 ^a (V)	$\lambda_{\max}^{b}(nm)$	$\lambda_{em}^{c}(nm)$	Φ (%)
1 2	0.85, 1.29 1.03, 1.68	342, 431 292, 405	494 451	65 73

 $^a~$ 0.10 M TBAHP/CH_2Cl_2, scan rate 100 mV s $^{-1}$, ref. SCE. $^b~$ 10 $^{-5}$ M in CH_2Cl_2.

^c In CH₂Cl₂ against perylene in cyclohexane as standard.



Figure 1. CV of compounds 1 (solid line) and 2 (dotted line) in 0.10 M TBAHP/ CH_2Cl_2 , scan rate 100 mV s⁻¹).

presents a larger Stokes shift (0.36 eV) than 2 (0.31 eV) due to larger conformational changes between fundamental and excited states related to the higher flexibility of its conjugated skeleton.



Figure 2. UV-vis absorption (line) and fluorescence emission (dotted line) spectra of compounds 1 (top) and 2 (bottom) in CH₂Cl₂.



Figure 3. Optimized geometries of compounds 1 (top) and 2 (bottom).

The optical properties of the compounds were also studied in the solid-state on spun-cast or vacuum deposited films. In both cases, the UV–vis absorption spectrum shows a bathochromic shift of λ_{max} of 25 and 21 nm for **1** and **2** respectively compared to solution what

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Theoretical data for compounds 1-2

Compd	HOMO ^a (eV)	LUMO ^a (eV)	$\Delta E \operatorname{Calcd}^{a}(eV)$	$\Delta E^{\rm b} ({\rm eV})$
1	-5.03	-2.22	2.81	2.88
2	-5.17	-2.08	3.09	3.06

^a DFT-calculated occupied (HOMO) and unoccupied (LUMO) molecular orbital energies, band gap calculated for **1–2**.

^b Estimated from UV-vis data in solution.

suggests enhanced intermolecular interactions in the solid state. In contrast, only compound **2** still retains some fluorescence emission (not quantified here) in the solid state.

The electronic properties of compounds **1** and **2** were evaluated by ab initio theoretical calculation using Gaussian 09 (DFT-B3LYP/ 6-31g (d, p)).¹² The optimized geometries of the two molecules are shown in Figure 3. Both compounds present a characteristic propeller shape typical of TPA derivatives. For compound **2**, each arm is perfectly planar but the benzene rings adjacent to the central nitrogen are not coplanar due to steric hindrance. In contrast, for compound **1**, periplanar interactions between the protons of phenyl and adjacent thiophene rings explain the twist angle observed between the two aromatic rings.

Table 2 lists the calculated HOMO, LUMO (degenerated due to the C3 geometry imposed for calculation) levels as well as calculated and experimental values of the energy gap (ΔE) for compounds **1–2**. Compound **1** which presents the most extended conjugated system shows lower LUMO and higher HOMO levels and consequently a smaller ΔE . Theoretical calculations are in good agreement with the electrochemical and spectroscopic data and confirm that **1** presents a lower oxidation potential and ΔE than **2**. The electronic levels and distributions of HOMO, LUMO, and higher and lower levels are presented in ESI (Figs. S4 and S5). While the HOMO level is mainly located on the central node with negligible coefficients on the perfluorinated adjacent cycles, the degenerated LUMO are dissymmetrical and localized on adjacent arms from the central node to the lateral functionality.

Although TPA is generally amorphous materials, crystals of compound **2** obtained by slow evaporation from a dichloromethane/hexane solution could be isolated and analyzed by X-ray diffraction.¹³ The molecule crystallizes in the centrosymmetric triclinic $p\bar{1}$ space group. The structure of the molecule is shown in Figure 4. As expected, the three C–N bonds are coplanar and the three phenyl rings grafted on the nitrogen atom present the



Figure 4. Crystallographic structure of compound 2.



Figure 5. Stacking mode of molecules along the *a* axis.



Figure 6. C-H···F contacts (red dotted lines) in one sheet of molecules **2** viewed along the *a* axis.

typical propeller shape of TPA derivatives.¹⁴ All vinylic bonds are in trans-configuration that is in agreement with NMR data.

In contrast to theoretical optimization, the conjugated system of compound ${\bf 2}$ is slightly bent and the two aromatic rings of each

arm present torsion angles of 31.2°, 38.6°, and 39.4°, respectively. These twists which are not due to intramolecular steric hindrance are imposed by intermolecular interactions as shown by the numerous short intermolecular distances observed in the crystal.

The packing arrangement of the molecules in the crystal is characterized by layers of molecules stacking along the *a* axis separated by short distances (3.37 Å, Fig. 5, ESI Fig. S6). In these stacks, the 3 PFP rings of each molecule are engaged in PFP–PFP interactions with two other molecules. Numerous short distances ranging from 3.19(9) and 3.39(5)Å shown in blue on Figure 5 are observed between fluorine and carbon atoms of the two superposed PFP rings.

Moreover, in layers, the molecules are imbricated within each other and present many C–H…F contacts. Figure 6 shows a set of molecules in a sheet, the red dotted lines symbolise the interactions between hydrogen and fluorine atoms. The distances d_{H-F} represented here range between 2.58 and 2.89 Å.

Finally, it may be noted that the structure is built from $C-H\cdots F$ interactions in sheets and from inter-PFP ring interactions in stacks thus allowing a strong three dimensional arrangement. These multiple interactions probably explain the deviation from planarity of the lateral arms for compound **2** in the crystal.

In conclusion we have synthesized two new TPA systems with peripheral PFP groups. The presence of these electron withdrawing groups leads to high oxidation potentials. On the other hand, the results of spectroscopic and X-ray diffraction analyses are consistent with the existence of multiple intermolecular interactions in the solid state. The reminiscence of fluorescence associated with strong intermolecular interaction in the solid states may allow the incorporation of such derivatives as active layer in OLEDs and in organic solar cells.

Acknowledgments

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Supplementary data

Supplementary data NMR spectra of compound **1–2**; solvatochromic studies for compounds **1–2**, HOMO, LUMO and higher and lower levels for compounds **1–2** associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.09.129.

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- 1.53 mmol Compound 1. То of ((perfluorophenyl)methylene) triphenylphosphorane 6 dissolved in 20 mL of THF at -78 °C, 200 mg (0.35 mmol) of trisaldehyde 5 dissolved in 30 mL of THF are dropped. The mixture is stirred 1 h at -78 °C then 12 h at room temperature. After evaporation of THF, the residue is dissolved in methylenechloride, washed with water and dried on magnesium sulfate. After evaporation of solvent, compound is purified threw chromatography on silica gel using toluene as eluent. 130 mg (35%) of yellow powder are isolated. ¹H NMR (C6D6): 7.47 (d, 2H, ³J = 8.5 Hz); 7.40 (d, 1H, ³J = 16.5 Hz); 7.09 (d, 2H, ³J = 8.5 Hz); 6.92 (d, 1H, ${}^{3}J$ = 3.5 Hz); 6.73 (d, 1H, ${}^{3}J$ = 16.5 Hz); 6.72 (d, 1H, ${}^{3}J$ = 3.5 Hz). ${}^{13}C$ NMR (C6D6) 147.1; 145.1; 141.2; 132.5; 132.4; 130.2; 129.5; 127.3; 124.9; 123.7; 111.5; ¹⁹F NMR -163.8 (td, 2F); -157.7 (t, 1F); -144.0 (dd, 2F); MP (DSC): 213 °C; HRMS (Calcd/Found, [M⁺], g mol⁻¹): 1067.0826/1067.0828. Compound **2**. Analogous procedure than for 1 starting from 0.18 mmol of 4 after chromatography on silica gel (hexane/toluene 7:3), 87 mg (25%) of a yellow solid are isolated. ¹H NRM (C6D6): 7.31 (d, 1H, ${}^{3}J$ = 16.5 Hz); 7.20 (d, 2H, ${}^{3}J$ = 9 Hz); 7.08 (d, 2H, ${}^{3}J$ = 9 Hz); 6.75 (d, 1H, ${}^{3}J$ = 16.5 Hz); ${}^{13}C$ NMR (C6D6): 147.8; 132.2; 128.5; 128.1; 127.8; 124.7; 111.7; MP (DSC): 212 °C; HRMS (Calcd/Found, [M⁺], g mol⁻¹): 821.1194/821.1192. (in both cases, carbons bearing fluorine which are known to produce large signals and low intensity were not observed).
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- 13 X-ray single-crystal diffraction data for 2 were collected at 293 K on a BRUKER KappaCCD diffractometer, equipped with a graphite monochromator utilizing MoK α radiation (λ = 0.71073 Å). The structure was solved by direct methods using SIR92 (Altomare et al., 1993) and refined on F² by full matrix leastsquares techniques using SHELXL97 (G.M. Sheldrick, 1998). All non-H atoms were refined anisotropically and absorption was corrected by SADABS program (Sheldrick, Bruker, 2000). The H atoms were included in the calculation without refinement. Crystallographic data for **2**: $C_{42}H_{18}F_{15}N$, M = 821.57, prism, $0.27 \times 0.22 \times 0.04 \text{ mm}^3$, triclinic, vellow space group p1. a = 11.836(1) Å, b = 12.166(3) Å, c = 13.015(2) Å, $\alpha = 95.22(1)^{\circ}$, $\beta = 98.84(1)^{\circ}$, $\gamma = 103.04(1)^{\circ}, \forall = 1/30.4(5) \text{ A}^{\circ}, Z = 2, \rho_{calc} = 1.577 \text{ g/cm}^{3}, \mu(\text{MoK}\alpha) = 0.149 \text{ mm}^{-1}, F(000) = 824, \theta_{min} = 2.20^{\circ}, \theta_{max} = 26.04^{\circ}, 33738 \text{ reflections collected} 6740 \text{ unious } (P_{abc} = 0.44)$ $\gamma = 109.04(1)^{\circ}, V = 1730.4(5) \text{ Å}^3,$ reflections collected, 6749 unique ($R_{int} = 0.10$), parameters/restraints = 523:0, $R_1 = 0.0732$ and $wR_2 = 0.1079$ using 3429 reflections with I>2 σ (I), $R_1 = 0.1617$ and $wR_2 = 0.1365$ using all data, GOF = 1.103, $-0.241 < \Delta \rho < 0.184$ eÅ⁻ CCDC-833959 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.
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