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Reactivity of Decafluorobenzophenone and decafluoroazobenzene towards aromatic diamines: a pratical entry to Donor-Acceptor systems.

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A series of Donor-Acceptor-Donor (D-A-D) and Acceptor-Donor- Acceptor (A-D-A) compounds has been prepared exploiting the relative ability of polyfluorinated azobenzenes and benzophenone to undergo aromatic nucleophilic substitution reactions with aromatic amines.
When fluorene and Carbazole-based diamines have been used and, working in high Donor Number solvent such as DMSO, an high para-regioselectivity is obtained. The prepared triads have been employed in the synthesis of oligomers with the aim of evaluating as photovoltaic material additives in optoelectronic applications.
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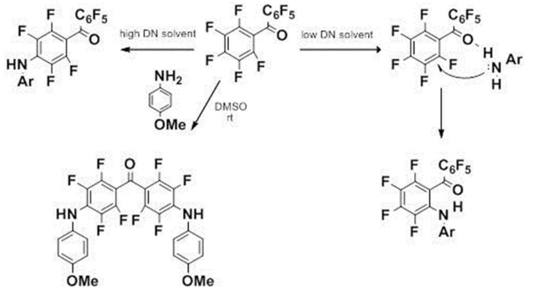
Introduction

Fluorine is the most electronegative element in the periodic table, it also has the lowest polarizability.
When bound to carbon, it forms the strongest bonds in organic chemistry, an average bond energy of around 480 kJ/mol[1], consequently fluorinated organic molecules usually show high thermal and photochemical stability.
The relative inertness of the C-F bond makes fluorinated molecules important in both medicinal chemistry, effecting drug activities[2,3] and Material sciences, in important fields such as liquid crystals displays, surfactants, catalysis, fuel cells, sensors[4], and Bulk Hetero-Junction (BHJ) solar cells[5].

Contrary to other halo-alkanes, aliphatic fluorine derivatives are practically inert toward nucleophilic substitution, while fluorinated aromatic systems are more reactive in aromatic nucleophilic substitutions since the fluorine atom shows a better nucleofugacity with respect to the other halogens.
This latter property has been recently exploited for realizing perfluorinated polymers starting from perfluorinated benzophenones or perfluorophenylsulfones by fluorine nucleophilic substitution with suitable polyols (diphenols and aliphatic diols). These latter have shown high negative thermooptical coefficients (i.e., the variation of refractive index as a function of temperature, *dn*/*dT*) and low thermal conductivities, interesting properties for optical guides [9-11], aerospace and electronic industry applications[12-17])
To the best of our knowledge, only a limited use of aliphatic and/or aromatic amines as nucleophiles are described [18-20] and no reports concerning the use of diamino-derivatives are reported in the literature.

Results and discussion

Recently we have reported on the reactivity of decafluorobenzophenone towards the nucleophilic substitution with aromatic amines and we have shown that *ortho/para* nucleophilic substitution regiochemistry can be controlled acting on solvent polarity. In particular we have found a correlation between the solvent Lewis basicity, expressed by Donor Number (DN) and the *ortho/para* substitution ratio. Indeed the low DN solvents favor hydrogen bonding between the N-H of the incoming aniline and the carbonyl group resulting in a *ortho* nucleophilic substitution, while in high DN solvents the C=O····H–N interaction is perturbed addressing the nucleophilic substitution in *para* position. In addition we have shown that the *ortho*-anilino-substituted derivatives were suitable starting materials for the synthesis of polifluorinated acridines and acridones.[21,22].
As expected, in these substitution reactions, good yields were observed with electron-rich aniline such as 4-methoxy or 4-dimethylamino-aniline.[22] In addition, when the reaction with 4-methoxy-aniline was performed in DMSO (high DN solvent), we have always observed the formation of the 4,4'-bis-anisidino-octafluoro-benzophenone even if stoichiometric amounts of amine were used. It appears evident that the two perfluorophenyl rings react almost independently and that the formation of mono or di-substituted derivates is meanly controlled by the equivalent of nucleophile used per equivalent of decafluorobenzophenone. Indeed, when decafluorobenzophenone was allowed to react with 2eq. of 4-methoxy-aniline in DMSO at room temperature, after 7h the 4,4'dianisidino-octafluoro-benzophenone was recovered in 95% yield. (scheme 1).



Scheme 1 Reactivity of decafluorobenzophenone towards para-methoxy-anilines

The hydrofluoric salt of para-anisidine is in equilibrium with the free amine due to the high DN [22] of DMSO which justifies the high yield achieved.

The 4,4'-para-anisidino-octaflurobenzophenone represents a Donor-Acceptor-Donor (D-A-D) system where the Donor part is expressed by para-anisidino moiety while octafluoro-benzophenone represents the acceptor counterpart. Recently these D-A systems have been introduced in bulk heterojunction polymeric photovoltaic cells for reducing their optical gap thus collecting a wider spectrum of sun radiation. The 4,4'-para-anisidino-octaflurobenzophenone shows a maximum absorption around 370nm and, in principle the absorption properties in these systems can be tuned acting on the electron donating properties of the substituent's on the starting anilines.

Indeed a red shift is espected when the methoxy group is replaced by a more electrondonating group such as the amino one. As an extension of this work, here we report on the results obtained when aromatic diamine's are employed. In particular our attention was addressed to the synthesis of Donor-Acceptor-Donor (D-A-D) and Acceptor-Donor-Acceptor (A-D-A) systems operating respectively with an excess of decafluorobenzophenone (A-D-A, approach 1) or aromatic diamine (D-A-D, approach 2). We have found interesting these 2 approaches since, in principle, the triads D-A-D and A-D-A so prepared, can be further mutually combined producing more elaborated systems (chart 1).

As aromatic diamines we have selected the 2,7-diamino-fluorene and 3,6-diamino-N-(2-ethylhexyl)-carbazole since these amine have been recently employed in the synthesis of polymeric system potentially useful in developing new organic photovoltaic cells. In particular new diaminofluorene dyes have been used in Dye Sensitized Solar Cells [23a,b] and aminocarbazole employed in polymers for organic phovoltaic cells [23c,d].

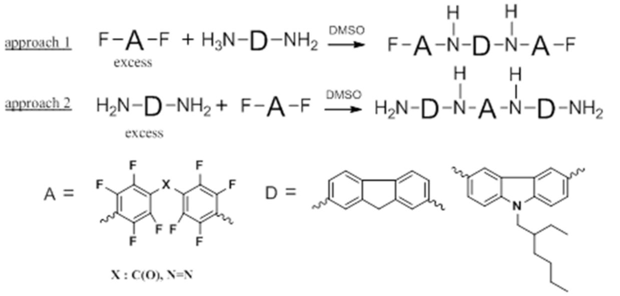
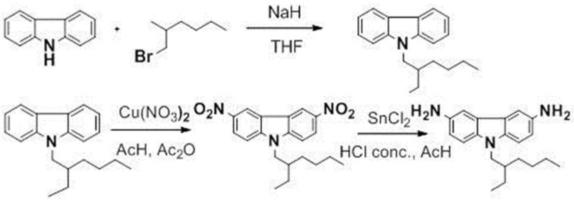


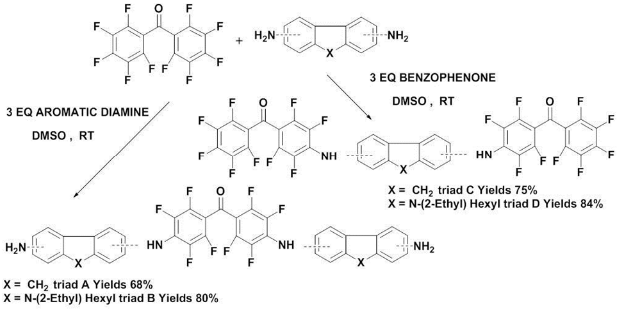
Chart 1 Approaches to the synthesis of A-D-A and D-A-D systems

The 2,7-diaminofluorene is commercially available while the 3,6-Diamino-N-(2-ethylhexyl)-carbazole has been prepared by alkylation of carbazole with 2-ethylhexylbromide, followed by double nitration of N-(2ethylhexyl)carbazole and reduction of the nitro gorup with $SnCl_2$ (scheme 2).[24]



Scheme 2 Synthesis of diamino-carbazole derivative

The reaction of 2,7-diaminofluorene and 3,6-Diamino-N-(2-ethylhexyl)-carbazole with an excess of decafluorobenzophenone (4 eq.) or the reaction of an excess of these amines (3 eq.) with decafluorobenzophenone both in DMSO at room temperature, affords the triads A-D-A (**C**), (**D**) and D-A-D (**A**), (**B**) respectively in satisfactory to good chemical yields (scheme 3)



Scheme 3 Synthesis of D-A-D and A-D-A employing diaminofluorene and diamino-carbazole.

All the new compounds have been fully characterized spectroscopically and in the figure 1 and table 1 are reported the absorption and emission properties of the triad A-D-A (**C**) and (**B**) and the triad D-A-D (**A**) and (**D**). All of the triad show maximum absorptions in the UV range centered around 370nm this reflects the limited π-conjugation of the benzophenone, lower absorption energies are observed when the acceptor unit is inside the triad. The triad **D** show maximum absorptions at slightly higher energy than **A** and **B**. The triads **A**, **B**, **C** show reasonable high Stoke shift in their emission properties while in triad **D** the emission practically coincides with the absorption.

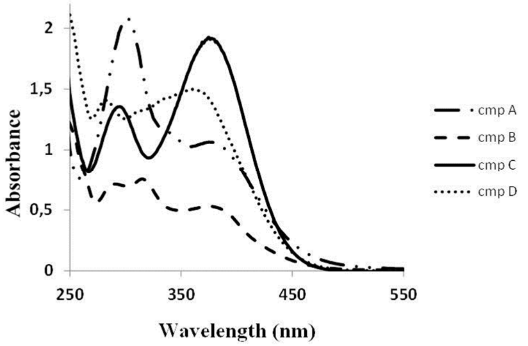
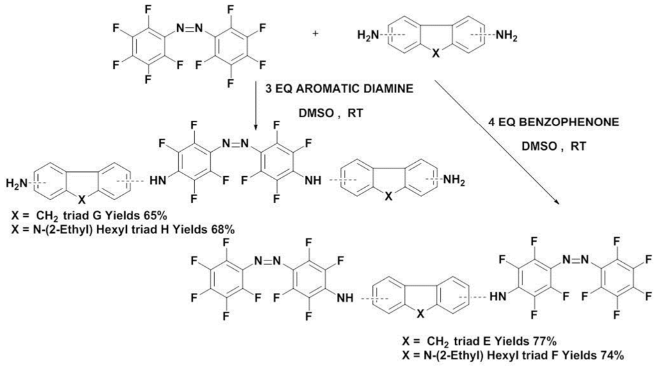


Figure 1 Absorption spectra of selected monomers A, B, C and D (10-5M CH2Cl2 solutions).

Triad	Abs λ (nm)	Emission λ_{max}(nm)
A	λ_1= 302 λ_2 =377	451 (λ_{ex}= 370)
B	λ1 = 290, λ2 =314 λ3 =373	453 (λ_{ex}= 370)
C	λ1=295 λ2 =380	517 (λ_{ex}= 380)
D	λ1 =282 λ2 =360	363 (λ_{ex}= 360)

Considering the analogy between decafluorobenzophenone and decafluoroazobenzene (C=O and N=N groups both units connecting the pentafluorophenyl rings) a similar reactivity towards nucleophiles is expected. Indeed reaction of polyfluoroazobenzene with sulfur, oxygen and nitrogen nucleophiles have been reported [25,26] but, to the best of our knowledge, no reports on the reactivity of decafluoroazobenzene towards aromatic diamines are present in the literature. In addition polyfluoroazobenzene systems have been also proposed as photoresponsive materials with potential application in optical storage devices [27] and liquid crystal displays.[28]

The decafluoroazobenzene has been prepared following the procedure reported in the literature, by oxidation of pentafluoroaniline with $Pb(AcO)_4$[26] by replacing benzene with methylenchloride. The decafluoroazobenzene was then allowed to react with the 2,7-diaminofluorene and 3,6-Diamino-N-(2-ethylhexyl)-carbazole following the same approach described for decafluorobenzophenone. By this, the triads A-D-A (**E**), (**F**), and D-A-D (**G**) and (**H**) have been synthesized in reasonable to good chemical yields.



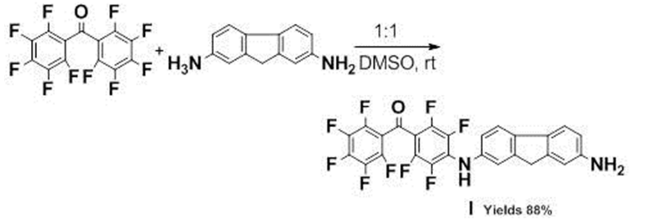
Scheme 4 Synthesis of triads with polyfluoroazobenzene acceptor and diammino fluorine and diamino-carbazole as donors.

In table 2 the absorption and emission properties of the triads E,F,G and H are displayed.

Triad	Abs λ (nm)	Emission λ_{max}(nm)
E	λ_1 = 285 λ_2 =453	684
F	λ1 = 386 λ2 =438	567
G	λ1 =296 λ2 =492	629
H	λ1 =391 λ2 =489	566

As expected a red shifting in optical properties is observed moving from benzophenone acceptor to the azobenzene one, this reflects a better conjugation between the two polyfluoroaromatic ring when the C=O function is replaced by the azo function. Also in this case absorptions at lower energies are observed when the acceptor is inside the triads and with diaminocarbazole as donor. A good Stoke shift, over 100nm in almost all triads, is observed which could be ascribed to more molecular rigidity), due to better conjugation, for the excited state in these systems when compared with benzophenone-based ones.

Finally by reacting stoichiometric amounts of diaminofluorene and decafluorobenzophenone in DMSO at room temperature the D-A dyad **I** has been obtained in satisfactory yields. (scheme 5)



Scheme 5 Synthesis of the diad benzophenone-fluorene **I**.

The diad **I** has both reactive amino and a pentafluorophenyl groups thus a polynucleophilic aromatic substitution reaction can be envisaged under thermal treatment affording oligomeric or polymeric materials. We have performed a Thermo-Gravimetric Analysis (TGA) in order to test the reactivity of this molecule under thermal stimulation and furthermore to distinguish at what temperature this occurs.

Indeed TGA provides the temperature at which the sample start to loose mass (HF is expected to be lost if a nucleophilic substitution occurs) and the nature of the lost molecules (analyzing the molecular mass). From TGA analysis we were able to determine that materials were lost starting at 80-90 °C and stops around 180 °C, a total loss of material of 10%. The elimination of HF was confirmed by mass analysis of the lost material (see experimental part). The TGA data seems to indicate that 180 °C is a suitable temperature for polymerization. With this information, the monomer **I** has been allowed to react in refluxing DMSO for 6 h. After this time the solvent was removed under reduced pressure and the optical (UV-Vis absorption) and spectroscopic properties (IR) of the collected material were compared with those of materials obtained from the TGA experiment. In figure 2 and 3 are reported the comparison of IR spectra and UV-Vis spectra of the material collected from the TGA experiment and that from the reaction in refluxing DMSO. It was found that in both conditions, the collected materials were almost identical.

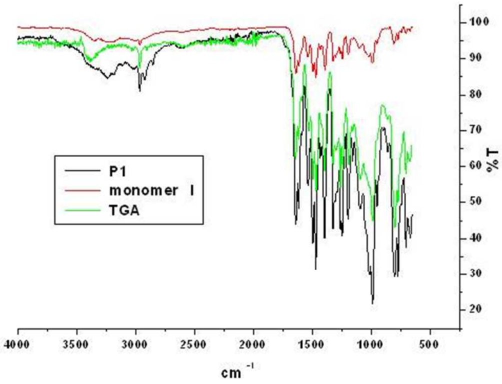


Figure 2 Comparison of IR spectrum of the material from TGA experiment (green line), monomer I (red line) and P1 (black line).

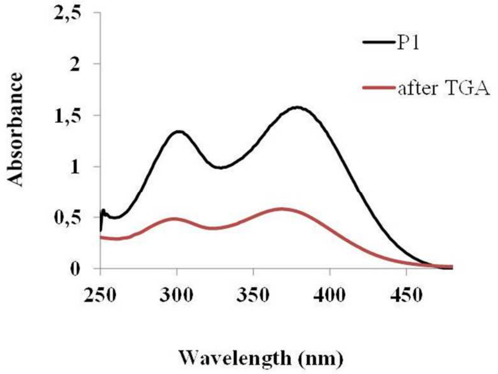
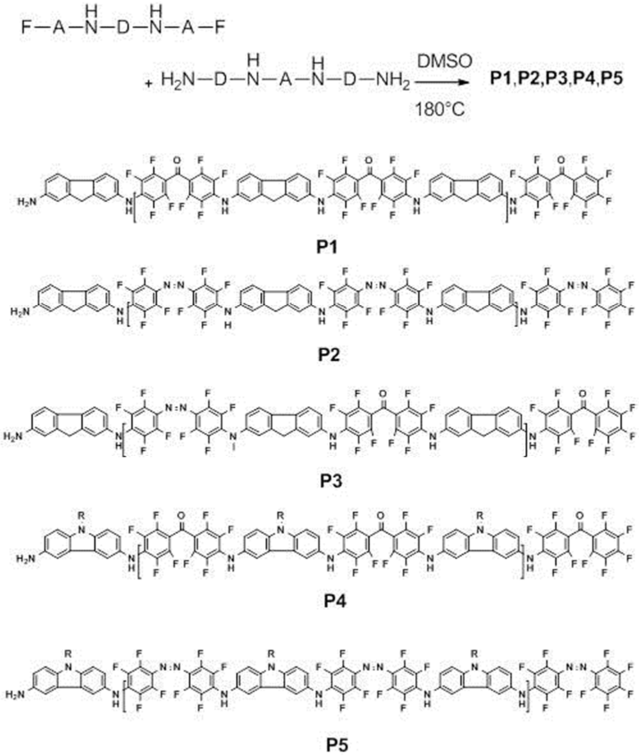


Figure 3 Comparison of UV-Vis spectrum of the materials from TGA experiment (red line) and that from reaction in DMSO (black line)

With this information, the triads (**A**)-(**G**) have been allowed to react in refluxing DMSO (180 °C), in different combinations. After the solvent was removed by distillation at reduced pressure the optical and electrochemical properties of the collected material was analyzed (scheme 6). The mixed oligomer **P3** obtained from monomers **C** and **G** containing both the octafluorobenzophenone and octafluoroazobenzene shows an absorbance in solution which is practically the sum of absorbance of oligomer **P1** and **P2** (see fig.S4 supporting information). All the oligomers show a reduction potential below -1.70V and oxidation potential over 0.25V with HOMO energy level in the range of -4.89 to -5.03 eV and LUMO energy level from 2.88 to 3.66 eV which correspond to an energy gap in the range of 2.10 to 1.37eV. The observed energy gap values for these systems fall in the interesting window for a their potential use as the active layer of bulk heterojunction (BHJ) organic solar cells (see fig.S1 supporting information).

All the oligomers show both slight differences between HOMO level and oxidation peaks with similar current intensity. The main differences between the are related to the position of LUMO energy level, that is consequence of different reduction behavior. Only oligomer **P2** and **P5** reduction peaks have intensity comparable to oxidation ones. However not one of these products has reversible oxidation and/or reduction behavior thus it is expected, from charge carrier transport properties, to show low efficiencies and consequently cannot be proposed as active materials in BHJ.

In table 3 are reported absorption and emission properties together with the HOMO/LUMO level optical and electrochemical energy gap (see also fig S4-8 supporting information).



Scheme 6. Synthesis of polymeric systems containingpolifluorobenzophenone and polifluoroazobenzene acceptorsand fluorene diamine and diaminocarbazole donor moieties.

Table 3, spectroscopic data of the oligomers **P1-P5**

oligomer (combined triads)	Abs λ [nm]	emission, λmax [nm]	HOMO/ LUMO (eV)	Egap (eV)
P1 (A+C)	λ1=300 λ2=378	460	-4.89/ -3.22	1.67
P2 (E+G)	λ1=299 λ2 =374 λ3 =490	625	-4.98/ -2.88	2.10
P3 (C+G)	λ1=299 λ2 =374 λ3 =490	565	-5.06/-3.67	1.39
P4 (B+D)	λ1= 283 λ2 =307 λ3=365		-5.05/-3.16	1.89
P5 (F+H)	λ1 =389 λ2 = 451		-5.03/-3.66	1.37

Fluorinated conjugated compounds have been reported as active components in organic solar cells [29-31] and have also been used as buffer layer materials (both conjugated and non conjugated) to improve the devices performances.[7, 32-36] This enhancement is attributed to the formation of a dipole layer at the anode interface, resulting from the negatively charged fluorine atoms, that facilitate the hole extraction process.[34]

In this latter field, polyvinylidenefluoride (PVDF)[6] and perfluoroalkyl fullerene[7,8] have been applied as buffer layer in Poli-3-hexyltiophene:phenyl-C61-butyric acid methyl ester (P3HT:PCBM) BHJ solar cells. In addition, it is reported that the introduction of small amount of perfluorinated compounds into the P3HT:PCBM-based BHJ results in an improvement of Power Conversion Efficiency (PCE)[35] indicating that the perfluorinated derivatives are both promising substrates and additives.

In particular, Wei et al. [7] found out that when a small amount of [6,6]-phenyl-C61-butyric acid 1H-pentadecafluoro-1-octyl ester is mixed with the active blend, it spontaneously migrates to the surface of the organic layer during spin-casting owing to the low surface energy of the fluorocarbon. In this way, a very thin buffer layer between the photoactive layer and the electrode is formed in one step, resulting in an enhancement of fill factor and PCE.

Based on these considerations and on the data obtained with these synthesized systems, being excluded a their use as active components in BHJ cells due to the irreversible redox behavior, we have looked at them as possible additives to P3HT:PCBM-based BHJ solar cells. Thus we have fabricated inverted polymer solar cells using a solution of poly(3-hexylthiophene (P3HT) and [6,6]-phenyl C61-butyric acid methylester (PCBM) containing 10% or 20% of the fluorinated oligomers (**P1**), and (**P4**) as additives. The average power conversion efficiencies of the resulting devices were in the range 1.9-2.4%, thus compared to 2.56% measured for a reference device without the fluorinated additive (table 4).

Table 4, photovoltaic parameters for the prepared cells using **P1** and **P4** as additive

Additive	FF av (Max)	Voc av (max)mV	Jsc av (max) Ma/cm^2	PCE av Max %
10% w P4	0.48 (0.50)	553 (555)	6.03 (7.29)	2.03 (2.03)
20% w P4	0.47 (0.59)	571 (590)	6.31 (7.12)	1.91 (2.39)
10% w P1	0.51 (0.58)	576 (602)	6.93 (7.32)	2.05 (2.48)
20% w P1	0.49 (0.61)	576 (614)	6.35 (7.05)	2.43 (2.60)
none	0.54 (0.60)	578 (588)	8.20 (8.59)	2.56 (2.85)

The Fill Factors and the short circuit current densities of the devices with the fluorinated additives are significantly lower than the reference devices but not dramatically lower especially (for P1) where the 20% of additive shows a PCE comparable with pristine blend. These preliminary results could be ascribed to a disfavored charge extraction process at the electrode interface, possible charge carriers recombination processes due to the presence of fluorinated additives in the active component.

Another aspect investigated has been to ascertain if **P1** and **P4** influence on the morphology of the blend P3HT/PCBM by collecting images of films by Atomic Force Microscopy (AFM). In figure 4 the morphologies of pristine P3HT/PCBM and those with 10% and 20% in weight of P1 and P4 respectively are reported.

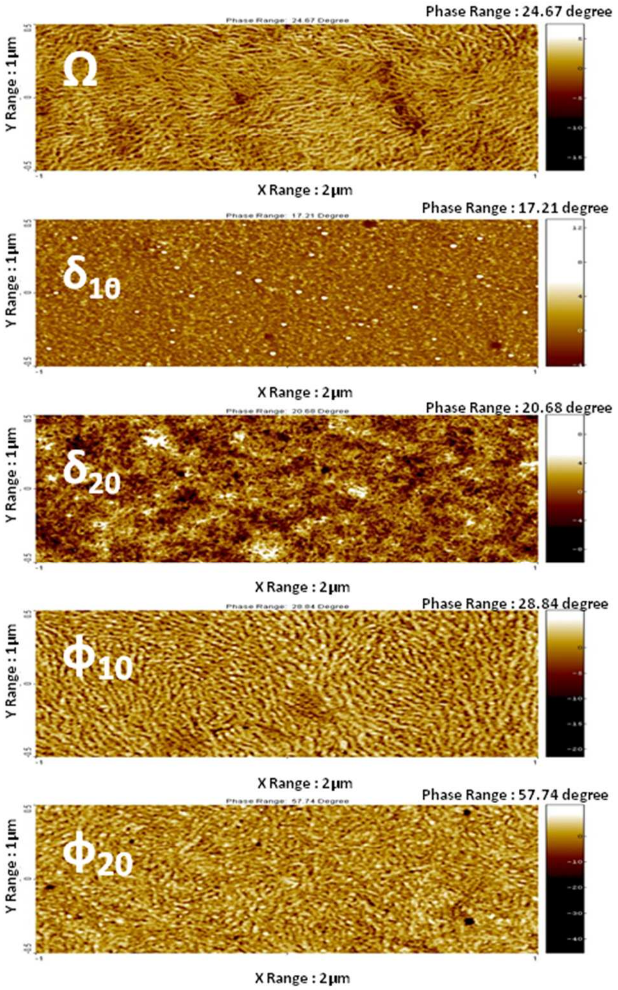


Figure 4 AFM Phase images of films of pristine P3HT/PCBM (40:60; A) with 10%w (B) and 20% (C) of P1 and with 10%w (D) and 20% (E) of P4 respectively.

AFM images of P3HT:PCBM:P1 blends (Figure 4 δ_{10} and δ_{20}) show that the surface morphology is remarkably changed compared to the P3HT:PCBM blend (figure 4 Ω), suggesting that the fluorinated additive indeed migrates toward the surface, as expected from the literature.[7] P3HT:PCBM:**P4** blends (Figure 4 ϕ_{10} and ϕ_{20}) exhibit a fibrillar morphology more similar to P3HT:PCBM, although in the blend containing 20% of **P4** the fibrils are less defined. It can be speculated that **P4** is more compatible with P3HT than **P1**, as it tends to dissolve in the amorphous phase, thus disfavorring the migration to the surface.

At this stage any correlation between the cell parameters and the nature of the additive and their action on the blend morphology are merely speculative since more work is required to investigate the influences of these additives on cell performance).

Conclusions

In conclusion, while exploring the reactivity of decafluorobenzophenone and decafluoroazobenzene toward aromatic diamines such as diminofluorene and diaminocarbazole a series of D-A-D and A-D-A triads have been synthesized and exploited in the synthesis of polymeric or oligomeric materials. In this work we have extended the study of the reactivity in nucleophilic substitution reaction of decafluoroazobenzene and decafluorobenzophenone towards aromatic diamine, a study that, to our best knowledge has never reported before. In addition, exploiting the control operated by the basic nature (expressed by Donor Number DN), high para regioselectivity have been observed in high DN solvents such as DMSO. Optical, spectroscopic and electrochemical properties of the prepared D-A-D and A-D-A triads have been evaluated and the reactivity of these systems exploited for the preparation of a series of new oligomeric D-A systems. The electrochemical characterization of D-A systems reported in this work seem, at the moment, to exclude any their possible use as active layer for Bulk Hetero-Junction cells. A potential use of these systems as additive in bulk heterojunction solar cells has been underlined. Indeed the preliminary results show that their addition (up to 20% in weight) to P3HT/PCBM-based Bulk Hetero-Junction, organic photovoltaics systems results in a lowering of the photovoltaic performances. The atomic force microscopy analysis seems to underline a correlation of power conversion efficiency reduction with the variation in the film morphology in presence of additives (**P1** and **P2**). This latter aspect deserves to be investigated in more details since a potential their application as morphology controlling additive can be envisaged. Work in this direction is ongoing in our research laboratories

Experimental

Material and Equipment

3,6-Diamino-N-(2-ethylhexyl)carbazole was prepared according to the described procedure.[24] Decafluoroazabenzene was prepared according to the described procedure. [26]

Solvents of analytical grade were used without further purification. Reagents were purchased from Sigma–Aldrich and used without further purification. Melting points were measured with an Electrothermal 9100 melting point instrument. UV spectra were recorded with a Perkin–Elmer Lambda 900 spectrophotometer. Fluorescence spectra were measured with an FP-Jasco 6200 Spectrofluometer. IR spectra were obtained with a Spectrum 100, FTIR Spectrometer Perkin– Elmer. NMR spectra were recorded in $CDCl_3$ with a Varian Mercury 400 Spectrometer (^{1}H 400 MHz, ^{19}F 376 MHz).

Electrochemical measurements were performed with an Autolab PGSTAT128N potentiostat/galvanostat in argon-purged acetonitrile/1,2-dichlorobenzene with 0.1M Bu_4NBF_4 as supporting electrolyte. A Glassy Carbon working electrode (Amel, surface 0.071 cm^2), a Platinum counterelectrode and an aqueous saturated calomel (SCE) reference electrode were used. The data have been referred to the Fc^+/Fc redox couple (ferricenium/ferrocene), according to IUPAC.

The melting point for triads G (cis/trans mixture) B, D, F and H, containing the carbazole moiety, have not reported since these compounds show a not defined solid-liquid transition. The diad I, has shown by TGA start to react around 80 °C and no melting has been observed.

Molecular structures and purity were analyzed by Gel Permeation Chromatography (GPC). Silica gel (230–400 mesh) was used for column chromatography.

Synthesis

General Procedure for the Synthesis of triads A-G

To a solution of decafluorobenzophenone (200mg ,0.55 mmol) and decafluoroazabenzene (200mg, 0.55mmol) in DMSO (3 mL) was added an excess of 2,7-diamminofluorene (MW 196, 3 equiv.), and the solution was stirred at room temperature .The reaction was monitored by TLC (alox; CH_2Cl_2). Then the solvent was removed under reduced pressure. The crude was purified by silica gel column chromatography, affording the desired product.

4-4'-(2,7diaminofluoren)-yl-2,3,5,6,2',3',5',6'-octafluorobenzophenone (triad A)

The crude solid was purified by Column Chromatography (Al_2O_3; CH_2Cl_2). mp 196 °C. Orange solid. (266 mg, 68%). ^{1}H NMR (400 MHz, DMSO) □□□ppm)= 3.73 (2H, s), 5.15 (NH_2, s), 6.57 (1H, dd, J= 1.8 and 8 Hz), 6.75 (1H, s), 7.00 (1H, d, J= 7.8 Hz), 7.18 (1H,s), 7.44 (1H, d, J= 8.1Hz), 7.52 (1H, d, J= 8.1 Hz), 9.07 (NH, broad, 1H). ^{19}F NMR (DMSO), □ (ppm)= -144.49 (2F, d, J = 24 Hz), -151,26 (2F, d, J= 24 Hz). MS (m/z) calcd for $C_{39}H_{22}F_8N_4O$ $[M]^+$ 714; found: 714. IR(cm^{-1}): 698, 799, 1016, 1088, 1188, 1259, 1324, 1397, 1470, 1499, 1523, 1640, 2962, 3226, 3357,3 444. $C_{39}H_{22}F_8N_4O$ (MW 714) calcd (%): C 65.55, H 3.10, N 7.84,; found (%): C 65.60, H 3.08, N 7.84. Optical properties reported in table 1.

4-4'-(2,7diaminofluoren)-yl-2,3,5,6,2',3',5',6'-octafluoroazobenzene (triad G cis+trans mixture)

The crude solid was purified by Column Chromatography (silica gel; CH_2Cl_2). Mp not defined. Dark violet solid. (254 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)= 6.66, 6.70, 7.19, 7.31, 7.41, 7.45, 7.51, 7.53, 7.55, 7.57, 7,62, 7.64. ^{19}F NMR (DMSO), δ (ppm)= -140 (2F), -147 (2F). HRMS (ESI positive) (m/z), calcd for $C_{38}H_{23}F_8N_6$, $[M+H]^+$: 715.185, found: 715.186. IR (cm^{-1}): 683, 802, 990, 1088, 1175, 1259, 1284, 1312, 1396, 1470, 1489, 1613, 1639, 2922, 3194, 3357 $C_{38}H_{22}F_8N_6$ (MW 714) calcd (%): C 63.87, H 3.10, N 11.76; found (%): C 63.80, H 3.11, N 11.70. Optical properties reported in table 2.

General Procedure for the Synthesis of triads B-H:

To a solution of decafluorobenzophenone (200mg, 0.5mmol) and decafluoroazabenzene (200mg, 0.5mmol) in DMSO (3 mL) was added an excess of 3,6-Diamino-N-(2-ethylhexyl)carbazole (MW 309 g/mol, 4 equiv.), and the solution was stirred at room temperature .The reaction was monitored by TLC (alox; CH2Cl2). Then the solvent was removed under reduced pressure. The crude was purified by silica gel column chromatography, affording the desired product.

4-4'-[3,6-Diamino-N-(2-ethylhexyl)carbazo)-yl]-2,3,5,6,2',3',5',6'-octafluorobenzophenone (triad B)

The crude solid was purified by Column Chromatography (silica gel; *n*-hexane/CH_2Cl_2, 1:1). Mp not defined. Orange solid. (413mg , 80%). ^{1}H NMR (400MHz, $CDCl_3$), δ (ppm)= 0.85-0.93 (6H, two t, J= 7.4Hz), 1.22-1.39 (8H, m), 2.04 (1H, m), 3.62 (NH), 4.08 (2H, CH_2-N, m), 6.30 (1H, s), 6.91 (1H, dd, J= 8.6, 2.2 Hz), 7.20 (2H, d, J= 8.7 Hz), 7.35 (1H, d, J= 2.1Hz), 7.72 (1H, s). ^{13}C NMR (400 MHz, $CDCl_3$)11.78, 14.88, 23.86, 25.28, 29.66, 31.87, 40.27, 48.50, 106.93, 109.82, 110.67, 115.40, 117.03, 122.01, 123.04, 123.85, 131.04, 137.09, 139.72, 140.17. ^{19}F NMR (DMSO), δ (ppm)= -143.33 (2F, m), -155.30 (2F, d, J= 18 Hz). IR (cm^{-1}): 748, 796, 990, 1200, 1236, 1262, 1292, 1317, 1395, 1492, 1534, 1634, 2337, 2928, 3345. HRMS (ESI positive) (m/z), calcd for $C_{53}H_{53}F_8N_6O$ $[M+H]^+$: 941.415, found: 941.416. $C_{53}H_{52}F_8N_6O$ (MW 940) calcd (%): C 67.65, H 5.57, N 8.93; found (%): C 67.60, H 5.52, N 8.90. Optical properties reported in table 1.

4-4'-[3,6-Diamino-N-(2-ethylhexyl)carbazo)-yl]-2,3,5,6,2',3',5',6'-octafluoroazobenzene (triad H)

The crude solid was purified by Column Chromatography (silica gel; *n*-hexane/CH_2Cl_2, 1:1). Mp not defined. Dark brown solid. (351mg, 68%). ^{1}H NMR (400MHz, $CDCl_3$), δ (ppm)= 0.79-0.93 (6H, two t, J= 7.4Hz), 1.04-1.42 (CH_2, 8H, m), 2.04 (CH, 1H, m), 2.98 (NH_2, s), 4.10 (CH_2-N, 2H, m), 6.17 (NH, 1H), 6.91 (1H, dd, J= 8.6 and 2 Hz), 7.20-7.22 (2H, m), 7.28 (1H, d, J= 8.8 Hz), 7.37 (1H, d, J= 2.1Hz), 7.73 (1H, s). ^{19}F NMR (DMSO), δ (ppm)= -144 (2F, m), -168 (2F, m). IR (cm^{-1}): 798, 1008, 1202, 1312, 1399, 1493, 1638, 2852, 2921. HRMS (ESI positive) (m/z), calcd for $C_{52}H_{53}F_8N_8$, $[M+H]^+$: 941.415, found: 941.668. $C_{52}H_{52}F_8N_8$ (MW 940) calcd (%): C 66.37, H 5.57, N 11.91; found (%): C 66.68, H 5.50, N 11.55. Optical properties reported in table 2.

General Procedure for the synthesis of triads C-D:

To a solution of 2,7-diamminofluorene (200mg, 1.02mmol) and 3,6-Diamino-N-(2-ethylhexyl) carbazole (200mg, 0.64mmol) in DMSO (3 mL) was added an excess of decafluorobenzophenone (MW 362 g/mol, 4 equiv.), and the solution was stirred at room temperature .The reaction was monitored by TLC (alox; CH_2Cl_2). Then the solvent was removed under reduced pressure. The crude was purified by silica gel column chromatography, affording the desired product.

(4,4'-(9H-fluorene-2,7-diyl)bis(azanediyl)bis(2,3,5,6-tetrafluoro-4,1-phenylene))bis((perfluorophenyl)methanone) (triad C)

The crude solid was purified by Column Chromatography (silica gel; *n*-hexane/CH_2Cl_2, 1:1). mp 197°C. yellow solid. (726 mg, 75%). ^{1}H NMR (400MHz, DMSO) δ (ppm)= 3.90 (CH_2, 2H), 7.14 (1H, d, J= 9Hz), 7.32 (1H, s), 7.76 (1H, d, J= 8.9Hz), 9.46 (NH,s). ^{19}F NMR (DMSO) δ (ppm)= -143.04 (2F, d, J= 22 Hz), -143.50 (2F, d, J= 32 Hz), -148.56 (1F, m), -150.92 (2F, d, J= 22 Hz), -160.38 (2F, m). IR (cm^{-1}): 772, 799, 989, 1093, 1187, 1260, 1326, 1399, 1469, 1490, 1527, 1610, 1641, 1673, 2963, 3348. HRMS (ESI positive) (m/z), calcd for $C_{39}H_{11}F_{18}N_2O_2$, $[M+H]^+$: 881.052, found: 881.049. $C_{39}H_{10}F_{18}N_2O_2$ (MW 880) calcd (%): C, 53.20, H 1.14, N 3.18; found (%): C 53.25, H 1.11, N 3.19. Optical properties reported in table 1.

(4,4'-(9-(2-ethylhexyl)-9H-carbazole-3,6-diyl)bis(azanediyl)bis(2,3,5,6-tetrafluoro-4,1-phenylene))bis((perfluorophenyl)methanone) (triad D)

The crude solid was purified by column chromatography (silica gel; *n*-hexane/CH_2Cl_2, 1:1). Mp not defined. Orange Solid. (533mg, 84%). ^{1}H NMR (400 MHz, CDCl3) δ (ppm)= 0.84-0.96 (CH_3, 6H, two t, J= 7.4 Hz),1.25-1.43 (CH_2, m, 8H), 2.05 (m, 1H), 4.18 (CH_2-N, 2H, dd, J= 2.7 and 7.4 Hz), 6.40 (s, 2H), 7.29-7.31(2H, d, J= 7.8 Hz), 7.37 (2H, d, J= 8.7 Hz), 7.84 (2H,s). ^{19}F NMR (DMSO) δ (ppm)= -142.01 (4F, m), -148.82 (1F, t, J= 25 and 50 Hz), -155.16 (2F, d, J= 18 Hz), -160.10 (2F, m). IR (cm^{-1}): 772, 987, 1050, 1127, 1185, 1290, 1326, 1398, 1500, 1540, 1640, 1672, 2853, 2928, 3376. HRMS (ESI positive) (m/z), calcd for $C_{46}H_{26}F_{18}N_3O_2$, $[M+H]^+$: 994.173, found: 994.173. $C_{46}H_{25}F_{18}N_3O_2$ (MW 993) calcd (%): C 55.60, H 2.54, N 4.23. found (%): C 55.63, H 2.57, N 4.28,. Optical properties reported in table 1.

General Procedure for the synthesis of triads E-F:

To a solution of 2,7-diamminofluorene (200mg, 1.02mmol) and 3,6-Diamino-N-(2-ethylhexyl)carbazole (200mg, 0.64mmol) in DMSO (3 mL) was added an excess of decafluoroazabenzene (MW 362 g/mol , 4 equiv.), and the solution was stirred at room temperature .The reaction was monitored by TLC (Al_2O_3; CH_2Cl_2). Then the solvent was removed under reduced pressure. The crude was purified by silica gel column chromatography, affording the desired product.

N^2-methyl-N^2,N^7-bis(2,3,5,6-tetrafluoro-4-((E)-(perfluorophenyl)diazenyl)phenyl)-9H-fluorene-2,7-diamine (triad E)

The crude solid was purified by Column Chromatography (silica gel; *n*-hexane/CH_2Cl_2, 1:1). mp 201 °C. Brown solid. (690 mg, 77%). ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm)= 2.62 (NH), 3.90 (CH_2, s, 2H), 3.92 (1H, s) , 6.26 (1H, s), 7.10 (1H, d, J= 7.6Hz), 7,70 (1H, d, J= 8.1Hz). ^{19}F NMR (DMSO) δ (ppm)= -148.22 (m), -149.81 (d, J= 22.2Hz), -151.41 (t, J= 39 and 20 Hz), -153.40 (d, J= 18 Hz), -161.10 (m), -161.87 (t, J= 44 Hz). IR (cm^{-1}): 794, 864, 1011, 1084, 1258, 1407, 1472, 1504, 1615, 1644, 2962, 3400. HRMS (ESI positive) (m/z), calcd for $C_{37}H_{11}F_{19}N_6$, $[M+H]^+$: 881.075, found: 881.076. $C_{37}H_{10}F_{19}N_6$ (MW 880) calcd (%): C 50.47, H 1.14, N 9.54; found (%): C 50.50, H 1.11, N 9.60. Optical properties reported in table 1.

9-(2-ethylhexyl)-N^2,N^7-bis(2,3,5,6-tetrafluoro-4-((E)-(perfluorophenyl)diazenyl)phenyl)-9H-carbazole-2,7-diamine (triad F)

The crude solid was purified by column chromatography (silica gel; *n*-hexane/CH_2Cl_2, 1:1). Mp not defined. Dark brown solid. (470mg, 74%). ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm)= 0.86-0.97 (CH_3, 6H, two t, J= 7.4Hz), 1.26-1.43 (CH_2, 8H, m), 2.08 (CH, m), 4.18 (CH_2-N, dd, J= 2.5 and 7.4 Hz), 6.35 (NH,1H), 7.30 (1H, d, J= 7.6 Hz), 7.37 (1H, d, J= 8.7 Hz), 7.82 (NH, d). ^{19}F NMR (DMSO) δ (ppm)= -148.18 (2F, d, J= 14 Hz), -150.18 (2F, d, J= 14 Hz), -152.04 (1F, t, J= 23 and 45 Hz), -155.93 (2F, d, J= 17 Hz), -162.03 (2F, dd, J= 14 and 23 Hz). IR (cm^{-1}): 802, 987, 1193, 1318, 1385, 1496, 1641, 2924, 3399. HRMS (ESI positive) (m/z), calcd for $C_{44}H_{26}F_{18}N_7$, $[M+H]^+$: 994.196, found: 994.197. $C_{44}H_{25}F_{18}N_7$ (MW 993) calcd (%): C 53.18, H 2.54, N 9.87. found (%): C 53.22, H 2.60, N 9.90. Optical properties reported in table 2.

General Procedure for the synthesis of dyad I:

To a solution of decafluorobenzophenone (200mg, 0.55mmol) in DMSO (3 mL) was added an equimolar quantity of 2,7-diamminofluorene and the solution was stirred at room temperature .The reaction was monitored by TLC (alox; CH_2Cl_2). Then the solvent was removed under reduced pressure. The crude was purified by silica gel column chromatography, affording the desired product.

4-(2,7-diamino-fluorenyl)-2,3,5,6,2',3',4',5',6'-nonafluoro-benzophenone (I)

The crude solid was purified by column chromatography (silica gel; *n*-hexane/CH_2Cl_2, 1:1). Mp not defined. Brown pale solid. (260 mg, 88%). ^{1}H NMR (400 MHz, DMSO) δ (ppm)= 3.81 (CH_2, 2H), 6.26 (1H, s), 6.70 (1H, dd, J= 2 and 9 Hz), 6.87 (1H, s), 7.05 (1H, d, J= 9 Hz), 7.20 (1H, s), 7.52 (1H, d, J= 9 Hz), 7.57 (1H, d. J= 9 Hz). ^{19}F NMR (DMSO) δ (ppm)= -143.46 (2F, d, J= 23 Hz), -143.50 (2F, d, J= 20 Hz), -149.17 (1F, m), -150.07 (2F, d, J= 25 Hz), -160.90 (2F, m). MS (ESI) (m/z) calcd for $C_{26}H_{11}F_9N_2O$ $[M]^+$: 538; found: 538. IR (cm^{-1}): 807, 987, 1191, 1243, 1321, 1389, 1469, 1491, 1534, 1637, 2963, 3200. $C_{26}H_{11}F_9N_2O$ (MW 538): calcd (%): C 58.01, H 2.06, N 5.20; found (%): C 58.12, H 2.10, N 5.30, (λ_{ex} 297nm, 369nm, λ_{em} 490nm)

General Procedure for the Synthesis of P1:

An equimolar quantity Monomer A and Monomer C has been reacted and stirred in DMSO at 180 °C for 6h. Then the solvent was removed under reduced pressure GPC =1203 (on the soluble component in THF). IR(cm^{-1}): 702, 771, 799, 986, 1094, 1194, 1244, 1322, 1393, 1469, 1493, 1534, 1613, 1638, 2962, 3240. E_{HOMO}=-4.89ev; E_{LUMO}=-3.22ev. BG= 1.67eV. Optical properties reported in table 3.

General Procedure for the Synthesis of P2:

An equimolar quantity Monomer E and Monomer G has been reacted and stirred in DMSO at 180 °C for 6h. Then the solvent was removed under reduced pressure. GPC= 1629 (on the soluble component in THF). IR(cm^{-1}): 795, 1010, 1090, 1258, 1397, 1469, 1499, 1614, 1639, 2961, 3238. E_{HOMO}=-4.98eV; E_{LUMO}=-2.88eV. BG= 2.10 eV. Optical properties reported in table 3.

General Procedure for the Synthesis of P3:

An equimolar quantity Monomer G and Monomer C has been reacted and stirred in DMSO at 180 °C for 6h. Then the solvent was removed under reduced pressure. GPC= 1195 (on the soluble component in THF). IR (cm^{-1}): 799, 989, 1098, 1259, 1325, 1395, 1470, 1639, 2962, 3246. E_{HOMO}=-5.06eV; E_{LUMO}=-3.67eV. BG= 1.39eV. Optical properties reported in table 3.

General Procedure for the Synthesis of P4:

An equimolar quantity Monomer D and Monomer B has been reacted and stirred in DMSO at 180 °C for 6h. Then the solvent was removed under reduced pressure. E_{HOMO}= -5.05eV; E_{LUMO}= -3.16eV. BG= 1.89eV. Optical properties reported in table 3.

General Procedure for the Synthesis of P5:

An equimolar quantity of Monomer F and Monomer H has been reacted and stirred in DMSO at 180 °C for 6h. Then the solvent was removed under reduced pressure. E_{HOMO}= -5.03eV; E_{LUMO}= -3.66eV. BG 1.37eV. Optical properties reported in table 3.

Gel permeation chromatography (GPC)

Molecular weights and molecular weight distributions were determined using gel permeation chromatography (GPC). GPC systems is constituted by a WATERS 1515 isocratic Pump, WATERS 2414 refractive index detector and four Waters Styragel columns (HR2, HR3, HR4, and HR5) working in series. The number-average molar molecular weight (Mn) and the polydispersity (PDI = Mw/Mn) were obtained using a calibration derived from PS standards (Sigma-Aldrich). All oligomers samples were prepared at 5 g L^{-1} concentrations and filtered through PTFE 0.2 µm filters. THF was used as eluent at a flow rate of 1.0 mL min^{-1}. (see supporting information)

Thermal analysis (TGA):

TGA was performed on a Mettler Toledo TGA/SDTA 851e module calibrated with indium (T_m = 156.60 °C) and aluminium (T_m =660.30 °C) The typical sample size is 6-8 mg for TGA and the temperature range used id 30-250°C at 5°C min^{-1}. Sample were placed I aopen alumina pans and were purged by a stream of dry nitrogenum flowing at 50 mL min^{-1}

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References

1 D. O'Hagan, *Chem. Soc. Rev.*, 2008, **37**, 308.
2. C. Sanbor and D. O'Hagan, *J. Fluorine Chem.*, 2006, **127**, 303.
3 K. L. Kirk, *J. Fluorine Chem.*, 2006, **127**, 1013.
4 K. A. Mauritz and R. B. Moore, *Chem. Rev.*, 2004, **104**, 4535.
5 P. Liu, H. Chen, S. Daniel, D. Hang, L. Zhao, H. Wang and Z. Zeng, *J. Fluorine Chem.*, 2013, **156**, 327-332.
6 S. O. Jeon, K. S. Yook and J. Y. Lee, *Org. Electron.*, 2009. **10**(8), 1583,
7 Q. Wei, T. Nishizawa, K.Tajima and K. Hashimoto, *Adv. Mat.*, 2008. **20**(11), 2211-2216.
8 M. Karakawa, T. Nagai, T. Irita, K. Adachi, Y. Ie and Y. Aso, *J. Fluorine Chem.*, 2012. **144**, 51-58.
9 J. Ding, F. Liu, M. Li, M. Day and M. Zhou, *J. Polym Sci. A: Polym Chem.*, 2002, **40**, 4205-4216.
10 Y. Qi, J. Jiang, C. L. Callender, M. Day and J. Ding, *Applied Optics*, 2006, **45**, 7480-7487.
11 J. Ding, X. Du, M. Day, J. Jiang, C. L. Callender and J. Stupak, *Macromolecules*, 2007, **40**, 3145-3153.
12 F. W Mercer, J. Wojtowicz, and D. Duff, *J Polym. Sci. Part A: Polym. Chem.* 1992, **30**, 1767.
13 F. W. Mercer, M. M. Fone, V .N. Reddy and A. A. Goodwin, *Polymer*, 1997, **38**, 1989.
14. A. A. Goodwin, F. W. Mercer and M. T. McKenzie., *Macromolecules*, 1997, **30**, 2767-2774.
15 H. Hendricks, K. S. Yau, A. R. Smith and W. B. Wan, *Mater. Res. Soc. Symp. Proc.*, 1995, **381**, 59-67.
16 K. Miyatake, K. Oyaizu, E. Tsuchida and A. S. Hay, *Macromolecules*, 2001, **34**, 2065-2071.
17 K. Kimura, Y. Tabuchi, Y. Yamashita, P. E. Cassidy, J. W. Fitch and Y. Okumura, *Polym. Advanced Technologies*, 2000, **11**, 757-765.
18 P. Kirsh, *Modern Fluoroorganic Chemistry,* Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2004.
19 A. Pažitný, T Solčán, and D. Vegh, *J. Fluorine Chem.*, 2009, **130**, 267-294.
20 L. Miozzo, A. Papagni and P. Del Buttero, *Targets in Heterocyclic Systems*, 2007, 181.
21 A. Papagni, P. Del Buttero, M. Moret, A. Sassella, L. Miozzo and G. Ridolfi, *Chem. Mat.*, 2003, **15**, 5010-5018.
22 P. Del Buttero, R. Gironda, M. Moret, A. Papagni, M. Parravicini, S. Rizzato and L. Miozzo, *Eur. J. Org. Chem.*, 2011, **12**, 2265-2271.
23 a) L. Lin, C.P. Lee, M. H. Yeh, A. Baheti, R. Vittal, K. R. Justin Thomas and K. C. Ho, *J. of Power Sources*, 2012, **215**, 122–129; b) A. Baheti, P. Singh, C. P. Lee, K. R. Justin Thomas and K. C. Ho, *J. Org. Chem*, 2011, **76** (12), 4910–4920 c) N. Blouin, A. Michauld, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletete, G. Durocher, Y. Tao and M. Leclerc, *J. Am. Chem Soc.*, 2007, **130** (2), 732-742 ; d) K. Karon, M. Lapkowski and G.Juozas, *Electrochim. Acta*, 2014, **123**, 176–182.
24 H. C. Kim, J. S. Kim, K. S. Kim, H. K. Park, S. Baek and M. Ree, *J. Polym Sci. A: Polym Chem.*, 2004, **42**, 825-834.
25 M. Matsui, *J. Fluorine Chem.*, 1999, **96**, 65-69.
26 J. M. Birchall., R. N. Haszeldine and J. E. G. Kemp, *J. Chem. Soc. C: Organic*, 1970, 449.
27 X. Xue, J. Zue, W.Zhang, Z. Zhang, and W. Zhu, *Polymer*, 2009, **50**, 4512-4519.
28 S. Leclair, L. Matthew, M. Giguere, S. Motallebi and Y.Zhao, *Macromolecules*, 2003. **36**, 9024-9032.
29 A. K. K. Kyaw, D. H. Wang, V. Gupta, W. L. Leong, L. Ke, G. C. Bazan and A. J. Heeger, *ACS Nano*, 2013, **7**, 4569-4577.

30 S. C. Price, A. C. Stuart and L. Yang, H. Zhou and W. Yoy, *J. Am. Chem. Soc.*, 2011, **133**(, 4625-4631.

31 J. R. Tumbleston, A. C. Stuart, E. Gann, W. You and H. Ade, *Adv Funct. Mater.*, 2013, **23**, 3463-3470.

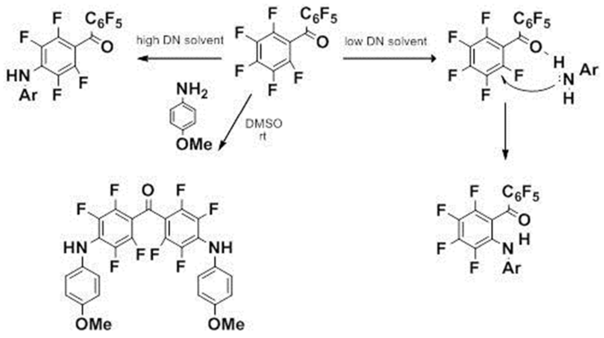
32 R. Po, C. Carbonera, A. Bernardi and N. Camaioni, *Energy & Environmental Science*, 2010, **4**, 285-310.

33 M. Manceau and S.Berson, *Nanotechnology*, 2014. **25**, 014018.

34 B. Kang, L.W. Tan and S. V. R. Silva, *Appl. Phys. Lett.*, 2008. **93**, 133302, 1-3.

35 S. Jeong, S.-H. Woo, H.-K. Lyu and Y. S. Han, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 1908–1914

36 J. S. Kim, J. H. Park, J. H. Lee, J. Jo, D. Y. Kim and K. Cho *Appl. Phys. Lett.*, 2007, **91**, 1-3.



Scheme 1 Reactivity of decafluorobenzophenone towards para-methoxy-anilines

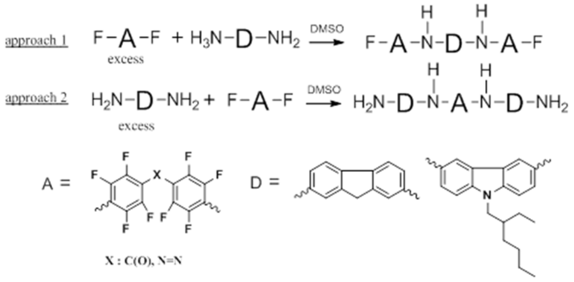
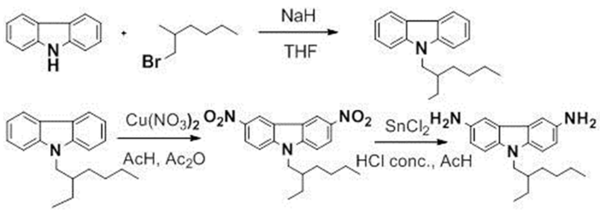
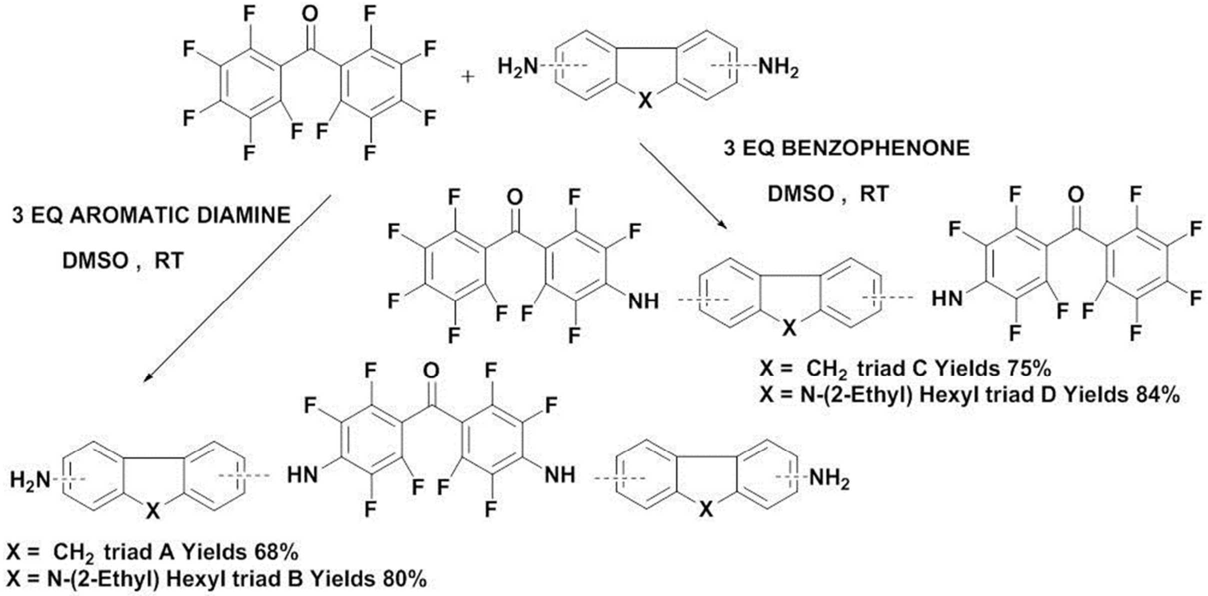


Chart 1 Approaches to the synthesis of A-D-A
and D-A-D systems



Scheme 2 Synthesis of diamino-carbazole derivative



Scheme 3 Synthesis of D-A-D and A-D-A employing diaminofluorene and diamino-carbazole.

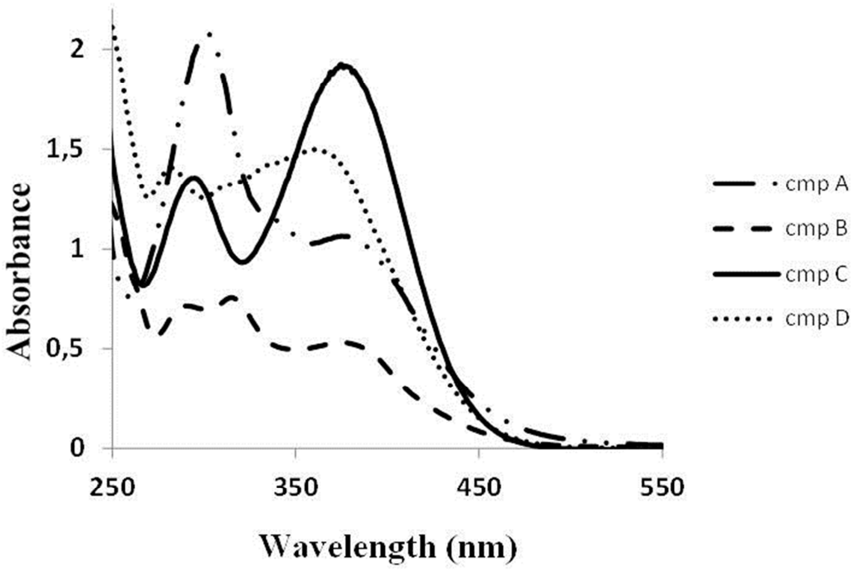
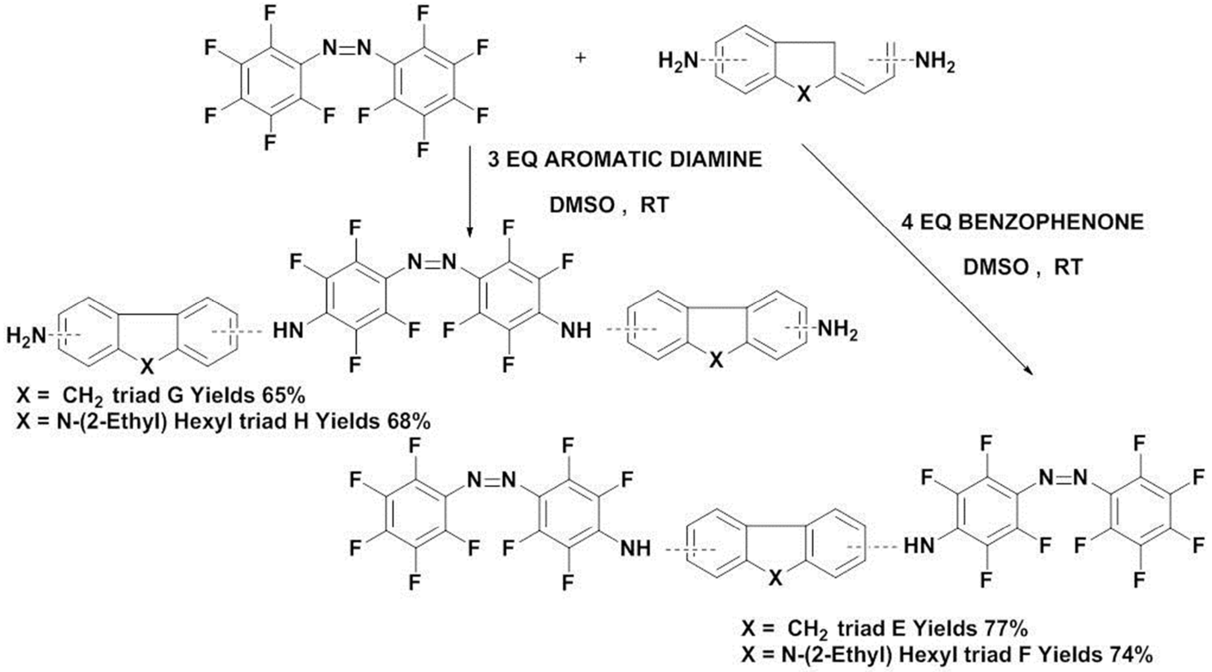
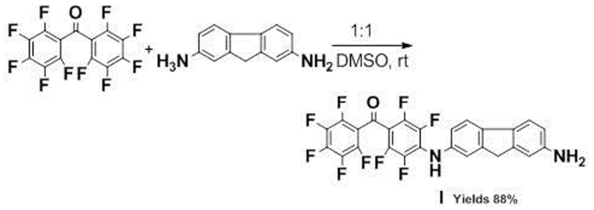


Figure 1 Absorption spectra of selected monomers A, B, C and D (10-5M CH2Cl2 solutions).



Scheme 4 Synthesis of triads with polyfluoroazobenzene acceptor and diammino fluorine and diamino-carbazole as donors.



Scheme 5 Synthesis of the diad benzophenone-fluorene I.

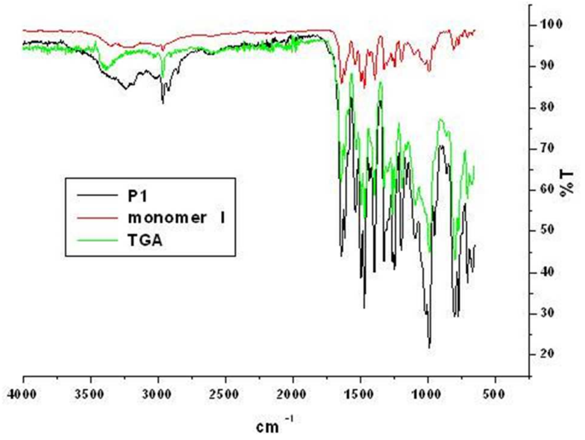


Figure 2 Comparison of IR spectrum of the material from TGA experiment (green line), monomer I (red line) and P1 (black line).

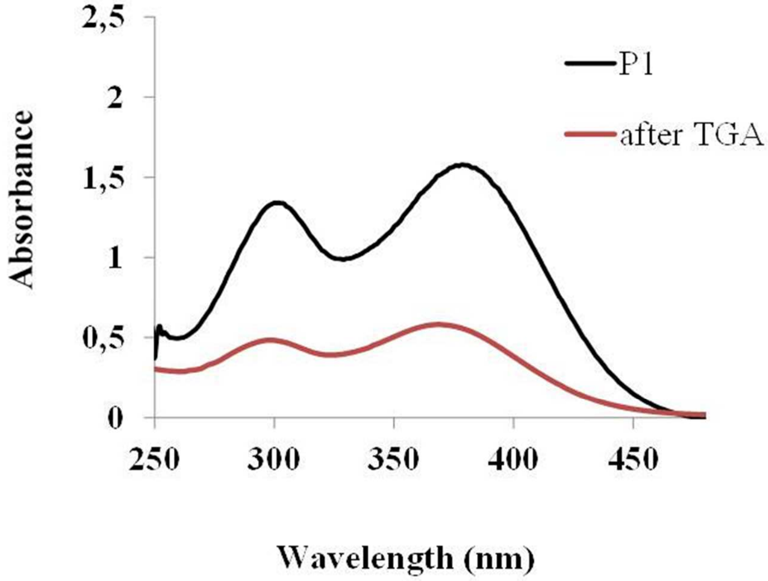
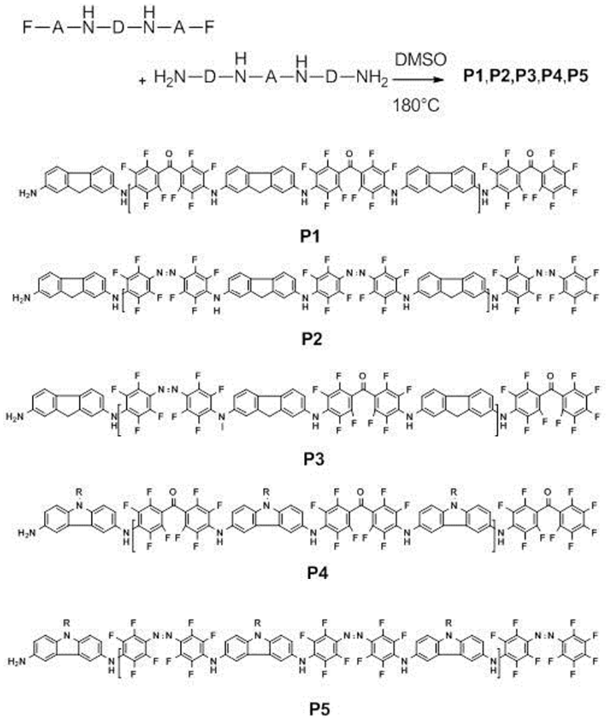


Figure 3 Comparison of UV-Vis spectrum of the materials from TGA experiment (red line) and that from reaction in DMSO (black line)



Scheme 6. Synthesis of polymeric systems containing polifluorobenzophenone and polifluoroazobenzene acceptors and fluorene diamine and diaminocarbazole donor moieties.

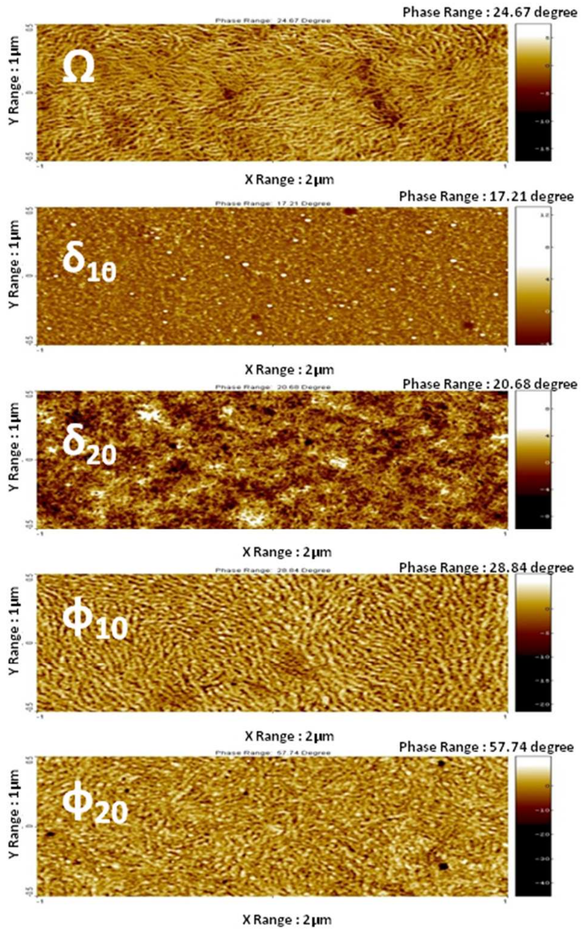
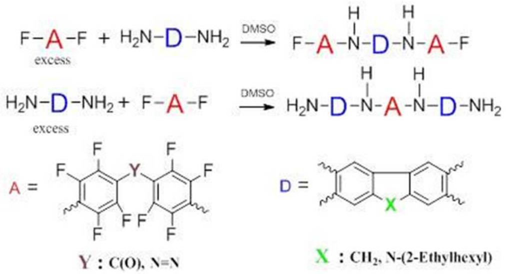


Figure 4 AFM Phase images of films of pristine 40P3HT:60PCBM (A) with 10%w (B) and 20% (C) of P1 and with 10%w (D) and 20% (E) of P4 respectively.

Graphical abstract



A series of Donor-Accepting-Donor (D-A-D) and Accepting-Donor-Accepting (A-D-A) compounds have been prepared and employed in the synthesis of oligomers potentially useful in optoelectronic applications