Reactivity of decafluorobenzophenone and decafluoroazobenzene towards aromatic diamines: a practical 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 have been prepared exploiting the relative ability of polyfluorinated azobenzenes and benzophenone to undergo aromatic nucleophilic substitution reactions with aromatic amines. A high *para*-regioselectivity is obtained when fluorene and carbazole-based diamines have been used in a high Donor Number solvent environment such as DMSO. The prepared triads have been employed in the synthesis of oligomers with the aim of evaluating them as photovoltaic material additives in optoelectronic applications.

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},[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 materials science, in important fields such as liquid crystal 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.

The 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). The latter have shown high negative thermo optical 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 is 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 the *ortho/para* nucleophilic substitution regiochemistry can be controlled by acting on solvent polarity. In particular we have found a correlation between the solvent Lewis basicity, expressed by the Donor Number (DN), and the *ortho/para* substitution ratio. Indeed low DN solvents favor hydrogen bonding between the N–H bond of the incoming aniline and the carbonyl group resulting in an *ortho* nucleophilic substitution, while in high DN solvents the C=O⋯H–N interaction is perturbed addressing the nucleophilic substitution in the *para* position. In addition we have shown that the *ortho*-anilino-substituted derivatives were suitable starting materials for the synthesis of polyfluorinated acridines and acridones.[21,22]

As expected, in these substitution reactions, good yields were obtained with electron-rich anilines such as 4-methoxy or 4-dimethylamino-aniline.[22] In addition, when the reaction with 4-methoxy-aniline was performed in DMSO (a high DN solvent), we have always observed the formation of 4,4′-bis-anisidino-octafluoro-benzophenone even if stoichiometric amounts
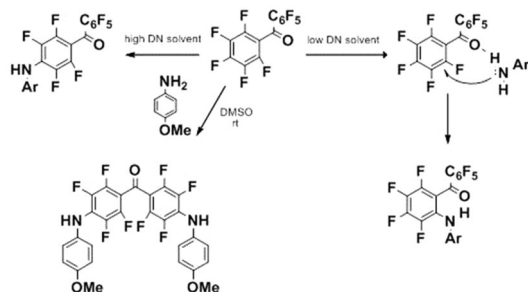
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Scheme 1 Reactivity of decafluorobenzophenone towards *para*-methoxy-anilines.

Chart 1 Approaches to the synthesis of A–D–A and D–A–D systems.

Scheme 2 Synthesis of diamino-carbazole derivatives.

of amines were used. This latter result underlines two aspects: (1) the two perfluorophenyl rings react almost independently, (2) the formation of mono or di-substituted derivatives is controlled by the equivalent of aniline used per equivalent of decafluoro-benzophenone. Indeed, when decafluorobenzophenone was allowed to react with 2 eq. of 4-methoxy-aniline in DMSO at room temperature, after 7 h 4,4′-dianisidino-octafluoro-benzophenone was recovered in 95% yield (Scheme 1).

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.

4,4′-*para*-Anisidino-octafluorobenzophenone represents a Donor–Acceptor–Donor (D–A–D) system where the donor part is expressed by a *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. 4,4′-*para*-Anisidino-octaflurobenzophenone shows a maximum absorption at around 370 nm and, in principle, the absorption properties of these systems can be tuned by acting on the electron donating properties of the substituents on the starting anilines.

Indeed a red shift is expected when the methoxy group is replaced by a more electron donating group such as the amino one. As an extension of this work, here we report on the results obtained when aromatic diamines are employed. In particular our attention was focussed on the synthesis of Donor–Acceptor–Donor (D–A–D) and Acceptor–Donor–Acceptor (A–D–A) systems operating, respectively, with an excess of decafluorobenzo-phenone (A–D–A, approach 1) or aromatic diamines (D–A–D, approach 2). We have found these two approaches interesting 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).

The aromatic diamines we have selected were 2,7-diamino-fluorene and 3,6-diamino-*N*-(2-ethylhexyl)-carbazole since these amines have been recently employed in the synthesis of a polymeric system potentially useful in developing new organic photovoltaic cells. In particular new diaminofluorene dyes have been used in dye sensitized solar sells[23a,b] and aminocarbazole employed in polymers for organic photovoltaic cells.[23c,d]

2,7-Diaminofluorene is commercially available while 3,6-diamino-*N*-(2-ethylhexyl)-carbazole has been prepared by alkylation
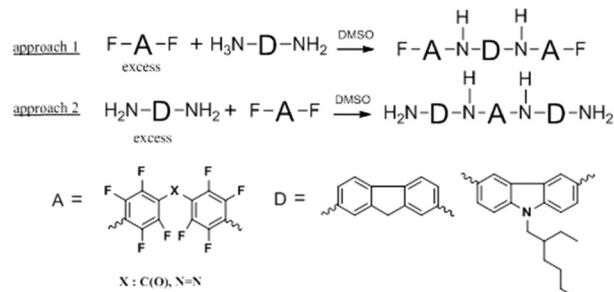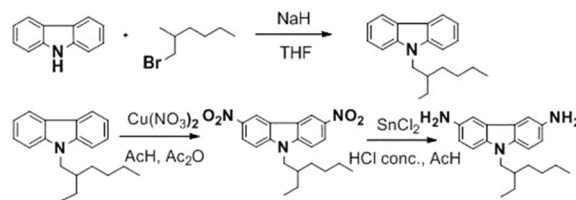
of carbazole with 2-ethylhexylbromide, followed by double nitration of *N*-(2-ethylhexyl)carbazole and the reduction of the nitro group with SnCl₂ (Scheme 2).[24]

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).

All the new compounds have been fully characterized spectro-scopically and the absorption and emission properties of triads A–D–A (**C**) and (**B**) and D–A–D (**A**) and (**D**) are reported in Fig. 1 and Table 1. All of the triads show maximum absorptions in the UV range centered at around 370 nm; this reflects the limited π-conjugation of the benzophenone and lower absorption ener-gies are observed when the acceptor unit is inside the triad. Triad **D** shows maximum absorptions at slightly higher energy than **A** and **B**. Triads **A**, **B**, and **C** show a reasonably high Stokes shift in their emission properties while in triad **D** the emission practically coincides with the absorption (Fig. 1 and Table 1).
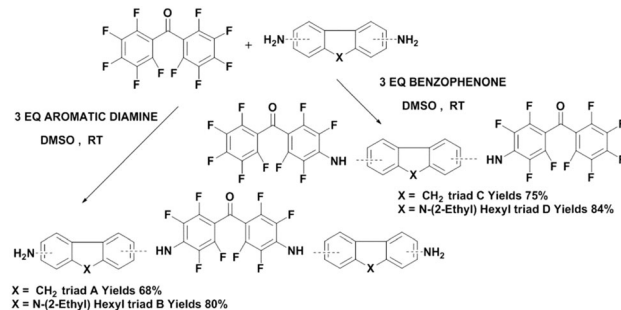
Scheme 3 Synthesis of D–A–D and A–D–A employing diaminofluorene and diamino-carbazole.
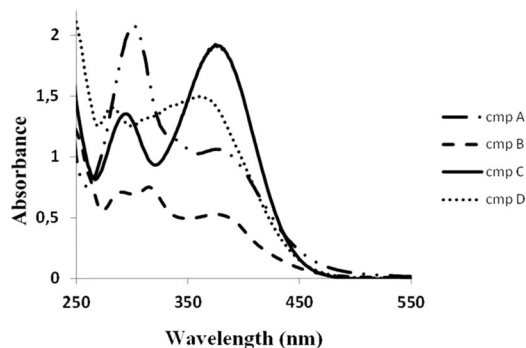
Fig. 1 Absorption spectra of selected monomers **A**, **B**, **C** and **D** (10^{-5} M CH$_2$Cl$_2$ solutions).

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

Table 1 Absorption and emission properties of the triads A, B, C and D

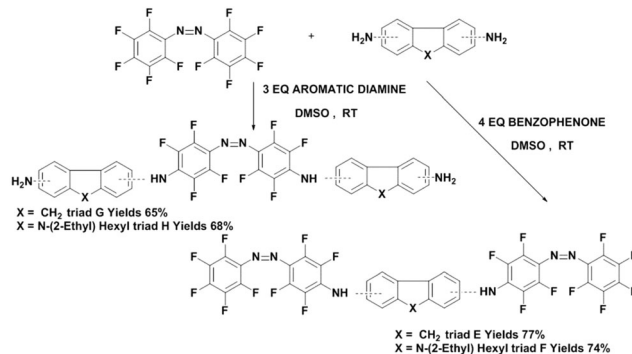| Triad	Abs λ (nm)	Emission λ_{max} (nm)
A	$\lambda_1 = 302$ $\lambda_2 = 377$	451 ($\lambda_{ex} = 370$)
B	$\lambda_1 = 290$, $\lambda_2 = 314$ $\lambda_3 = 373$	453 ($\lambda_{ex} = 370$)
C	$\lambda_1 = 295$ $\lambda_2 = 380$	517 ($\lambda_{ex} = 380$)
D	$\lambda_1 = 282$ $\lambda_2 = 360$	363 ($\lambda_{ex} = 360$)

Table 2 Absorption and emission properties of the triads E, F, G and H

Triad	Abs λ (nm)	Emission λ_{max} (nm)
E	$\lambda_1 = 285$ $\lambda_2 = 453$	684
F	$\lambda_1 = 386$ $\lambda_2 = 438$	567
G	$\lambda_1 = 296$ $\lambda_2 = 492$	629
H	$\lambda_1 = 391$ $\lambda_2 = 489$	566

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, the reaction of polyfluoroazobenzene with sulfur, oxygen and nitrogen nucleophiles has 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 also been proposed as photoresponsive materials with potential applications in optical storage devices[27] and liquid crystal displays.[28]

Decafluoroazobenzene has been prepared following the procedure reported in the literature, by oxidation of pentafluoroaniline with Pb(AcO)$_4$[26] and by replacing benzene with methylene chloride. Decafluoroazobenzene was then allowed to react with 2,7-diaminofluorene and 3,6-diamino-N-(2-ethylhexyl)-carbazole following the same approach described for decafluorobenzophenone. By this, triads A–D–A (**E**), (**F**), and D–A–D (**G**) and (**H**) have been synthesized in reasonable to good chemical yields (Scheme 4).

The absorption and emission properties of triads **E**, **F**, **G** and **H** are displayed in Table 2.

As expected a red shift in optical properties is observed moving from the benzophenone acceptor to the azobenzene one, this reflects a better conjugation between the two polyfluoroaromatic rings 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 a donor. A good Stokes shift, over 100 nm 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 D–A dyad **I** was obtained in satisfactory yields (Scheme 5).

Dyad **I** has both reactive amino and 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 reaction occurs.

Indeed, TGA provides the temperature at which the sample starts to lose its 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 the loss of materials started at 80–90 °C and stopped at 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 seem to indicate that 180 °C is the suitable temperature for polymerization. With this information, 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 Fig. 2 and 3 the comparison of IR
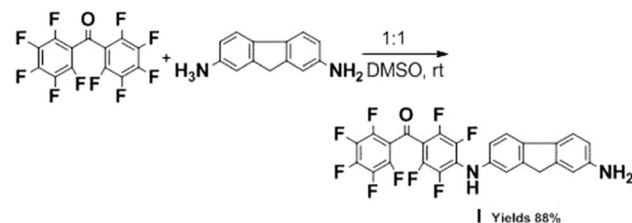
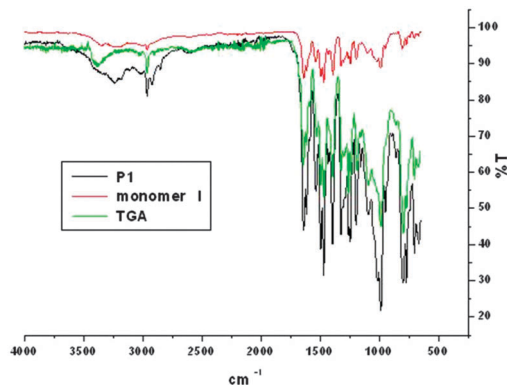Scheme 5 Synthesis of dyad benzophenone-fluorene **I**.

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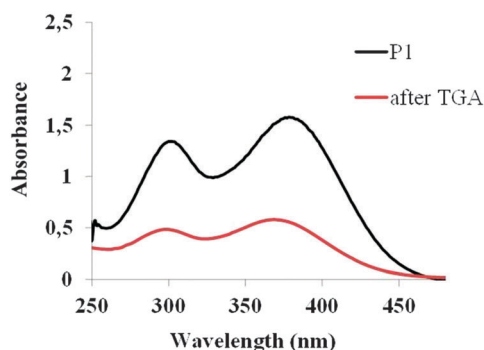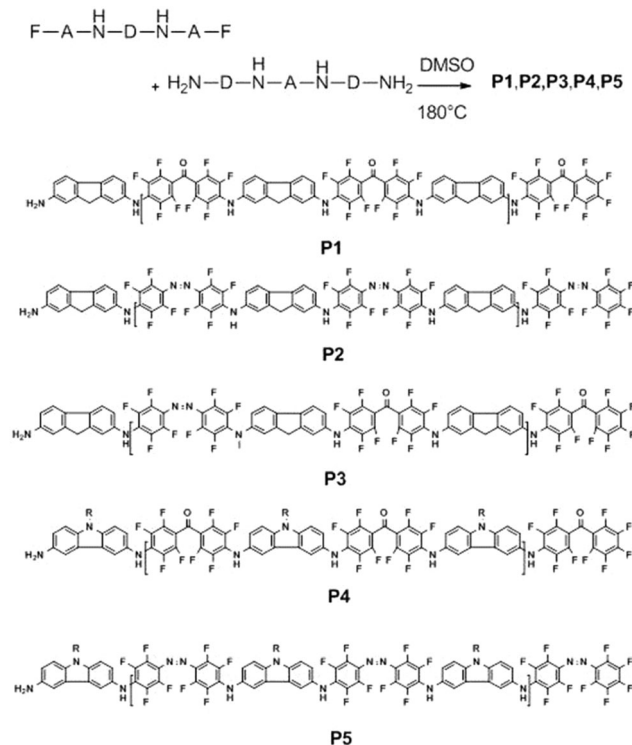

Fig. 3 Comparison of the UV-Vis spectrum of the materials from TGA experiment (red line) and that from reaction in DMSO (black line).

Scheme 6 Synthesis of polymeric systems containing polyfluorobenzophenone and polyfluoroazobenzene as acceptors and fluorene diamine and diamino carbazole as donor moieties.

spectra and UV-Vis spectra of the material collected from the TGA experiment and that from the reaction in refluxing DMSO is reported. It was found that under both conditions, the collected materials were almost identical.

With this information, 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 were analyzed (Scheme 6). The mixed oligomer **P3** obtained from monomers **C** and **G** containing both octafluorobenzophenone and octafluoroazobenzene shows an absorbance in solution which is practically the sum of absorbance of oligomers **P1** and **P2** (see Fig. S4, ESI†). All the oligomers show a reduction potential below −1.70 V and an oxidation potential over 0.25 V with the HOMO energy level in the range of −4.89 to −5.03 eV and the LUMO energy level from 2.88 to 3.66 eV which correspond to an energy gap in the range of 2.10 to 1.37 eV. The observed energy gap values for these systems fall in the interesting window for their potential use as the active layer of bulk heterojunction (BHJ) organic solar cells (see Fig. S1, ESI†).

All the oligomers show slight differences between the HOMO level and oxidation peaks with a similar current intensity. The main differences between them are related to the position of the LUMO energy level, that is, the consequence of different reduction behavior. Only the reduction peaks of oligomers **P2** and **P5** have intensity comparable to oxidation ones. However, none of these products have reversible oxidation and/or reduction behavior, as is expected from charge carrier transport properties, to show low efficiencies and consequently cannot be proposed as active materials in BHJ.

In Table 3 absorption and emission properties together with the HOMO/LUMO level optical and electrochemical energy gaps are reported (see also Fig. S4–S8, ESI†).

Table 3 Spectroscopic data of oligomers **P1–P5**

Oligomer (combined triads)	Abs λ (nm)	Emission, λ_{max} (nm)	HOMO/LUMO (eV)	E_{gap} (eV)
P1 (**A** + **C**)	$\lambda_1 = 300$ $\lambda_2 = 378$	460	−4.89/−3.22	1.67
P2 (**E** + **G**)	$\lambda_1 = 299$ $\lambda_2 = 374$ $\lambda_3 = 490$	625	−4.98/−2.88	2.10
P3 (**C** + **G**)	$\lambda_1 = 299$ $\lambda_2 = 374$ $\lambda_3 = 490$	565	−5.06/−3.67	1.39
P4 (**B** + **D**)	$\lambda_1 = 283$ $\lambda_2 = 307$ $\lambda_3 = 365$		−5.05/−3.16	1.89
P5 (**F** + **H**)	$\lambda_1 = 389$ $\lambda_2 = 451$		−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 device 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, which facilitates the hole extraction process.[34]

In the latter field, polyvinylidenefluoride (PVDF)[6] and perfluoroalkyl fullerene[7,8] have been applied as buffer layers in poly-3-hexylthiophene:phenyl-C61-butyric acid methyl ester (P3HT:PCBM) BHJ solar cells. In addition, it is reported that the introduction of a 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 the fill factor and PCE.
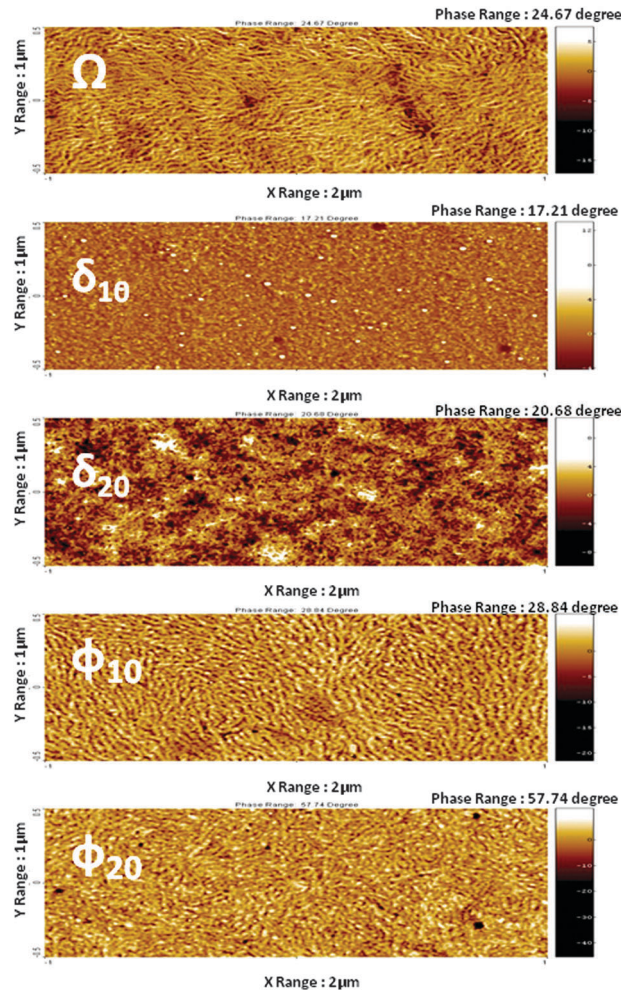
Based on these considerations and on the data obtained with these synthesized systems, their use as active components in BHJ cells being excluded due to the irreversible redox behavior, we have looked at them as possible additives to P3HT:PCBM-based BHJ solar cells. Thus we have fabricated inverted polymer 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 of 1.9–2.4%, thus compared to 2.56% measured for a reference device without the fluorinated additive (Table 4).

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 a pristine blend. These preliminary results could be ascribed to a disfavored charge extraction process at the electrode interface, possible charge carrier 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

Fig. 4 AFM phase images of films of pristine P3HT/PCBM (40 : 60; Ω) with 10%w (δ_{10}) and 20% (δ_{20}) of **P1** and with 10%w (Φ_{10}) and 20% (Φ_{20}) of **P4** respectively.

collecting images of films by Atomic Force Microscopy (AFM). In Fig. 4 the morphologies of pristine P3HT/PCBM and those with 10% and 20% in weight of **P1** and **P4**, respectively, are reported.

AFM images of P3HT:PCBM:**P1** blends (Fig. 4, δ_{10} and δ_{20}) show that the surface morphology is remarkably changed compared to the P3HT:PCBM blend (Fig. 4, Ω), suggesting that the fluorinated additive indeed migrates toward the surface, as expected from the literature.[7] P3HT:PCBM:**P4** blends (Fig. 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 disfavoring 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.

Table 4 Photovoltaic parameters for the prepared cells using **P1** and **P4** as additives

Additive	FF av (max)	V_{oc} av (max) (mV)	J_{sc} av (max) (Ma cm^{-2})	PCE av Max (%)
10 wt% **P4**	0.48 (0.50)	553 (555)	6.03 (7.29)	2.03 (2.03)
20 wt% **P4**	0.47 (0.59)	571 (590)	6.31 (7.12)	1.91 (2.39)
10 wt% **P1**	0.51 (0.58)	576 (602)	6.93 (7.32)	2.05 (2.48)
20 wt% **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)

Conclusions

In conclusion, while exploring the reactivity of decafluoro-benzophenone and decafluoroazobenzene toward aromatic diamines such as diaminofluorene 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 the nucleophilic substitution reaction of decafluoroazabenzene and decafluorobenzophenone towards aromatic diamine, a study that, to the best of our knowledge, has never been reported before. In addition, exploiting the control operated by the basic nature (expressed by the Donor Number (DN)), high *para* regioselectivity has 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 seems, at the moment, to exclude any of their possible use as active layers for Bulk Hetero-Junction cells. A potential use of these systems as additives in bulk heterojunction solar cells has been underlined. Indeed the preliminary results show that their addition (up to 20% in weight) to the P3HT/PCBM-based Bulk Hetero-Junction and organic photovoltaic 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 the presence of additives (**P1** and **P2**). The latter aspect deserves to be investigated in more detail since their potential application as morphology controlling additives can be envisaged. Work in this direction is ongoing in our research laboratories.

Experimental

Materials 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 using an Electrothermal 9100 melting point instrument. UV spectra were recorded on a Perkin–Elmer Lambda 900 spectrophotometer. Fluorescence spectra were measured using an FP-Jasco 6200 Spectrofluorometer. IR spectra were obtained using a Spectrum 100, FTIR Spectrometer Perkin–Elmer. NMR spectra were recorded in CDCl$_3$ using a Varian Mercury 400 Spectrometer (^{1}H 400 MHz, ^{19}F 376 MHz).

Electrochemical measurements were performed using an Autolab PGSTAT128N potentiostat/galvanostat in argon-purged acetonitrile–1,2-dichlorobenzene with 0.1 M Bu$_4$NBF$_4$ as a supporting electrolyte. A Glassy Carbon working electrode (Amel, surface 0.071 cm^2), a platinum counter electrode 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 points for triads **G** (*cis/trans* mixture) **B**, **D**, **F** and **H**, containing the carbazole moiety, have not been reported since these compounds do not show a defined solid–liquid transition. It has been shown by TGA that dyad **I** starts to react at 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 (200 mg, 0.55 mmol) and decafluoroazabenzene (200 mg, 0.55 mmol) in DMSO (3 mL) was added an excess of 2,7-diaminofluorene (M_W 196, 3 equiv.), and the solution was stirred at room temperature. The reaction was monitored by TLC (alox; CH$_2$Cl$_2$). Then the solvent was removed under reduced pressure. The crude was purified by silica gel column chromatography, affording the desired product.

4-4′-(2,7-Diaminofluoren)-yl-2,3,5,6,2′,3′,5′,6′-octafluorobenzo-phenone (triad A). The crude solid was purified by column chromatography (Al$_2$O$_3$; CH$_2$Cl$_2$). mp 196 °C. Orange solid (266 mg, 68%). ^{1}H NMR (400 MHz, DMSO), δ (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* = 8.1 Hz), 7.52 (1H, d, *J* = 8.1 Hz), 9.07 (NH, broad, 1H). ^{19}F NMR (DMSO), δ (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$_8$N$_4$O [M]$^+$ 714; found: 714. IR(cm^{-1}): 698, 799, 1016, 1088, 1188, 1259, 1324, 1397, 1470, 1499, 1523, 1640, 2962, 3226, 3357, 3444. C$_{39}$H$_{22}$F$_8$N$_4$O (M_W 714) calcd (%): C 65.55, H 3.10, N 7.84; found (%): C 65.60, H 3.08, N 7.84. Optical properties are reported in Table 1.

4-4′-(2,7-Diaminofluoren)-yl-2,3,5,6,2′,3′,5′,6′-octafluoroazo-benzene (triad G *cis* + *trans* mixture). The crude solid was purified by column chromatography (silica gel; CH$_2$Cl$_2$). 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$_8$N$_6$, [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$_8$N$_6$ (M_W 714) calcd (%): C 63.87, H 3.10, N 11.76; found (%): C 63.80, H 3.11, N 11.70. Optical properties are reported in Table 2.

General procedure for the synthesis of triads B–H

To a solution of decafluorobenzophenone (200 mg, 0.5 mmol) and decafluoroazabenzene (200 mg, 0.5 mmol) in DMSO (3 mL) was added an excess of 3,6-diamino-*N*-(2-ethylhexyl)carbazole (M_W 309 g mol^{-1}, 4 equiv.), and the solution was stirred at room temperature. The reaction was monitored by TLC (alox; CH$_2$Cl$_2$). 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$_2$Cl$_2$, 1 : 1). Mp not defined. Orange solid (413 mg, 80%). ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm) = 0.85–0.93 (6H, two t, J = 7.4 Hz), 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 = 2.1 Hz), 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$_8$N$_6$O [M + H]$^+$: 941.415, found: 941.416. C$_{53}$H$_{52}$F$_8$N$_6$O (M$_W$ 940) calcd (%): C 67.65, H 5.57, N 8.93; found (%): C 67.60, H 5.52, N 8.90. Optical properties are 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$_2$Cl$_2$, 1 : 1). Mp not defined. Dark brown solid (351 mg, 68%). ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm) = 0.79–0.93 (6H, two t, J = 7.4 Hz), 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 = 2.1 Hz), 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$_8$N$_8$, [M + H]$^+$: 941.415, found: 941.668. C$_{52}$H$_{52}$F$_8$N$_8$ (M$_W$ 940) calcd (%): C 66.37, H 5.57, N 11.91; found (%): C 66.68, H 5.50, N 11.55. Optical properties are reported in Table 2.

General procedure for the synthesis of triads C–D

To a solution of 2,7-diamminofluorene (200 mg, 1.02 mmol) and 3,6-diamino-N-(2-ethylhexyl) carbazole (200 mg, 0.64 mmol) in DMSO (3 mL) was added an excess of decafluorobenzophenone (M$_W$ 362 g mol^{-1}, 4 equiv.), and the solution was stirred at room temperature. The reaction was monitored by TLC (alox; CH$_2$Cl$_2$). 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$_2$Cl$_2$, 1 : 1). mp 197 °C. Yellow solid (726 mg, 75%). ^{1}H NMR (400 MHz, DMSO), δ (ppm) = 3.90 (CH$_2$, 2H), 7.14 (1H, d, J = 9 Hz), 7.32 (1H, s), 7.76 (1H, d, J = 8.9 Hz), 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$_2$O$_2$, [M + H]$^+$: 881.052, found: 881.049. C$_{39}$H$_{10}$F$_{18}$N$_2$O$_2$ (M$_W$ 880) calcd

(%): C, 53.20, H 1.14, N 3.18; found (%): C 53.25, H 1.11, N 3.19. Optical properties are 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$_2$Cl$_2$, 1 : 1). Mp not defined. Orange solid. (533 mg, 84%). ^{1}H NMR (400 MHz, CDCl$_3$), 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$_3$O$_2$, [M + H]$^+$: 994.173, found: 994.173. C$_{46}$H$_{25}$F$_{18}$N$_3$O$_2$ (MW 993) calcd (%): C 55.60, H 2.54, N 4.23. Found (%): C 55.63, H 2.57, N 4.28. Optical properties are reported in Table 1.

General procedure for the synthesis of triads E–F

To a solution of 2,7-diamminofluorene (200 mg, 1.02 mmol) and 3,6-diamino-N-(2-ethylhexyl)carbazole (200 mg, 0.64 mmol) in DMSO (3 mL) was added an excess of decafluoroazabenzene (M$_W$ 362 g mol^{-1}, 4 equiv.), and the solution was stirred at room temperature. The reaction was monitored by TLC (Al$_2$O$_3$; CH$_2$Cl$_2$). 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$_2$Cl$_2$, 1 : 1). mp 201 °C. Brown solid (690 mg, 77%). ^{1}H NMR (400 MHz, 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 = 7.6 Hz), 7,70 (1H, d, J = 8.1 Hz). ^{19}F NMR (DMSO) δ (ppm) = −148.22 (m), −149.81 (d, J = 22.2 Hz), −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$_6$ (M$_W$ 880) calcd (%): C 50.47, H 1.14, N 9.54; found (%): C 50.50, H 1.11, N 9.60. Optical properties are 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$_2$Cl$_2$, 1 : 1). Mp not defined. Dark brown solid (470 mg, 74%). ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm) = 0.86–0.97 (CH$_3$, 6H, two t, J = 7.4 Hz), 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$_7$ (M$_W$ 993) calcd (%): C 53.18, H 2.54, N 9.87. Found

(%): C 53.22, H 2.60, N 9.90. Optical properties are reported in Table 2.

General procedure for the synthesis of dyad I

To a solution of decafluorobenzophenone (200 mg, 0.55 mmol) 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%). ^1H 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} 297 nm, 369 nm, λ_{em} 490 nm).

General procedure for the synthesis of P1

An equimolar quantity of monomers **A** and **C** was reacted and stirred in DMSO at 180 °C for 6 h. 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} = −4.89 eV; E_{LUMO} = −3.22 eV. BG = 1.67 eV. Optical properties are reported in Table 3.

General procedure for the synthesis of P2

An equimolar quantity of monomers **E** and **G** was reacted and stirred in DMSO at 180 °C for 6 h. 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} = −4.98 eV; E_{LUMO} = −2.88 eV. BG = 2.10 eV. Optical properties are reported in Table 3.

General procedure for the synthesis of P3

An equimolar quantity of monomers **G** and **C** was reacted and stirred in DMSO at 180 °C for 6 h. 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} = −5.06 eV; E_{LUMO} = −3.67 eV. BG = 1.39 eV. Optical properties are reported in Table 3.

General procedure for the synthesis of P4

An equimolar quantity of monomers **D** and **B** was reacted and stirred in DMSO at 180 °C for 6 h. Then the solvent was removed under reduced pressure. E_{HOMO} = −5.05 eV; E_{LUMO} = −3.16 eV. BG = 1.89 eV. Optical properties are reported in Table 3.

General procedure for the synthesis of P5

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

Gel permeation chromatography (GPC)

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

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 is 30–250 °C at 5 °C min^{-1}. Samples were placed in open alumina pans and were purged by a stream of dry nitrogen flowing at 50 mL min^{-1}.

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