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A comprehensive study of substituent effects on poly(dibenzofulvene)s†

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We herein report the first cross comparison of 14 poly(dibenzofulvene) derivatives (13 novel examples and the parent poly(dibenzofulvene)) in order to understand how the choice of substituent affects the physical properties of this interesting class of semiconducting polymers. Electron withdrawing substituents decreased the polymerization reactivity and resulted in very low molecular-weight products. Di-substituted poly(dibenzofulvene)s were found to be much less soluble than the mono-analogues which can be explained by the Hansen solubility parameter system. Analysis based on absorption, emission and electrochemistry profiles suggests that polymer solubility is a very important factor that controls the degree of stacking present in the polymer due to synthetic issues. For the first time, the thermal analysis of the parent poly(dibenzofulvene) and its derivatives is reported and it was believed that depolymerization occurred much earlier than the melting transition. We have also demonstrated the orthogonal synthesis of dibenzofulvene monomers using three distinct routes (lithiation, oxidation and Wittig) to cope with functional group compatibility.

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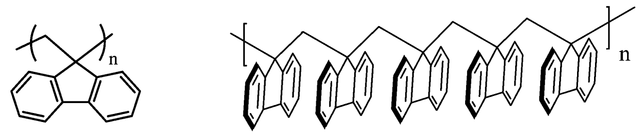
Introduction

Poly(dibenzofulvene) (**poly(DBF)**) is an interesting polymer in which the pendant fluorene moieties have been shown by Nakano *et al.* to adopt a π-stacking conformation (Fig. 1), which gives rise to a number of characteristic observations in the photophysics and electrochemistry profiles of the polymer.[1–4] In terms of practical application, **poly(DBF)** has a great potential to serve as an excellent organic transistor which has stacked fluorenes as a delocalization tunnel for charge transport, contrary to typical conducting polymers such as polythiophene and polyaniline that delocalize charges through the conjugated main chain.[5,6] For instance, **poly(DBF)** exhibits a high hole mobility of $\sim 3 \times 10^{-4}$ cm^2 V^{-1} s^{-1} which is of the same order of magnitude as the inorganic selenium semiconductor.[7] Recently, Li and coworkers prepared a novel π-stacked polymer (**PVMSiF**) by replacing the nitrogen atom in poly(9-vinylcarbazole) with silicon.[8] **PVMSiF** possessed excellent nanofuse property with an ON–OFF ratio as high as 4×10^6, which was attributed to the reversible π-stacking conformation of the polymer under hole/electron transport. Thanks to the absence of extended main-chain conjugation, **poly(DBF)** is also more advantageous than traditional conducting polymers in that it is colorless and stable towards photo-oxidation.



Poly(DBF)

Fig. 1 Chemical structure of **poly(DBF)** (left) and a schematic showing π-stacking of fluorene moieties in the polymer chain (right).

While **poly(DBF)** is an attractive transistor or nanofuse material, it is surprising that the number of reported **poly(DBF)** derivatives is still very limited so far. These include alkyl,[9–11] thiophene,[12] ether[13] and *N*-alkylated amino[14] groups and most of them were reported independently without cross comparison with each other. Substituent effects can play a significant role in the physical properties of π-stacked polymers. For example, the molecular weight of poly(2,7-di-*tert*-butyldibenzofulevene) was limited to the trimer due to the steric bulk of the *tert*-butyl groups.[9] Moreover, the molecular weights, photophysical behaviors and propensity to thermal depolymerization of poly(benzofulvene) (**poly(BF)**)have been found to be substituent-dependent.[15] It must be pointed out that **poly(BF)** and **poly(DBF)** are two very different classes of polymers because, while the former can have a very high number-average molecular weight (M_n) up to $\sim$1 700 000 g mol^{-1}, the latter can only achieve an M_n of several thousand g mol^{-1} due to high steric hindrance at the polymerization site. Therefore, there is a definite need to study how the substituents affect the physical properties of **poly(DBF)**.

In this contribution, we prepared 13 novel[16] mono- and di-substituted **poly(DBF)**s containing a wide range of substituents

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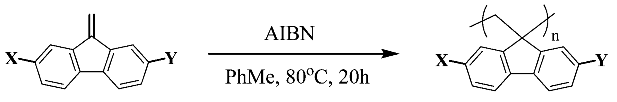


Mono-substituted			Di-substituted		
X	Y		X	Y	
H	H	**Poly(DBF)**	NO_2	OPr	**Poly(NO2PrODBF)**
MeO	H	**Poly(MeODBF)**	NO_2	OHex	**Poly(NO2HexODBF)**
NMe_2	H	**Poly(NMe2DBF)**	Br	OMe	**Poly(BrMeODBF)**
F	H	**Poly(FDBF)**	Br	OPr	**Poly(BrPrODBF)**
Br	H	**Poly(BrDBF)**	Br	OHex	**Poly(BrHexODBF)**
I	H	**Poly(IDBF)**	Br	Br	**Poly(Br2DBF)**
CN	H	**Poly(CNDBF)**			
NO_2	H	**Poly(NO2DBF)**			

Scheme 1 A list of mono- and di-substituted **poly(DBF)**s generated by free-radical polymerization in this study.

such as electron-donating groups (*e.g.* MeO and NMe_2), electron-withdrawing (*e.g.* CN and NO_2) groups and halogens (*e.g.* F, Br and I) which are shown in Scheme 1. We chose the free-radical method for polymerization because it enjoys the greatest functional group tolerance. We shall present how substituents affect the photophysical and electrochemical profiles of the polymers. We found that polymer solubility is an important parameter in that it controls the degree of stacking present in the **poly(DBF)**s. We shall also present the thermal analysis of the parent **poly(DBF)** and its derivatives, which, to the best of our knowledge, has never been reported before.

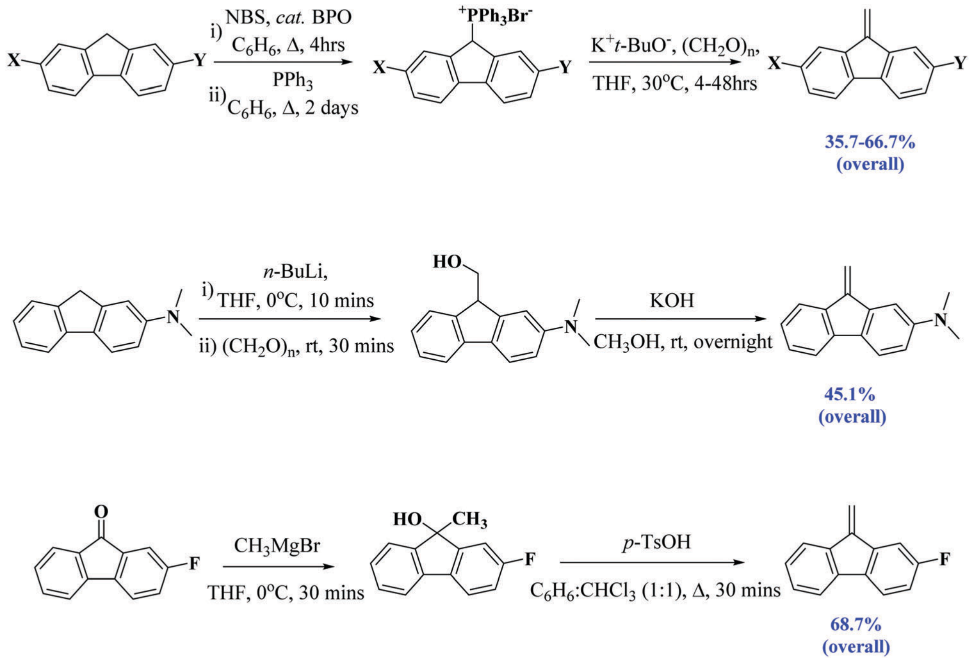
Results and discussions

Monomer synthesis

All substituted dibenzofulvene monomers were prepared by the Wittig route (Scheme 2, top) reported by us previously,[18] with the exception of 2-dimethylaminobenzofulvene and 2-fluorodibenzofulvene. 2-Dimethylaminobenzofulvene could not be prepared *via* the Wittig route because the C9-bromination of the 2-dimethylaminofluorene intermediate was seriously interrupted by the ring bromination due to the strong activation effect of the electron-donating dimethylamino group, and thus the monomer was prepared by the lithiation route (Scheme 2, middle). On the other hand, 2-fluorodibenzofulvene was prepared by the oxidation route (Scheme 2, bottom) simply because 2-fluorofluorenone was much more commercially available than 2-fluorofluorene. Therefore, we have demonstrated that the three synthetic routes to dibenzofulvene monomers can be used in an orthogonal manner.

Polymer synthesis

Table 1 summarizes the polymerization conditions, yields and molecular weight distributions of the substituted **poly(DBF)**s. All polymerizations were affected at 80 °C with AIBN as an initiator in degassed toluene under nitrogen atmosphere for 20 h. Despite higher stereochemical defect formation using a more diluted monomer concentration,[2] **poly(NO2DBF)** and **poly(Br2DBF)** employed lower monomer concentrations due to limited solubilities of their monomers in toluene. It has been reported that high molecular-weight **poly(DBF)** was intractable,[2] therefore an usually heavy initiator loading of 5.0 mol% was employed as the molecular weight control. For polymers with solubilizing groups (alkyl or alkoxy), a lighter loading of 2.5 mol%



Scheme 2 Preparation of dibenzofulvene monomers *via* the Wittig route (top). Preparation of 2-dimethylaminobenzofulvene by the lithiation route (middle). Preparation of 2-fluorodibenzofulvene by the oxidation route (bottom).

Table 1 Summary of polymerization conditions,[a] yields and molecular weight distributions of the substituted **poly(DBF)**s

	[M] (g mL^{-1})	Initiator (mol%)	Yields in soluble[b]/soluble/total (%/%/%)	M_n[c] (X_n)	PDI
Poly(DBF)	0.10	5.0	15.0/16.8/31.8	1409 (7.9)	1.35
Poly(MeODBF)	0.10	2.5	0/42.9/42.9	2313 (11.1)	2.03
Poly(NMe2DBF)	0.10	2.5	0/25.0/25.0	3752 (17.0)	2.13
Poly(FDBF)	0.10	5.0	0/36.9/36.9	1610 (8.2)	1.87
Poly(BrDBF)	0.10	5.0	38.4/29.7/68.1	1141 (4.4)	1.78
Poly(IDBF)	0.10	5.0	53.1/31.3/84.4	1335 (4.4)	1.69
Poly(CNDBF)	0.10	5.0	45.6/21.1/66.7	506, 325, 116 (—)	—
Poly(NO2DBF)	0.05	5.0	26.1/29.1/55.2	515, 306 (—)	—
Poly(NO2PrODBF)	0.10	2.5	70.9/23.9/94.8	348 (—)	—
Poly(NO2HexODBF)	0.10	2.5	0/60.1/60.1	2194 (6.8)	1.66
Poly(BrMeODBF)	0.10	2.5	69.1/6.3/75.4	—	—
Poly(BrPrODBF)	0.10	2.5	45.8/17.2/63.0	1212 (3.8)	1.78
Poly(BrHexODBF)	0.10	2.5	0/39.8/39.8	3304 (9.3)	1.67
Poly(Br2DBF)	0.05	5.0	51.6/0/51.6	—	—

[a] All polymerizations were affected at 80 °C with AIBN as an initiator in degassed toluene under nitrogen atmosphere for 20 h. [b] Insoluble in THF. [c] With respect to the polystyrene standards.

was employed. Many substituted **poly(DBF)**s in this study have both soluble and insoluble fractions (THF used as the extracting solvent). According to the infrared absorption analysis (Fig. S10 and S11, ESI†), the insoluble fraction has the same chemical structure as the soluble counterpart and thus it can be deduced that the former fraction contains polymer aggregates with a higher molecular weight than the latter fraction.[2] In the pioneering work on the parent **poly(DBF)** by Nanako *et al.*, they obtained total yields and M_ns from 22 to 73% and from 250 to 2190, respectively, which agree well with our results.[2] Monomers with heavy halogens and electron withdrawing substituents were found not to polymerize smoothly. For example, **poly(BrDBF)** and **poly(IDBF)** gave significantly smaller molecular weights than the fluorine analogue, **poly(FDBF)**, which can be attributed to the steric hindrance of heavy halogens.[9] In addition, **poly(CNDBF)** and **poly(NO2DBF)** gave only oligomers (M_n < 500). Given that the cyano group should not have caused significant side reactions during the polymerization (because AIBN contains the cyano functionality as well) and that it imposes little steric hindrance due to its linearity, it seems to be appropriate to attribute the lack of polymerization reactivity to the electronic effect exerted by the electron-withdrawing effect of cyano and nitro groups.

The ^{1}H NMR spectra of **poly(MeODBF)** and **poly(NMe2DBF)** and their corresponding fluorenes are shown in Fig. 2. In these

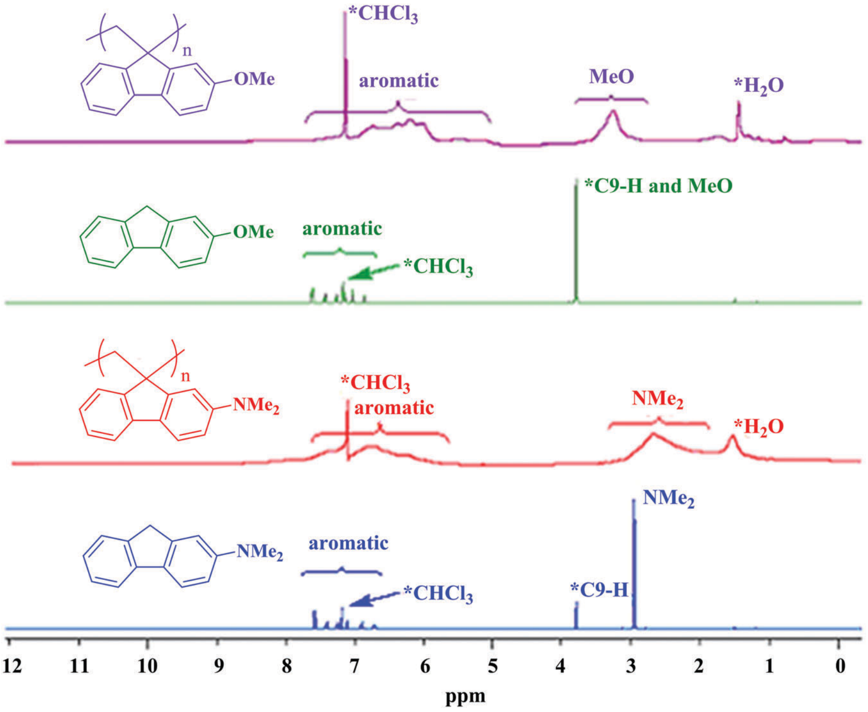


Fig. 2 ^{1}H NMR spectra of **poly(MeODBF)** and **poly(NMe2DBF)** and their corresponding fluorenes to demonstrate anisotropic shielding as the consequence of π-stacking conformation in the polymers.

polymers, both the aromatic and methyl protons exhibit significant upfield shifts compared with the monomeric fluorenes which is attributed to anisotropic shielding in the π–π stacking system.[4,5] Similar phenomena are observed in poly(benzofulvene),[19,20] and oligophenylurea.[21] On the other hand, poly(9,9′-dimethyl-2-vinylfluorene), a close analogue to **poly(DBF)** but without π–π stacking, does not show such an upfield shift for the aromatic protons.[4]

Polymer solubilities

The solubility of the substituted **poly(DBF)**s can be defined as the relative ratio of the soluble fraction to the insoluble counterpart. We believe that solubility is a very important parameter of the **poly(DBF)**s because we noticed that more soluble **poly(DBF)**s (*i.e.* high ratio of soluble fraction yield to insoluble counterpart) demonstrate higher molecular weights which greatly affect their photophysical and electrochemical properties (*vide infra*). For example, by lengthening the alkoxy group, molecular weights were enhanced from **poly(NO2PrODBF)** to **poly(NO2HexODBF)** and from **poly(BrPrODBF)** to **poly(BrHexODBF)**, because the less soluble propoxy-substituted polymers suffered more seriously from premature precipitation of the insoluble growing chain during polymerizations.[22] In addition, **poly(NMe2DBF)**, with the highest molecular weight among all **poly(DBF)**s, is totally soluble. We noted that di-substituted **poly(DBF)**s have much lower solubilities than the mono-substituted analogues. For example, even with additional solubilizing alkoxy groups, di-substituted **poly(BrMeODBF)** and **poly(NO2PrODBF)** are significantly less soluble than mono-substituted **poly(BrDBF)** and **poly(NO2DBF)**, respectively. Furthermore, **poly(Br2DBF)** is completely insoluble. These observations can be explained by the well-noted Hansen solubility parameter (δ) system[23] using the following expression:

$$\Delta\delta = \sqrt{\left[2\left(\delta_{\mathrm{dp}} - \delta_{\mathrm{ds}}\right)\right]^2 + \left[\delta_{\mathrm{pp}} - \delta_{\mathrm{ps}}\right]^2 + \left[\delta_{\mathrm{hp}} - \delta_{\mathrm{hs}}\right]^2} \qquad (1)$$

where the first subscripts "d", "p" and "h" refer to the dispersion force, polarity and hydrogen-bonding, respectively; and the second subscripts "p" or "s" refer to the polymer and solvent, respectively. Simply put, a small $\Delta\delta$ results in a good solubility of the polymer in the particular solvent in question. δ_{h} should be irrelevant because π–π stacking is not a hydrogen-bonding interaction and there is no –OH or –NH substituent used in this study which can form hydrogen bonds. For the di-substituted **poly(BrMeODBF)** and **poly(NO2PrODBF)**, the polar parameters (δ_{p}) should be the main factors that result in their low solubilities. As demonstrated in Fig. 3, bromine and nitro groups are electron-withdrawing and make the phenyl ring attached to be electron-deficient (shown in red), whereas the alkoxy group is electron-donating and makes the other phenyl ring electron-rich (shown in blue). As a result, it is likely that in the di-substituted **poly(DBF)**s the electron-deficient and electron-rich phenyl rings will be stacked with each other in an alternate fashion due to electrostatic attraction. Therefore, δ_{pp} is much larger than δ_{ps} followed by a large $\Delta\delta$ and insolubility. In the case of **poly(Br2DBF)** which is totally insoluble, the dispersion force parameter of the polymer (δ_{dp}) is much larger than that of the solvent (δ_{ds}) due to the additional large bromine atom with a significant amount of polarizable electron density. Based on the same reason, a trend of decreasing solubilities is also observed from mono-substituted **poly(FDBF)** to **poly(IDBF)** when the size of halogens increases (Table 1).

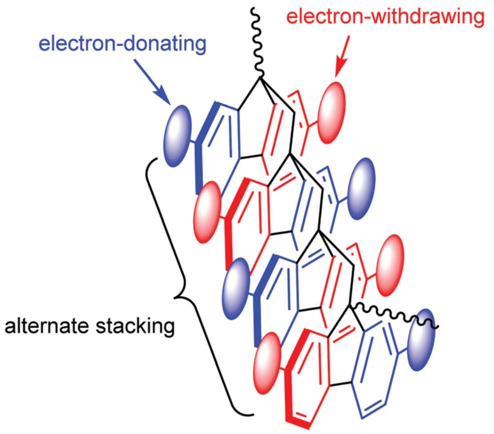


Fig. 3 Alternate stacking of electron-rich (blue) and electron-deficient (red) phenyl rings in the di-substituted **poly(BrRODBF)**s and **poly(NO2RODBF)**s due to favorable dipole interactions, where R denotes general alkyl groups. δ_{pp} is hence much larger than δ_{ps}.

Photophysical and electrochemical properties

The absorption, photophysical and electrochemical properties of the substituted **poly(DBF)**s are summarized in Table 2. The lowest-energy absorption peak wavelengths of the substituted **poly(DBF)**s and their corresponding fluorenes were recorded and the difference between them ($\Delta\lambda$) were compiled. A positive $\Delta\lambda$ (*i.e.* bathochromic shift after polymerization) is the result of the stacking conformation of the adjacent fluorene moieties in the polymer chain.[4] The bathochromic shift has been shown to level off when the number of stacking fluorene units approaches 5.[4] Therefore, it is reasonable for low molecular-weight polymers such as **poly(CNDBF)**, **poly(NO2DBF)** and **poly(NO2PrODBF)** to have negligible $\Delta\lambda$ (-1 to 2 nm). As the $\Delta\lambda$ depends on the molecular weight, it follows naturally that **poly(DBF)**s with solubilizing substituents exhibit a larger $\Delta\lambda$, which is confirmed by the comparison between **poly(NO2PrODBF)** and **poly(NO2HexODBF)** as well as between **poly(BrPrODBF)** and **poly(BrHexODBF)**. In addition, the magnitude of $\Delta\lambda$ was found to depend on the nature of the substituent. For example, while **poly(DBF)**, **poly(MeODBF)** and **poly(NMe2DBF)** have considerably higher molecular weights among the polymers studied, their $\Delta\lambda$s (6, 13 and 10 nm respectively) are considerably different. This suggests that the effectiveness of conjugation between adjacent stacked fluorene moieties might be affected by substituents. Therefore, caution must be taken when using $\Delta\lambda$ to estimate the degree of π–π stacking present in the polymers. In general, a very small $\Delta\lambda$ (*e.g.* <5 nm) may translate to little or non-existent stacking, whereas a large $\Delta\lambda$ (*e.g.* >10 nm) may suggest the presence of a considerable amount of stacking (Fig. 4).

The cyclic voltammograms of the substituted **poly(DBF)**s showed that all of them underwent irreversible oxidations except for

Table 2 Photophysical and electrochemical data of the substituted **poly(DBF)**s in this study

	Absorption[a]		Emission[b]	Electrochemistry[c]	
	$\lambda_{polymer}/\lambda_{fluorene}$[d] (nm nm^{-1})	$\Delta\lambda$[e] (nm)	$\lambda_{polymer}/\lambda_{defect}$ (nm nm^{-1})	$E_{ox,polymer}/E_{ox,fluorene}$[f] (V/V *vs.* Fc/Fc$^+$)	ΔE_{ox}[g] (mV)
Poly(DBF)	309/303	6	403/322	0.859/0.999	−140
Poly(MeODBF)	323/310	13	409/333	0.807/0.854	−47
Poly(NMe2DBF)	339/329	10	437/371	0.213/0.246	−33
Poly(FDBF)	311/305	6	397/321	0.955/1.032	−77
Poly(BrDBF)	317/307	10	402/338	1.057/1.053	4
Poly(IDBF)	317/308	9	404/334	1.025/1.019	6
Poly(CNDBF)	314/312	2	428/336	1.132/1.125	7
Poly(NO2DBF)	329/330	−1	432/375	1.273/1.281	−8
Poly(NO2PrODBF)	355/355	0	535/402	0.951/0.940	11
Poly(NO2HexODBF)	360/355	5	537/401	0.864/0.935	−71
Poly(BrMeODBF)[h]	—	—	—	—	—
Poly(BrPrODBF)	319/313	6	401/339	0.843/0.866	−23
Poly(BrHexODBF)	326/313	13	403/340	0.805/0.872	−67
Poly(Br2DBF)[h]	—	—	—	—	—

[a] Measured in THF at a concentration of 100 ppm. [b] Measured in THF at a concentration of 10 ppm. [c] Measured in THF under nitrogen atmosphere with 0.1 M *n*-Bu$_4$NPF$_6$ as the supporting electrolyte. [d] Absorption maxima of the corresponding substituted fluorenes. [e] $\Delta\lambda = \lambda_{polymer} - \lambda_{fluorene}$. [f] Oxidation potential of the corresponding substituted fluorenes. [g] $\Delta E_{ox} = E_{ox,polymer} - E_{ox,fluorene}$. [h] Not measured due to the lack of the soluble part.

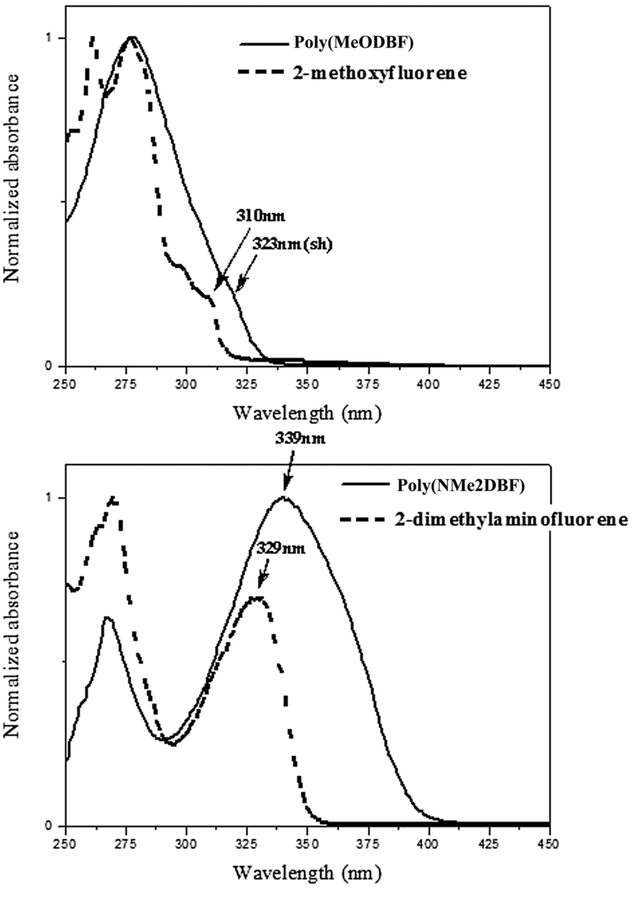


Fig. 4 Normalized absorption spectra of **poly(MeODBF)** (top) and **poly(NMe2DBF)** (bottom) together with their corresponding fluorenes, showing red-shifts in the lowest-energy absorption peaks after polymerization due to stacking conformation.

poly(NMe2DBF) (Fig. S17 and S18, ESI†). The HOMO levels of the substituted **poly(DBF)**s are determined from the ferrocene internal standard and the LUMO levels are estimated from the optical band gaps of the polymers from absorption onset wavelengths, and the results are summarized in Table S1 (ESI†). The strongly electron-donating dimethylamino group (**poly(NMe2DBF)**) raises the HOMO level to −5.01 eV, whereas the potent electron-withdrawing cyano (**poly(CNDBF)**) and nitro groups (**poly(NO2DBF)**, **poly(NO2PrODBF)** and **poly(NO2HexODBF)**) deepen the LUMO levels to −2.58 eV and from −3.07 eV to −3.14 eV respectively. For the rest of the **poly(DBF)**s, the HOMO and LUMO levels are in general −5.6 eV and −2.0 eV, respectively. The oxidation potentials of the polymers are compared with those of the corresponding fluorenes and the differences (ΔE_{ox}s) are listed in Table 2. A negative ΔE_{ox} results from the additional stabilization of the resulting radical cation by delocalization through π-stacking present in the polymers.[4] In most cases, ΔE_{ox} agrees well with $\Delta\lambda$ reported in the aforementioned absorption analysis. For example, ΔE_{ox} becomes progressively more negative (*i.e.* more pronounced π-stacking in the polymer) from **poly(NO2PrODBF)** to **poly(NO2HexODBF)** and from **poly(BrPrODBF)** to **poly(BrHexODBF)** due to the increase in molecular weights. Yet, the case of halogen-substituted **poly(DBF)**s is less trivial. While **poly(FDBF)** shows a clear agreement between ΔE_{ox} and $\Delta\lambda$, **poly(BrDBF)** and **poly(IDBF)** do not. One plausible explanation is that while $\Delta\lambda$ measures the ground state properties of the polymers, ΔE_{ox} involves the stability of the radical cation (*i.e.* excited species).[4] We deduce that $\Delta\lambda$ probably gives a more accurate picture than ΔE_{ox} about the degree of stacking present in the **poly(DBF)**s because the polymer chain in the excited state has such a high energy that a weak secondary interaction like π–π stacking may be broken, or that the excited polymer chain interacts with the solvent or another chain which is not relevant to the π stacking in the polymers.

All substituted **poly(DBF)**s showed both characteristic excimer[3,4] and defect (*i.e.* monomeric fluorene) emissions (see Fig. 5 for examples). The presence of defects is inevitable under high temperature conditions used in free-radical polymerization.[2]

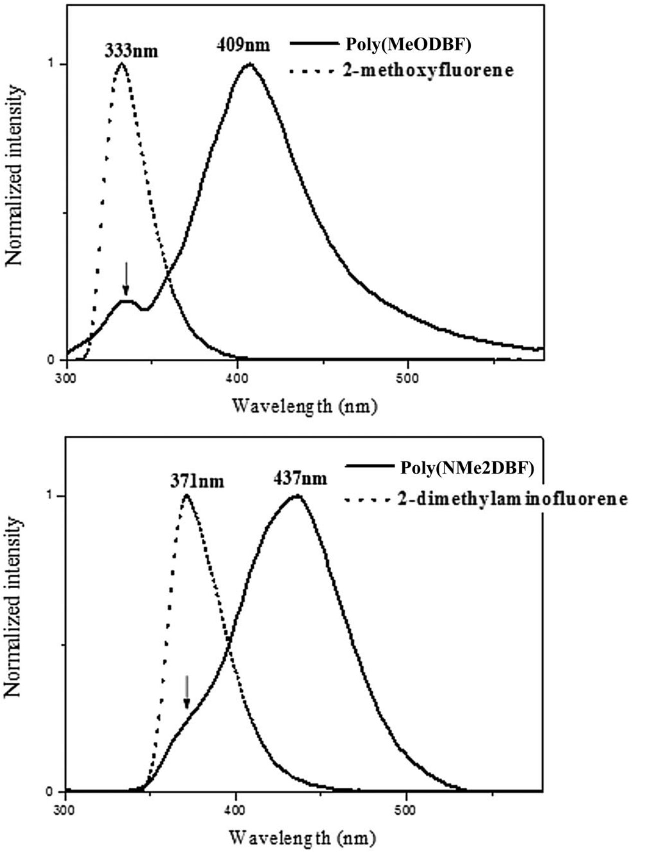


Fig. 5 Normalized emission spectra of **poly(MeODBF)** (top) and **poly(NMe2DBF)** (bottom) showing both excimer and defect emissions. The arrows indicate the emissions from defects in the polymer chains which agree very well with the emission of the corresponding fluorenes.

We found that the relative emission intensity of the excimer to the defect is not a reliable indicator of the degree of stacking present in the polymer chain. For example, **poly(CNDBF)** showed exclusively excimer emission at 428 nm with very small defect emission at 324 nm (Fig. S16, ESI†). However, both GPC and absorption analyses suggest that **poly(CNDBF)** has a small molecular weight followed by limited degree of stacking. Indeed, unlike absorption and electrochemical properties which depend on the stacking of several adjacent fluorene units, excimer emission could be observed in much smaller oligomers, even in dimers.[4]

Table 3 DSC and TGA data of the substituted **poly(DBF)**s, both soluble and insoluble parts

	DSC[a]		TGA[b]	
	T_{peak}[c]/ΔH[d] (°C/kJ mol^{-1})		T_{onset}[e] (°C)	
	Soluble part	Insoluble part	Soluble part	Insoluble part
Poly(DBF)	171/2.05	178/2.95	290	331
Poly(MeODBF)	236/5.18	—	327, 596	—
Poly(NMe2DBF)	227/8.20	—	338	—
Poly(FDBF)	Not observed	—	285	—
Poly(BrDBF)	164/4.24	166/5.32	277	331
Poly(IDBF)	158/4.48	156/6.48	254	369
Poly(CNDBF)	188/9.91	201/11.14	273, 592[f]	346, 662
Poly(NO2DBF)	220/13.69	230/14.50	300	338
Poly(NO2PrODBF)	230/19.83	236/21.55	315	362
Poly(NO2HexODBF)	228/22.55	—	342	—
Poly(BrMeODBF)	—	206/12.07	—	346
Poly(BrPrODBF)	204/11.15	209/12.59	281	354
Poly(BrHexODBF)	196/12.32	—	300	—
Poly(Br2DBF)	—	209/9.08	—	338, 585

[a] Under nitrogen atmosphere at a heating rate of 20 °C min^{-1}. [b] Under nitrogen atmosphere at a heating rate of 40 °C min^{-1}. [c] Temperature of endotherm peak. [d] Enthalpy change associated with the endotherm. [e] Temperature at 5% weight loss. [f] Second phase of weight loss.

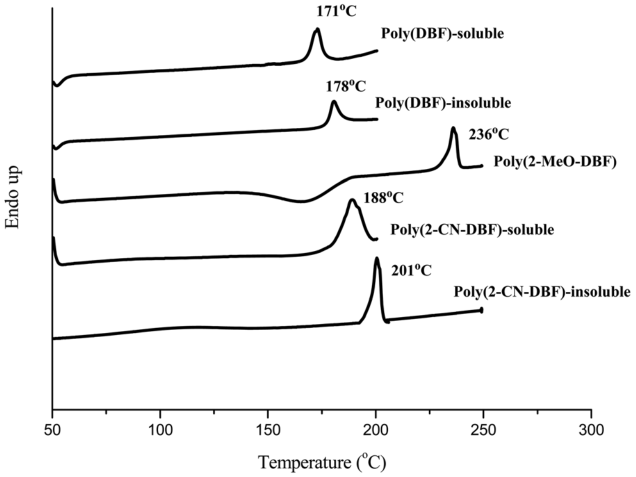


Fig. 6 DSC traces of some substituted **poly(DBF)**s in this study.

Thermal properties

The thermal properties of the substituted **poly(DBF)**s were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) and the data are summarized in Table 3. Previous studies of **poly(DBF)** focused heavily on the conformation[4,24] of the pendant fluorene units and charge transport[5–7] and this study, to the best of our knowledge, reveals for the first time the thermal behaviors of **poly(DBF)** and its derivatives. The DSC trace (Fig. 6) of the parent soluble **poly(DBF)** shows an endotherm with a temperature peak (T_{peak}) at 171 °C with an enthalpy change (ΔH) of 2.05 kJ mol^{-1}. The annealed sample after the DSC experiment was analyzed by ^{1}H NMR and GPC techniques and it was found that the dibenzofulvene monomer was regenerated (*i.e.* characteristic peak at δ = 6.0 ppm) and that the polymer was decomposed into species with lower molecular weights (Fig. S19, ESI†). Thus, the endotherm can be assigned to either depolymerization or melting processes. Given the large steric bulk at the vinyl functional group in **DBF** monomers at which polymerization occurs, it can be inferred that the ceiling temperature (T_c) for this type of polymers should be low. For example, a sterically hindered polymer like poly(α-methyl styrene) has a T_c as low as 61 °C (under the conditions of a neat α-methyl styrene monomer).[25] In addition, free-radical polymerizations of the parent **poly(DBF)** at 80 °C reported by Nakano's group[2] and us consistently produced polymers with low molecular weights (*e.g.* $X_n < 10$), further suggesting low T_cs for this class of polymers. Therefore, it is very unlikely that the depolymerizations of **poly(DBF)**s were initiated at high temperatures like above 170 °C (DSC endotherms shown in Fig. 6). On the other hand, the ΔH of the endotherms (Fig. 6) has a magnitude close to typical melting process for polymers.[26] Furthermore, ΔH depends largely on the nature of the substituent. For example, the ΔHs of soluble **poly(NO2DBF)**, **poly(NO2PrODBF)** and **poly(NO2HexODBF)** are 13.69 kJ mol^{-1}, 19.83 kJ mol^{-1} and 22.5 kJ mol^{-1}, respectively which suggests that additional heat was used to melt the alkoxy chains. The length of the alkoxy chains in the three polymers should have little effect on the depolymerization process because of their remote distance from the polymerization site. Depolymerization processes for vinyl polymers have been reported to show either a sharp[15] or a broad[19,27] peak in DSC analysis. **DBF** monomers, due to their large steric bulk at the polymerization site, should have a low heat of polymerization (ΔH_p).[25] Therefore, it is safe to assume that the depolymerizations of the substituted **poly(DBF)**s occurred at a much lower temperature before the melting endotherms and were hardly discernible in DSC analysis because the depolymerization endotherms were too broad and low. While the insoluble part of the substituted **poly(DBF)**s have practically the same T_{peak} as their soluble counterparts, their ΔHs are invariably higher which can be explained by the presence of stronger inter-chain interactions in the insoluble part. The substituted **poly(DBF)**s show moderate thermal stability with their onset decomposition temperature (T_{onset}, defined as 5 wt% loss) ranging from 254 °C to 369 °C. The insoluble part always has a higher T_{onset} compared with their soluble counterpart.

Conclusions

This study is the first comprehensive cross comparison of substituent effects on **poly(DBF)**s and it contributes to the understanding of the structure–property relationship of π-stacked polymers, which is relatively underexplored. Di-substituted **poly(DBF)**s are much less soluble than the mono-analogues which can be explained by the Hansen solubility parameters. Solubility should not be overlooked because it controls the degree of stacking present in the **poly(DBF)**s. Lastly, it is believed that depolymerization occurred much earlier than the melting transition in DSC analysis which means that **poly(DBF)**s have limited thermal stability.

Experimental

General information

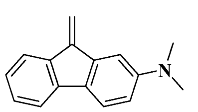
Fluorene, 2-bromofluorene, 2-iodofluorene, 2,7-dibromofluorene, paraformaldehyde, 2-fluorofluorenone, *p*-toluenesulfonic acid, *n*-butyllithium (1.6 M in hexane solution) and methylmagnesium bromide (3.0 M in ether solution) were purchased from Sigma Aldrich. Toluene used in polymerization was distilled freshly once from calcium hydride and AIBN were recrystallized from methanol before use. Other solvents were of analytical grade and used as received.

^1H and ^{13}C NMR spectra were recorded on a Bruker-AF301 AT 400 MHz spectrometer using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. High resolution mass spectrometry (HRMS) was carried out using a Bruker autoflex MALDI-TOF mass spectrometer. Melting points were measured on a MEL-TEMP capillary tube apparatus and uncorrected. Infrared spectra were recorded using a Nicolet Magna 550 Series II FTIR spectrometer using KBr pellets. UV-vis absorption spectra were measured in THF at a 100 ppm concentration using a Varian Cary 200 spectrophotometer. Fluorescence spectra were also measured in THF at a 10 ppm concentration using a Perkin Elmer LS55 luminescence spectrometer. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer Pyris Diamond DSC under nitrogen purge at a heating rate of 20 °C min^{-1}. Thermogravimetric analyses (TGA) were achieved using a Perkin-Elmer TGA-6 thermal analyzer under nitrogen at a heat rate of 40 °C min^{-1}. Cyclic voltammetry (CV) measurements were performed on a BAS CV-50W electrochemical analyzer adapted with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode. All measurements were affected in 0.1 M THF solution with tetrabutylammonium hexafluorophosphate as the electrolyte and ferrocene as the internal standard. Molecular weights were determined by gel permeation chromatography (GPC) using a HP 1050 series HPLC with THF as the eluent and a UV absorption detector (at 254 nm) calibrated against polystyrene MW standards.

Synthesis

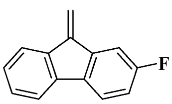
2-*N*,*N*-Dimethylaminofluorene was prepared according to the literature.[28] 2-Fluorofluorene was prepared by the Wolff–Kishner reduction of 2-fluorofluorenone.[29] 2-Methoxyfluorene, 2-cyanofluorene, 2-nitrofluorene, 2-nitro-7-alkoxyfluorenes and 2-bromo-7-alkoxyfluorenes were prepared according to the literature.[18] Except for 2-*N*,*N*-dimethylaminodibenzofulvene and 2-fluorodibenzofulvene, the synthesis of other **DBF** monomers have been reported previously.[18]

2-*N*,*N*-Dimethylaminodibenzofulvene



To an ice-water cooled solution of 2-*N*,*N*-dimethylaminofluorene (500 mg, 2.39 mmol) in dry THF, 1.6 M *n*-butyllithium (1.49 mL, 2.39 mmol) was dropwise added. The reaction mixture was stirred for 10 min. Paraformaldehyde (71.7 mg, 2.39 mmol) was then added in a single portion. After 30 minutes, the reaction was quenched by pouring into water. The mixture was extracted with DCM several times. The combined organic was dried with anhydrous magnesium sulfate. After concentration, the crude was purified by flash column chromatography using an eluent (EtOAc : hexanes = 1 : 2, v : v, with 3% Et_3N as an additive) to give 9-hydroxymethyl-2-*N*,*N*-dimethylaminofluorene (275 mg, 1.15 mmol). The alcohol was then mixed with potassium hydroxide (1 g) in methanol (10 mL) and allowed to stir overnight. DCM was then added and the reaction mixture was filtered through a short plug of silica gel. After concentration, the crude was purified by flash column chromatography using an eluent (DCM : hexanes = 1 : 5, v : v, with 3% Et_3N as an additive) to offer 2-*N*,*N*-dimethylaminodibenzofulvene (238 mg, 45.1%) as a yellow solid. Mp 118 °C; δ_H ($CDCl_3$) 7.64 (1H, d, *J* = 7.6 Hz, ArH), 7.52 (2H, d, *J* = 8.0 Hz, ArH), 7.29 (1H, dt, *J* = 7.6 and 0.8 Hz, ArH), 7.15 (1H, dt, *J* = 7.6 and 0.8 Hz, ArH), 7.11 (1H, d, *J* = 2.4 Hz, ArH), 6.76 (1H, dd, *J* = 8.0 and 2.4 Hz, ArH), 6.15 (1H, s, vinyl), 6.12 (1H, s, vinyl), 3.03 (6H, s, NMe_2); δ_C ($CDCl_3$) 150.53, 144.03, 141.03, 139.50, 137.68, 129.69, 128.73, 125.14, 120.71, 120.40, 118.43, 113.44, 106.71, 105.08, 41.08; HRMS (MALDI) [M^+] calcd for $C_{16}H_{15}N$: 221.1204; found: 221.1195.

2-Fluorodibenzofulvene



To an ice-water cooled solution of 2-fluoro-9-fluorenone (500 mg, 2.72 mmol) in dry THF, 3.0 M methylmagnesium bromide (1.1 mL, 3.26 mmol) was added dropwise. After stirring for 30 minutes, the reaction was quenched by pouring into water. The mixture was extracted with chloroform several times. The combined organic fractions were dried with anhydrous magnesium sulfate. After concentration *in vacuo*, the crude alcohol was mixed with *p*-toluenesulfonic acid (2.34 g, 13.6 mmol) and refluxed in 10 mL benzene/chloroform (1 : 1) for 30 minutes. The solvent was then removed and the crude was purified by column chromatography using hexane as the eluent to offer 2-fluorodibenzofulvene as a colorless oil (331 mg, 68.7%). δ_H ($CDCl_3$) 7.70 (1H, d, *J* = 7.6 Hz, ArH), 7.63–7.58 (2H, m, ArH), 7.39–7.33 (2H, m ArH), 7.27 (1H, dt, *J* = 7.6 and 0.8 Hz, ArH), 7.08–7.03 (1H, m, ArH), 6.09 (1H, s, vinyl), 6.03 (1H, s, vinyl); δ_C ($CDCl_3$) 163.96, 161.53, 142.78, 142.75, 140.13, 140.04, 139.45, 138.02, 136.16, 136.14, 128.95, 126.75, 121.06, 120.82, 120.73, 119.47, 115.80, 115.56, 114.09, 108.93, 108.46, 108.23; HRMS (MALDI) [M^+] calcd for $C_{14}H_9F$: 196.0688; found: 196.0677.

General polymerization procedures

Freshly prepared monomers (250 mg), a catalytic amount of AIBN (2.5 mol% or 5.0 mol%) and distilled toluene (2.5 or 5.0 mL) were added into a Schlenk tube. The system was then degassed by five freeze–pump–thaw cycles. The polymerization was then affected by stirring at 80 °C for 20 h under nitrogen atmosphere. For monomers that produced only soluble products, the polymerization mixture was a homogeneous solution at the end of the reaction. The polymers were collected by precipitation in hexane twice. On the other hand, for monomers that yielded both soluble and insoluble products, the polymerization mixture was a suspension. The suspension was first precipitated in hexane. The polymer thus obtained was soaked in three successive batches of 10 mL THF to resolve the soluble and insoluble fractions. The solids that remained insoluble in THF were identified as the insoluble fraction. The filtrates thus collected were concentrated. The soluble fractions were recovered by precipitation again in hexane.

Acknowledgements

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