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A facile approach to the synthesis of substituted dibenzofulvenes-precursors to pi-stacked poly(dibenzofulvene)s

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ABSTRACT

A series of novel substituted (2-methoxy, 2-nitro, 2-bromo, 2-iodo, 2-cyano, and 2-acetyl) and di-substitiuted (2-bromo-7-methoxy, 2-bromo-7-propoxy, 2-bromo-7-hexoxy, 2-nitro-7-propoxy, 2-nitro-7-hexoxy, and 2,7-di-bromo) dibenzofulvenes have been prepared from the corresponding fluorenes with fair to very good overall yields (35.7–66.7%) based on the Wittig chemistry. The new approach enjoyed much simpler experimental procedures and has the advantage of higher functional group tolerance. Preliminary results on their polymerization using solution free-radical approach are also presented.

1. Introduction

It is well known that 1,1-diphenylethylene cannot be polymerized due to steric hindrance, its coplanar analog dibenzofulvene (DBF), however, can undergo addition polymerization effectively.[1] The conductivity of traditional main-chain conductive polymers derived from extensive delocalization of conjugated π-electrons, whereas the conductivity for poly(dibenzofulvene) (poly(DBF)) resulted from unique stacking conformation of the fluorene moieties.[2] The π-stacked fluorene moieties allow efficient charge tunneling leading to a hole mobility of 2.7×10^{-4} $cm^2\,V^{-1}\,s^{-1}$ at 299 K (under an electric field 7×10^5 V/cm),[3] which is unusually high for a side-chain polymer. Enhanced charge mobility due to π–π stacking has also been proposed as the underlying principle behind charge transport within DNA strands.[4,5,6] In addition, the solubility of side-chain polymers is general better than main-chain conducting polymers. Optical clarity due to restricted π-electrons delocalization also rendered poly(DBF) a novel organic opto-electronic materials.[2]

In the past, there have been two major routes for the preparation of DBF monomer. One of them involved lithiation at the 9-position of fluorene followed by hydroxymethylation using paraformaldehyde. The carbinol was then subjected to base-catalyzed dehydration to afford the DBF monomer (Fig. 1). DBF has been prepared from commercially available 9-hydroxymethylfluorene using this route but produced a meager yield of 37.2%.[1] Similarly, 2,7-di-*tert*-butyldibenzofulvene has been synthesized via the two-step process starting from 2,7-di-*tert*-butylfluorene with only 54.9% overall yield.[7] It was necessary to maintain strict stoichiometric balance between the lithiation reagent and fluorene or otherwise the yield would drop significantly.[8] Another drawback to this approach has been the use of air-sensitive organometallic reagent. Fluorenyllithium is known to attack molecular oxygen.[9] Thus the solvent used for the reaction has to be dried thoroughly and degassed. The use of organometallic regents also raises an issue with functional-group tolerance when preparing substituted DBF.

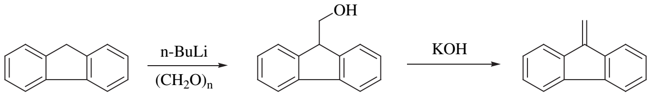

Figure 1. Synthesis of DBF via the lithiation route.

An alternative route to prepare DBF would be first oxidizing fluorene to fluorenone, followed by a nucleophilic attack on the keto group by methylmagnesium bromide to produce an alcohol. Finally, the alcohol was subjected to acid-catalyzed dehydration to yield the DBF monomer (Fig. 2).[10] The oxidation step was carried out typically using dichromate salts in acetic acid under slight heating while *p*-toluenesulfonic acid would be used in the acid-catalyzed dehydration reaction step. Although higher yield was resulted, this approach again utilized air-sensitive organometallic reagent, which greatly limited the choice of functional groups in the

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DBF to be prepared. In addition, chromium salts bring toxicity and waste disposal problems that need to be resolved.

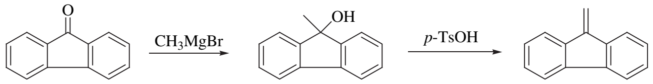
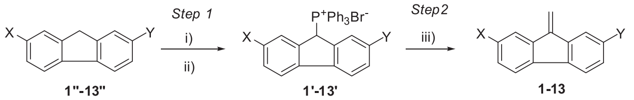


Figure 2. Synthesis of DBF via the oxidation route.

2. Results and discussion

In this manuscript, an alternative route for the preparation of DBF with a range of electron-donating and withdrawing substituents is reported. The methodology presented here is facile, high yield and without using air-sensitive reagents. The underlying chemistry is the extremely well-known Wittig reaction. As shown in Figure 3, the first step was bromination at the 9-position of the fluorene moiety (**1**″–**13**″) followed by preparation of its phosphonium salt using triphenylphosphine in a one-pot manner. Details on the preparation of the substituted fluorenes (**1**″–**13**″) are given as Supplementary data except for **4**″, **5**″, and **13**″, which were obtained commercially. The phosphonium salts offered the corresponding ylides upon deprotonation and reacted with paraformaldehyde to produce the desired DBFs. The yields for the two reaction steps and reaction times for the second step are given in Table 1. In general, the yields for the first reaction step were between 50 and 70% and the reaction times for the second step affording 70% to near quantitative yield were from 4 to 48 h depending on the chemistry of the substituted groups.



i) NBS, *cat.* BPO, C_6H_6, reflux, 4hrs; ii) PPh_3, C_6H_6, reflux, 2 days; iii) $K^+t\text{-}BuO^-$, THF, $(CH_2O)_n$, 30°C, 4-48hrs

Figure 3. Synthetic scheme for the substituted DBFs from their corresponding fluorenes.

Table 1
Summary of reaction yields and times for step 1 and step 2 employing the Wittig approach

Entry	X	Y	Yield for step 1 (**1**′–**13**′) (%)	Reaction time for step 2 (**1**–**13**) (hrs)	Yield for step 2 (**1**–**13**) (%)
1	H	H	62.0	12	99.7
2	OMe	H	67.0	4	99.5
3	NO_2	H	61.8	48	81.4
4	Br	H	61.0	12	∼93[a]
5	I	H	59.2	12	79.5
6	CN	H	67.2	24	84.1
7	Ac	H	58.9	24	79.6
8	Br	OMe	53.8	4	98.8
9	Br	OPr	59.3	4	∼50[a]
10	Br	OHex	50.7	4	82.0
11	NO_2	OPr	53.3	24	80.3
12	NO_2	OHex	49.5	24	72.2
13	Br	Br	61.5	12	68.8

[a] Notes: Products were ***oil-like*** and some insoluble solids were obtained spontaneously upon solvent removal. The yield was calculated according to product fraction which is soluble in toluene.

The new route allowed the preparation of a range of substituted DBFs (**2**–**13**) that have not been previously reported. The substituents include X=H, OMe, NO_2, Br, I, CN, Ac, and Y=H, OR (where R=Me, Pr, Hex), Br. It is expected that substituents with different electronic and steric properties would affect the optical properties and solubility of the resulting π-stacked poly(DBF)s. The chemistry also affected thermal stability of the resulting polymers, such as the tendency for depolymerization or degradation.[11,12]

Initial trial on the synthesis of DBF (**1**) was attempted with 9-fluorenone as the carbonyl participant and deprotonated methyltriphenylphosphonium bromide as the ylide for the Wittig reaction. However, only trace amount of product was obtained. This was attributed to the highly electrophilic nature of DBF in situ formed, which was then attacked by the non-stabilized ylide.[13] With this understanding in mind, the role for the carbonyl group and ylide for the Wittig reaction was interchanged, i.e., paraformaldehyde was used to provide the carbonyl group while 9-fluorenylphosphonium bromide was used as the ylide precursor. As a result the yield (**1**′–**13**′) increased drastically. This is because ylide from 9-fluorenylphosphonium salt was stabilized by the strong delocalization of electron density over the planar fluorene moiety and as a result the stabilized ylide was compatible with the DBF products.

Indeed, protons at the 9-position of the fluorenes are particularly active. It has been reported that fluorene could be easily metalated by potassium hydroxide in ether at room temperature.[14] Deprotonation of a hydrocarbon using merely potassium hydroxide is extremely rare. It should be attributed to the efficient charge delocalization of the resulting anion over the two aromatic rings together with coplanar conformation. It was noted that the acidity of fluorene (p*K*a: ∼20.5)[15] is much higher than that of diphenylmethane (p*K*a: ∼35).[16]

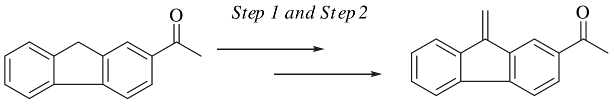
The substituted DBFs have been fully characterized by ^1H, ^{13}C NMR, melting point analysis, infra-red spectroscopy (spectra for **3**, **6**, **7**, **12** are provided as Fig. 7(a–d) in Supplementary data) and high-resolution mass spectrometry. A characteristic ^1H NMR peak for the vinyl protons at about 6.0 ppm was detected. The splitting of this NMR peak provided further information on the chemical structure of the resulting DBFs. For symmetrically substituted DBFs like the parent DBF (**1**) and 2,7-di-bromo-DBF (**13**), this vinyl proton peak appeared as a singlet (e.g., NMR spectra for (**1**) and (**13**) are given in Fig. 6 (a) and 6 (b) in Supplementary data), whereas for the unsymmetrically substituted DBFs (**2**–**11**) the vinyl proton peaks were two singlets (e.g., NMR spectra for unsymmetrical 2-acetyl-DBF (**7**) and 2-methoxy-DBF (**2**) are given in Fig. 6(c) and 6(d) in Supplementary data). However, 2-NO_2-7-HexO-DBF (**12**) did not show two singlets probably because its vinyl protons were accidentally equivalent in ^1H NMR.[17] The results indicated the two vinyl protons can be non-equivalent for asymmetrically substituted DBFs. The two vinyl proton peaks in all unsymmetrically substituted DBFs (except **12**) are barely singlets, i.e., there is no coupling among these geminal protons.

Elucidation on the structure of the substituted 9-fluorenyltriphenylphosphonium bromide intermediates (**1**′–**13**′) was attempted using NMR spectroscopy.[18] It was, however, hampered by the poor solubility of the phosphonium salts in deuterated solvents. Nevertheless, the chemical structure for some of the phosphonium salts can be implied by the yields and structures of the final products. For example, DBF (**1**) as well as 2-methoxy-DBF (**2**) were prepared from their corresponding phosphonium salts with nearly quantitative yields (99.7% and 99.5%, respectively), which implied the chemical structure as well as high purity of the salts. Because the phosphonium salts of **1**′–**13**′ were all prepared from the corresponding substituted fluorenes via the same side-chain bromination and S_N2 displacement by triphenylphosphine, they therefore should possess the chemical structures as suggested in Figure 3.

There were several precautions to achieve high yields for the parent and substituted DBFs. Firstly, the substituted DBFs were rather sensitive to heat. We observed DBF (**1**) readily converted into insoluble solids, probably polymers[19], as the temperature of the water bath for the rotary evaporator exceeded 40 °C. A small amount of insoluble solids was detected for some of the substituted DBFs at temperature as low as 32 °C. It is therefore suggested 30 °C should be the maximum temperature for subsequent workup processes. Secondly, the monomers were sensitive to oxygen. It has been reported that DBF was able to carry out solid-state copolymerization with oxygen.[20] Thirdly, the monomers might be moisture sensitive. In one occasion, insoluble material was formed when a DCM solution of DBF was extracted with DI water. Cho stated that DBF had to be stored under anhydrous condition.[21] Stability of substituted DBFs might also be related to their physical states. The monomers 2-Br-7-MeO-DBF (**8**) and 2-Br-7-HexO-DBF (**10**) remained stable in the solid state format, whereas 2-Br-7-PrO-DBF (**9**), which was a greenish oil, produced substantial quantity of insoluble solids upon solvent removal and was suspected to be the result of self-induced polymerization. The reasons underlying this observation are not clear and could be related to the stability of the monomer when exposed to ambient UV irradiation.

Table 1 indicated that DBFs with electron-withdrawing substituents, such as 2-nitro (**3**) and 2-cyano (**6**) needed a longer reaction time to achieve high yield whereas those with electron-donating substituents, such as 2-methoxy (**2**) and 2-bromo-7-methoxy (**8**) accomplished excellent yields within relatively short reaction time. This is expected as the electronic property of the substituents affected the electron density of their ylides and thus the rate of nucleophilic attack onto formaldehyde.

We have previously suggested either the traditional lithiation or oxidation route has limited functional group tolerance. Derivatives, such as 2-cyano (**6**) and 2-acetyl-DBF (**7**) that cannot be prepared using the traditional routes have been accomplished here using the methodology presented above. For example, 2-acetyl-DBF (**7**) was prepared successfully with a 46.9% overall yield starting from 2-acetylfluorene, as shown in Figure 4. If either *n*-butyllithium or methylmagnesium bromide was employed in the reaction, the acetyl group would have been destroyed.



7, overall: 46.9%

Figure 4. Synthesis of 2-acetyl-DBF via the Wittig route.

Free-radical initiated solution polymerizations for the substituted DBFs (all except **7**) have been attempted (see Fig. 5). The yields and number-averaged number of repeating units (X_n) have been summarized in Table 2. The molecular weights (MW) of the THF soluble fraction have been measured by gel permeation chromatography using polystyrene MW standards. As previously reported by Nakano et al.[1,2,20] both soluble and insoluble fraction were obtained for the π-stacked DBF polymer. The insoluble fraction was most likely higher molecular weight and crystalline materials. In general, it was found that the overall yield increased with the addition of any substituted group in comparison to the neat monomer **1**. The amount of soluble fraction increased with an increase in the size of the solubilizing alkoxy group (e.g., **10**>**9**>**8**, **12**>**11**). The substituted polymers became fully soluble when the mono-substituent was methoxy (**2**) or one of the di-substituent was hexoxy (**10**, **12**). The number-averaged number of repeating units (X_n) was also found to be among highest for the polymers (**2**, **10**, **12**) that were fully soluble. For DBF polymers with bulky substituted side-group (such as Br, I, NO_2), their X_n are lowered probable due to severe steric hindrance imposed at the vinylic linkages. For the polymers **3**, **6**, **11**, their X_n were lower than unity because the MW was not determined using universal MW calibration. Further study on the substituted DBF polymers, such as the electronic and steric effects of the substituted group on the thermal, optical and electrical properties will be reported in a paper to follow.

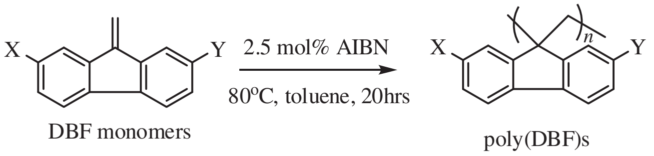


Figure 5. Polymerization scheme of substituted DBFs.

Table 2
Summary of polymerization results of substituted DBFs

Entry	X	Y	% Insoluble[a]	% Soluble[b]	Total yield (%)	X_n[c]
1	H	H	15.0	16.8	31.8	7.9
2	OMe	H	0	42.9	42.9	11.1
3	NO_2	H	26.1	29.1	55.2	0.19
4	Br	H	38.4	29.7	68.1	4.4
5	I	H	53.1	31.3	84.4	4.4
6	CN	H	45.6	21.1	66.7	0.37
7[d]	Ac	H	NA	NA	NA	NA
8	Br	OMe	69.1	6.3	75.4	NA
9	Br	OPr	45.8	17.2	63.0	3.8
10	Br	OHex	0	39.8	39.8	9.3
11	NO_2	OPr	70.9	23.9	94.8	0.82
12	NO_2	OHex	0	60.1	60.1	6.8
13	Br	Br	51.6	Trace	51.6	NA

[a] Polymer yield of insoluble fraction in THF.
[b] Yield of soluble fraction in THF.
[c] Number-averaged number of repeating units for the soluble fraction.
[d] Polymerization not yet carried out for this monomer.

3. Conclusion

The advantages of the Wittig approach presented in this report have been its simplicity and ease of handling. Neither organometallic reagents nor pre-dried solvents were required. All reactions were carried out under ambient conditions and open atmosphere. The purification of the substituted DBFs by column chromatography is particularly efficient due to the excellent reaction yield and cleanliness of the reaction. As a result, a series of novel substituted DBFs have been prepared successfully employing the Wittig approach with good yields. The DBF monomers prepared have been polymerized using solution free-radical polyaddition method. Preliminary results indicating the yield, solubility, and molecular weights of the polymers are affected critically by the chemistry of the substituted groups. Details on the properties of the DBF polymers and relationship to the chemistry of the substituted groups will be the subject of a forthcoming paper.

4. Experimental section

4.1. General

All reagents and chemicals, unless otherwise stated, were purchased from commercial sources and used without further purification. *N*-bromosuccinimide was recrystallized from hot water, followed by vacuum drying at about 40 °C. Analytical grade solvents were used as received. Melting points were taken on a MEL-TEMP capillary tube apparatus and were uncorrected. Infrared spectra were recorded using KBr pellets on the Nicolet

Magna 550 Series II FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-AF301 AT 400 MHz spectrometer. High resolution mass spectrometry was carried out using a Bruker Autoflex MALDI–TOF mass spectrometer. The synthesis of the substituted fluorenes (**1′**–**13′**) is reported as Supplementary data.

4.2. General procedures for the preparation of substituted 9-fluorenyltriphenylphosphonium bromides

*4.2.1. Fluorenyl-9-triphenylphosphonium bromide (**1′**).* Fluorene (5.00 g, 30.1 mmol), *N*-bromosuccinimide (5.36 g, 30.1 mmol), and benzoyl peroxide (182 mg, 0.75 mmol) in benzene (50 mL) were refluxed for 4 h. Two additional portions of benzoyl peroxide (182 mg, 0.75 mmol) were added at one-hour interval. The reaction mixture was cooled to room temperature and benzene was removed by rotary evaporator to near completion. The crude solids obtained were washed with warm water (~100 mL) followed by cold methanol (~20 mL) to remove all residue moisture. After air-drying, the crude solids and triphenylphosphine (11.9 g, 45.1 mmol) were mixed in benzene (50 mL) and refluxed further for two days. Upon cooling, the precipitates were collected, thoroughly washed with ether, and dried. The resulting compound is a white solid (9.17 g, 60.2%).

Other substituted fluorenyl-9-triphenylphosphonium bromides (**2′**–**13′**) were prepared similarly. Their yields are summarized in Table 1.

4.3. General procedures for the preparation of substituted DBFs

*4.3.1. Dibenzofulvene (DBF) (**1**).* To a suspension of fluorenyl-9-triphenylphosphonium bromide (1.0 g, 1.98 mmol) in *untreated* THF (10 mL) was added potassium *tert*-butoxide (222 mg, 1.98 mmol)[22] and stirred for 30 min. Paraformaldehyde (1.78 g, 59.4 mmol) was then added in a single portion, and the reaction mixture was stirred for 12 h in a 30 °C oil bath. Hexane (~25 mL) was then added and the whole reaction mixture was filtered through a plug of silica, followed by washing with DCM several times. The filtrate was concentrated by rotary evaporator and subjected to flash column chromatography using hexane as the eluent. The compound (351 mg, 99.7%) is a colorless oil, which crystallized upon drying under high-vacuum. Mp 53.4–54.5 °C (lit.[1] 50–52 °C); δ_H (CDCl$_3$) 6.08 (2H, s, vinyl), 7.29 (2H, t, *J* 7.4, ArH), 7.36 (2H, t, *J* 7.4, ArH), 7.68 (2H, d, *J* 7.4, ArH), and 7.72 (2H, d, *J* 7.4, ArH); δ_C (CDCl$_3$) 107.76, 119.73, 120.99, 127.03, 128.72, 138.00, 140.13, and 143.33; HRMS (MALDI) calcd for $C_{14}H_{10}$: 178.0783; found: 178.0768.

*4.3.2. 2-Methoxydibenzofulvene (2-MeO-DBF) (**2**).* Slight greenish solids, mp 103.5–105.1 °C; δ_H (CDCl$_3$) 3.85 (3H, s, OCH$_3$), 6.00 (1H, s, vinyl), 6.02 (1H, s, vinyl), 6.89 (1H, dd, *J* 8.3 and 2.4, ArH), 7.19 (1H, t, *J* 7.5, ArH), 7.23 (1H, d, *J* 2.4, ArH), 7.30 (1H, t, *J* 7.5, ArH), 7.54 (1H, d, *J* 8.3, ArH), 7.55 (1H, d, *J* 7.5, ArH), and 7.65 (1H, d, *J* 7.5, ArH); δ_C (CDCl$_3$) 55.61, 106.47, 107.76, 114.88, 119.00, 120.57, 120.90, 125.98, 128.82, 133.38, 137.89, 139.76, 140.28, 143.41, and 159.59; HRMS (MALDI) calcd for $C_{15}H_{12}O$: 208.0888; found: 208.0859.

*4.3.3. 2-Nitrodibenzofulvene (2-NO$_2$-DBF) (**3**).* Tan colored solids, mp not observed up to 200 °C; δ_H (CDCl$_3$) 6.25 (1H, s, vinyl), 6.26 (1H, s, vinyl), 7.42–7.48 (2H, m, ArH), 7.77–7.82 (3H, m, ArH), 8.28 (1H, dd, *J* 8.3 and 1.9, ArH), and 8.56 (1H, d, *J* 1.9, ArH); δ_C (CDCl$_3$) 110.93, 116.59, 119.86, 121.13, 131.46, 124.35, 129.11, 129.37, 137.95, 138.70, 139.38, 141.74, 145.71, and 147.21; HRMS (MALDI) calcd for $C_{14}H_9NO_2$: 223.0633; found: 223.0647; IR (KBr pellet) 1330 cm^{-1} (NO$_2$ sym stretch) and 1520 cm^{-1} (NO$_2$ asym stretch).

*4.3.4. 2-Bromodibenzofulvene (2-Br-DBF) (**4**).* Slightly greenish oil; δ_H (CDCl$_3$) 5.99 (1H, s, vinyl), 6.04 (1H, s, vinyl), 7.28 (1H, t, *J* 7.4, ArH), 7.33 (1H, t, *J* 7.4, ArH), 7.41–7.47 (2H, m, ArH), 7.59 (1H, d, *J* 7.4, ArH), 7.66 (1H, d, *J* 7.4, ArH), and 7.77 (1H, d, *J* 1.4, ArH); δ_C (CDCl$_3$) 109.03, 119.76, 120.81, 121.00, 121.01, 124.27, 127.37, 128.89, 131.45, 137.66, 138.89, 139.15, 139.82, and 142.33; HRMS (MALDI) calcd for $C_{14}H_9{}^{79}Br$: 255.9888; found: 255.9865.

*4.3.5. 2-Iododibenzofulvene (2-I-DBF) (**5**).* White solids, mp 78.8–80.1 °C; δ_H (CDCl$_3$) 6.02 (1H, s, vinyl), 6.08 (1H, s, vinyl), 7.30–7.42 (3H, m ArH), 7.63–7.71 (3H, m, ArH), and 8.02 (1H, d, *J* 1.2, ArH); δ_C (CDCl$_3$) 92.07, 109.11, 119.89, 121.08, 121.44, 127.63, 128.95, 130.26, 137.40, 137.48, 139.27, 139.56, 140.04 and 142.27; HRMS (MALDI) calcd for $C_{14}H_9{}^{127}I$: 303.9749; found: 303.9762.

*4.3.6. 2-Cyanodibenzofulvene (2-CN-DBF) (**6**).* Yellowish solids, mp not observed up to 200 °C; δ_H (CDCl$_3$) 6.14 (1H, s, vinyl), 6.19 (1H, s, vinyl), 7.39 (1H, t, *J* 7.4, ArH), 7.42 (1H, t, *J* 7.4, ArH), 7.63 (1H, dd, *J* 7.9 and 1.4, ArH), 7.72–7.78 (3H, m, ArH), and 7.95 (1H, d, *J* 1.4, ArH); δ_C (CDCl$_3$) 110.10, 110.47, 119.47, 120.31, 120.81, 121.38, 124.75, 128.85, 129.27, 132.54, 138.34, 138.37, 138.52, 141.72, and 143.98; HRMS (MALDI) calcd for $C_{15}H_9N$: 203.0735; found: 203.0766; IR (KBr pellet) 2224 cm^{-1} (nitrile).

*4.3.7. 2-Acetyldibenzofulvene (2-Ac-DBF) (**7**).* Tan colored solids, mp 116.7–118.0 °C; δ_H (CDCl$_3$) 2.65 (3H, s, COCH$_3$), 6.19 (1H, s, vinyl), 6.23 (1H, s, vinyl), 7.41 (1H, t, *J* 7.4, ArH), 7.45 (1H, t, *J* 7.4, ArH), 7.77–7.81 (3H, m, ArH), 8.02 (1H, dd, *J* 7.9 and 1.5, ArH), and 8.35 (1H, d, *J* 1.5, ArH); δ_C (CDCl$_3$) 26.80, 109.31, 119.58, 120.72, 120.91, 121.25, 128.33, 129.03, 129.45, 135.94, 138.14, 138.90, 139.13, 142.56, 144.39, and 197.82; HRMS (MALDI) calcd for $C_{16}H_{12}O$: 220.0888; found: 220.0854; IR (KBr pellet) 1650 cm^{-1} (carbonyl).

*4.3.8. 2-Bromo-7-methoxydibenzofulvene (2-Br-7-MeO-DBF) (**8**).* Greenish solids, mp 122.5–123.6 °C; δ_H (CDCl$_3$) 3.89 (3H, s, OCH$_3$), 6.02 (1H, s, vinyl), 6.05 (1H, s, vinyl), 6.91 (1H, dd, *J* 8.3 and 2.3, ArH), 7.22 (1H, d, *J* 2.3, ArH), 7.40–7.44 (2H, m, ArH), 7.52 (1H, d, *J* 8.3, ArH), and 7.76 (1H, s, ArH); δ_C (CDCl$_3$) 55.60, 106.48, 109.00, 115.13, 119.63, 120.28, 120.68, 124.18, 131.51, 132.41, 139.11, 139.49, 139.76, 142.46, and 159.85; HRMS (MALDI) calcd for $C_{15}H_{11}{}^{79}BrO$: 285.9993; found: 285.9985.

*4.3.9. 2-Bromo-7-propoxydibenzofulvene (2-Br-7-PrO-DBF) (**9**).* Greenish oil; δ_H (CDCl$_3$) 1.10 (3H, t, *J* 7.4, alkyl), 1.87 (2H, m, alkyl), 4.00 (2H, t, *J* 6.6, OCH$_2$), 6.02 (1H, s, vinyl), 6.05 (1H, s, vinyl), 6.92 (1H, dd, *J* 8.3 and 2.3, ArH), 7.24 (1H, d, *J* 2.3, ArH), 7.40 (1H, d, *J* 8.0, ArH), 7.44 (1H, dd, *J* 8.0 and 1.4, ArH), 7.51 (1H, d, *J* 8.0, ArH), and 7.77 (1H, d, *J* 1.4, ArH); δ_C (CDCl$_3$) 10.63, 22.70, 69.88, 107.14, 108.94, 115.59, 119.56, 120.26, 120.67, 124.16, 131.49, 132.21, 139.20, 139.47, 139.77, 142.49, and 159.40; HRMS (MALDI) calcd for $C_{17}H_{15}{}^{79}BrO$: 314.0306; found: 314.0324.

*4.3.10. 2-Bromo-7-hexoxydibenzofulvene (2-Br-7-HexO-DBF) (**10**).* Greenish solids, mp 98.5–99.7 °C; δ_H (CDCl$_3$) 0.88 (3H, t, *J* 7.4, alkyl), 1.34–1.38 (4H, br, alkyl), 1.47–1.49 (2H, br, alkyl), 1.83 (2H, m, alkyl), 4.04 (2H, t, *J* 6.5, OCH$_2$), 6.04 (1H, s, vinyl), 6.07 (1H, s, vinyl), 6.93 (1H, dd, *J* 8.3 and 2.1, ArH), 7.25 (1H, d, *J* 2.1, ArH), 7.39–7.49 (2H, m, ArH), 7.54 (1H, d, *J* 8.3, ArH), and 7.79 (1H, s, ArH); δ_C (CDCl$_3$) 14.09, 22.65, 25.77, 29.30, 31.62, 68.40, 107.16, 108.95, 115.63, 119.55, 120.27, 120.67, 124.18, 131.51, 132.21, 139.20, 139.47, 139.77, 142.52, and 159.43; HRMS (MALDI) calcd for $C_{20}H_{21}{}^{79}BrO$: 356.0776; found: 356.0759.

*4.3.11. 2-Nitro-7-propoxydibenzofulvene (2-NO$_2$-7-PrO-DBF) (**11**).* Orange solids, mp not observed up to 200 °C; δ_H (CDCl$_3$) 1.05 (3H, t, *J* 7.5, alkyl), 1.84 (2H, m, alkyl), 4.00 (2H, t, *J* 6.6, OCH$_2$), 6.17 (1H, s, vinyl), 6.18 (1H, s, vinyl), 6.96 (1H, dd, *J* 8.4 and 2.3, ArH), 7.26 (1H, d, *J* 2.3, ArH), 7.61 (1H, d, *J* 8.4, ArH), 7.63 (1H, d, *J* 8.4, ArH), 8.21 (1H, dd, *J* 8.4 and 2.0, ArH), and 8.46 (1H, d, *J* 2.0, ArH); δ_C (CDCl$_3$) 10.56, 22.60, 69.97, 107.04, 110.74, 116.40, 116.43, 118.79, 122.21, 124.64, 130.92, 138.43, 141.38, 141.81, 146.14, 146.23 and 160.76; HRMS (MALDI) calcd for $C_{17}H_{15}NO_3$: 281.1052; found: 281.1044.

*4.3.12. 2-Nitro-7-hexoxydibenzofulvene (2-NO_2-7-HexO-DBF) (**12**).* Yellowish solids, mp 94.2–96.1 °C; δ_H ($CDCl_3$) 0.90 (3H, t, *J* 7.2, alkyl), 1.33–1.40 (4H, br, alkyl), 1.41–1.52 (2H, br, alkyl), 1.81 (2H, m, alkyl), 4.02 (2H, t, *J* 6.4, OCH2), 6.15 (2H, s, vinyl), 6.95 (1H, dd, *J* 8.4 and 2.0, ArH), 7.24 (1H, d, *J* 2.0, ArH), 7.58 (1H, d, *J* 8.4, ArH), 7.60 (1H, d, *J* 8.2, ArH), 8.19 (1H, dd, *J* 8.2 and 2.0, ArH), and 8.43 (1H, d, *J* 2.0, ArH); δ_C ($CDCl_3$) 14.09, 22.64, 25.74, 29.23, 31.60, 68.47, 106.98, 110.72, 116.36, 116.39, 118.75, 122.18, 124.61, 130.87, 138.39, 141.36, 141.78, 146.12, 146.18, and 160.76; HRMS (MALDI) calcd for $C_{20}H_{21}NO_3$: 323.1521; found: 323.1499; IR (KBr pellet) 1330 cm^{-1} (NO_2 sym stretch), 1510 cm^{-1} (NO_2 asym stretch) and 2930 cm^{-1} (alkane).

*4.3.13. 2,7-Dibromodibenzofulvene (2,7-di-Br-DBF) (**13**).* White crystals, mp not observed up to 200 °C; δ_H ($CDCl_3$) 6.08 (2H, s, vinyl), 7.49–7.54 (4H, m, ArH) and 7.84 (2H, d, *J* 0.8, ArH); δ_C ($CDCl_3$) 110.48, 121.17, 121.29, 124.48, 131.80, 138.04, 139.55, and 141.46; HRMS (MALDI) calcd for $C_{14}H_8{}^{79}Br_2$: 335.8972; found: 335.8956.

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Supplementary data

Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2010.03.046.

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17. It should be noted the vinyl protons for **12** can be resolved into two singlets when a different deuterated solvent *d*-benzene was used. δ_H (C_6D_6) 0.98 (3H, t, *J* 7.2, alkyl), 1.30–1.46 (6H, m, alkyl), 1.70–1.74 (2H, m, alkyl), 3.74 (2H, t, *J* 6.4, OCH_2), 5.61 (1H, s, vinyl), 5.77 (1H, s, vinyl), 6.94 (1H, dd, *J* 8.4 and 2.4, ArH), 7.04 (1 H, d, *J* 8.4, ArH), 7.26 (1H, d, *J* 2.4, ArH), 7.30 (1H, d, *J* 8.4, ArH), 8.08 (1H, dd, *J* 8.4 and 2.0, ArH), and 8.39 (1H, d, *J* 2.0, ArH); δ_C (C6D6) 14.25, 22.99, 26.07, 29.53, 31. 89, 68.31, 107.20, 110.71, 116.52, 116.68, 118.82, 122.37, 124.64, 131.38, 138.56, 141. 69, 142.00, 145.84, 146.85, and 161.09.
18. (2-bromo-7-hexoxyfluorenyl)-9-triphenylphosphonium bromide: δ_H ($CDCl_3$) 0.87 (3H, t, *J* 7.2), 1.25–1.31 (6H, br), 1.55–1.58 (2H, br), 3.32–3.36 (1H, m), 3.64–3.70 (1H, m), 6.66 (1H, s), 6.77 (1H, dt, *J* 8.4 and 2.0), 7.11 (1H, d, *J* 8.0), 7.23–7.29 (3 H, m), 7.49–7.54 (6 H, br), 7.63–7.66 (3 H, m), 7.94–7.99 (6H, br), and 8.53 (1H, d, *J* 8.8); δ_P ($CDCl_3$) 30.54; (b) (2-nitro-7-hexoxyfluorenyl)-9-triphenylphosphonium bromide: δ_H ($CDCl_3$) 0.87 (3H, t, *J* 7.2), 1.28–1.34 (6H, br), 1.58–1.63 (2H, br), 3.32–3.38 (1H, m), 3.67–3.72 (1H, m), 6.67 (1H, s), 6.77 (1H, d, *J* 8.4), 7.44–7.56 (9H, m), 7.66–7.69 (5H, m), 7.96–7.99 (8H, br), and 8.94 (1 H, d, *J* 8.2, ArH); δ_P ($CDCl_3$) 30.44.
19. According to our experience, whether polymerization has occurred or not can be accomplished by a solubility test. DBF is highly soluble in solvent like DCM and THF, whereas its polymer is not.
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22. It is important to keep the equivalence of potassium *tert*-butoxide NOT larger than the phosphonium salts as polymerization of the products can be initiated by this weak nucleophile even at −78 °C.[1]