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Bis(Diaryliodonium) Perfluorosulfonimide Zwitterions as Potential Photo Acid Generators

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Abstract

Three examples of bis(diaryliodonium) perfluorosulfonimide (BDI-PFSI) zwitterions have been prepared as a potential new class of ionic photo-acid generators for chemically amplified photoresist formulations.

Keywords: Iodonium, photo-acid generators, acid diffusion, zwitterions

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1. Introduction

Potential Photo Acid Generators (PAGs) will produce an acid by the following simplified reaction mechanism upon irradiation with UV light¹. Onium salt PAGs have played an enabling role in the development of high photosensitivity resists for microlithography. Both diaryliodonium and triarylsulfonium salts have been extensively utilized². Expectations are that onium PAGs will continue to be important in the application of deep ultraviolet (DUV) and extreme ultraviolet (EUV) technologies for decreasing feature size in semiconductor devices as well as other applications^{3,4}. EUV lithography (EUVL) is a rapid advancing lithography technology, which uses an EUV wavelength, currently expected to be 13.5 nm.⁵ DUV refers to a range of light on the violet side of the color spectrum, far beyond what the human eye can see. Often, 248nm (KrF) and 193nm (ArF) excimer lasers are used⁶. The design and selection of a PAG depends on many factors as expertly summarized by Crivello and Ito²⁻⁴.

Perfluoroalkylsulfonimide (PFSI) onium salts have been shown to have excellent properties as PAGs ^{7, 8}. The very acidic bis((perfluoroalkyl)sulfonyl)imides produced are as effective as perfluoroalkyl sulfonic acids from PFSA based onium salts. In addition the larger moleculear size of the PFSIs can have a favorable effect on acid diffusion as minimum feature size decreases.

Herein we describe a series of novel zwitterionic bis(diaryliodonium) α,ω perfluoroalkylsulfonimides (BDI-PFSI) as potential PAGs (Figure 1). These diffunctional materials may offer advantages in lower PAG concentration and solubility in resist formulations.



This research evolved from earlier work with iodinanes stabilized by bis((trifluoromethyl)sulfonyl)imides anions and iodonium zwitterions based on sulfonamide anions ^{9, 10}.

Results and Discussion Preparation of BDI-PFSI zwitterions

The syntheses of the BDI-PFSI zwitterions are outlined in Scheme 1. 4-iodobenzenesulfonamide 1 and perfluororalkyl disulfonyl fluorides **4a-c** are coupled, and the products **5a-c** are isolated as the Cesium salts. The Cs salts are then oxidized with persulfate in sulfuric acid in the presence of benzene to form the BDI-PFSI zwitterionic compounds **6a-c**.



Scheme 1. Synthesis of Symmetric BDI-PFSI Zwitterions **6a-c** ($R_F = (CF_2)_4$, **a**; (CF₂)₆, **b**; (CF₂CF₂OCF₂CF₂) **c**.

The starting perfluororalkyl disulfonyl fluorides (**4a-4c**) are prepared in three steps (**Scheme 2**) from commercially available α , ω -diiodoperfluoroalkyl compounds I(CF₂)_nI. The reaction chemistry is an extension and refinement of earlier work in China ¹¹ and in our laboratory ¹².

$$IR_{F}I \xrightarrow{Na_{2}S_{2}O_{4} / NaHCO_{3}} NaSO_{2}R_{F}SO_{2}Na \xrightarrow{Cl_{2}} ClSO_{2}R_{F}SO_{2}Cl \xrightarrow{KF} FSO_{2}R_{F}SO_{2}F$$

$$2a-c \qquad 3a-c \qquad 4a-c$$
Scheme 2. Surthesis of Parfluence llud Disulfered Electrides 45.5

Scheme 2. Synthesis of Perfluororalkyl Disulfonyl Fluorides **4a-c**

The sodium-sulfinate salts **2a-c** are not isolated and are converted to the sulfonyl chlorides **3a-c**. The chlorination is carried out by the reverse dropwise addition of the dilute aqueous solution of **2a-c** to chlorine saturated water. In this way the $\Gamma(aq)$ from the deiodosulfination is rapidly converted to ICl₃ and the intermediate I₂ and ICl do not react with **2a-c** to form the unstable -CF₂SO₂I which form -CF₂I groups on decomposition. If chlorine is not present in large excess as in the addition of Cl₂(g) to the aqueous **2a-c**, then substantial amounts of the -CF₂SO₂Na functions are converted back to $-CF_2I$ and separation of the mixtures is difficult. Finally, conversion of **3** to **4** is a high yield reaction and the progress is easily monitored by ¹⁹F NMR.

The coupling reaction of **1** with **4** proceeds well with very dry acetonitrile and DIPEA catalyst. The presence of water leads to hydrolysis of the sulfonyl fluoride. The isolation of **5** as the cesium salts is greatly facilitated by the low solubility of **5**-Cs in water. This low solubility is as

counter intuitive. Conversion of **5** to **6** is carried out using Beringer's methodology [10] 13 and applied to the earlier synthesis of DI-PFSI zwitterions (Figure 2) 10 .



Figure 2. DI-PFSI Zwitterions (R=H; or R=F)

2.2 Properties of BDI-PFSI Zwitterions

The new zwitterionic compounds **4a-c** are similar in many ways to the previously isolated DI-PFSI zwitterions. They have high thermal stability with decomposition onset for **4a-b** beginning near 240° C. In comparison, the two DI-PFSI zwitterions (R=H; or R=F) (Figure 2) decompose at 305 and 294° C, respectively ¹⁴. The difference in polarity of the DI – vs - BDI zwitterions is apparent by the low solubility of the latter in CH₃CN. Both types of zwitterions have good solubility in DMSO.

Table 1 ε (molar absorptivity) values for **6 a-b** are given and a value for a DI-PFI for comparison. The BDI zwitterions are clearly somewhat more absorbing at a given wavelength and all have large ε values at 193 nm.

	$\epsilon (\text{cm}^{-1} \text{ M})$	
Compound	193 nm	254 nm
PhI ⁺ PhSO ₂ N ⁻ SO ₂ CF ₃	$1.17 \mathrm{x} \ 10^5$	16.86×10^3
$(PhI^+PhSO_2N^-SO_2C_2F_4)_2$ 6a	3.21×10^5	42.56×10^3
$(PhI^+PhSO_2N^-SO_2C_3F_6)_2$ 6b	$2.17 \mathrm{x} \ 10^5$	35.85×10^3

Table 1 ε values for DI-PFSI and BDI-PFSIs

3. Conclusions

Three novel bis(diaryliodonium) perfluoroalkylsulfonimide BDI-PFSI zwitterions of the type (Figure 1) were prepared in good yield. They are very unusual examples of zwitterionic structures. The compounds have high thermal stability, are soluble in polar organic solvents and strongly absorb UV light. Based on known PAGs used in photoresists, these new compounds have potential for utilization as PAGs.

4. Experimental

4.1 General considerations

¹H and ¹F NMR spectroscopic studies were carried on a Bruker AC 200 (¹H 200.33MHz and ¹⁹F 188.13 MHz) or JEOL ECX-300 (¹H 300.53 MHz and ¹⁹F 282.78 MHz). All chemical shifts are quoted in ppm using the high-frequency position convention. NMR spectra were measured using solutions of 1-2 mmol/L (unless otherwise stated) in an appropriate deuterated solvent. ¹H NMR spectra were referenced to external TMS, and ¹⁹F chemical shifts were referenced to internal CFCl₃. The infrared spectra were recorded on Perkin-Elmer 1600 and 2000 series FTIR spectrometers. Liquids were run as a film between two KCl plates. Unless indicated otherwise, samples were a minimum of 99.5% pure by ¹⁹F NMR spectroscopy. Thermogravimetric analyses were obtained under nitrogen on a Perkin-Elmer TGA7 with heating rates of 20 °C/min. The sample size for the TGA was normally 10–20 mg. The UV-Vis absorptions were measured on a Shimadzu UV-3101PC spectrophotometer with CH₃CN solution. Extinction coefficients of samples at 193 and 248 nm were calculated based on absorption at these two wavelengths and have estimated error limits of +/-10%. Sample concentration was adjusted so that the absorbance at the wavelength of interest was close to 2.5 in order to minimize effects of possible PAG photodecomposition on the measured ε values. Each sample was run in triplicate and the ε values reported are averages.

The starting materials perfluoroalkyl disulfonyl fluorides **4a-c** were prepared by published methods ^{11, 12}. All other starting materials were from commercial sources and were used as received except where noted.

4.2 Preparation of p-IPhSO₂NH₂**1**

p-iodobenzenesulfonyl chloride (9.08 g, 0.03 mol), 10 mL acetonitrile and 30 mL water were added into a 100-mL round-bottomed flask. Then around 15 mL of NH₃ gas was bubbled into the mixture. The solution was refluxed for 8 hours at 100 °C, and the volatile material was removed using a rotary evaporator. The solid crude product was then recrystallized from a water solution and filtered. The pure product 7.64 g of p-iodobenzenesulfonyl amide **1** was obtained with a yield of 90% after drying under high vacuum for 2 hours.

Alternatively, in a 250-mL three-necked round bottom flask, p-iodobenzenesulfonyl chloride (9.08 g, 0.03 mol) was added. Then ca. 30 mL of ammonia was condensed into the flask at -60 °C and the flask was allowed to slowly warm to room temperature over 8 hours. The crude product was washed with 40 mL water and dried under the vacuum to give 8.07 g purified amide **1** with a yield of 95%.

$$I \xrightarrow{H^{a}} SO_{2}NH_{2}$$

¹H NMR (CD₃CN, ppm): (ab, δ_a 7.89 (2H, d), δ_b 7.60 (2H, d), J_{ab} = 10 Hz, δ_c 5.70 (2H, s) (**note:** The ¹H for this and related compounds represents an aa'bb' spin system but it appears as a deceptively simple ab system with J/ δ near 0.5. The $\delta_{a,b}$ for all compounds are taken as the midpoint of the second order doublets as an approximation as if it is a classic ab spin system. The J_{a,b} is assigned as that of a classic ab spin system. No effort was made to analyze the spectra further.)

4.3 Preparation of NaSO₂R_fSO₂Na 2a-c

In a typical procedure $(IC_2F_4)_2$ (45.40 g, 0.1 mol) was dissolved in 100 mL of acetonitrile and 200 mL of water in a 500-mL round-bottomed flask. The solution was made basic with NaHCO₃ (30.00 g, 0.36 mol) and then fresh Na₂S₂O₄ (50.00 g 0.28 mmol, the ratio is 1:2.8) was slowly added with good stirring at 22° C. After 20 h, fluorine-19 NMR spectroscopy indicated the reaction was complete by disappearance of the $-CF_2I$ signal. The solution (NaSO₂C₂F₄)₂ and other byproducts are light yellow.

 $\begin{array}{l} \underline{2a\;(NaSO_2CF_2{}^aCF_2{}^b)_2} & {}^{19}\text{F\;NMR\;(CD_3CN,\,ppm):\;} \delta_a - 121.6(4\text{F},\,m)\;,\; \delta_b - 129.6(4\text{F},\,m).\\ \underline{2b\;(NaSO_2CF_2{}^aCF_2{}^bCF_2{}^c)_2} & {}^{19}\text{F\;NMR\;(CD_3CN,\,ppm):\;} \delta_a - 121.3(4\text{F},\,m)\;,\; \delta_b - 121.7(4\text{F},\,m)\;,\; \delta_c - 129.8(4\text{F},\,m).\\ \underline{2c\;(NaSO_2CF_2{}^aCF_2{}^b)_2O} & {}^{19}\text{F\;NMR\;(CD_3CN,\,ppm):\;} \delta_a - 81.9(4\text{F},\,m)\;,\; \delta_b - 132.6(4\text{F},\,m). \end{array}$

4.4 Preparation of ClSO₂R_fSO₂Cl **3a-c**

In a typical procedure, 100-mL of water was added to the $(NaSO_2C_2F_4)_2$ solution above. At 0 °C, chlorine was bubbled into another 100 mL of ice water in a 1000-mL flask. While continuously bubbling Cl₂ gas, the $(NaSO_2C_2F_4)_2$ solution was slowly added from a dropping funnel. Each drop instantly gave a red-brown color in the solution, and then quickly turned back to light yellow. After the reaction was complete, the white solid was filtered out and redissolved in CH₂Cl₂. Then, the resulting solution was washed with water and dried over anhydrous Na₂SO₄ for at least 48 hours. Finally 31.90 g of white product (ClSO₂C₂F₄)₂ was obtained after removing

the Na_2SO_4 crystals by filtration, followed by removal of CH_2Cl_2 under vacuum. The yield was 80% for the two reactions.

 $\frac{3a (CISO_2CF_2^{a}CF_2^{b})_2}{3b (CISO_2CF_2^{a}CF_2^{b}CF_2^{c})_2}$ (yield, 88%). $\frac{3b (CISO_2CF_2^{a}CF_2^{b}CF_2^{c})_2}{(PF NMR (CDCl_3, ppm): \delta_a - 104.7(4F, m), \delta_b - 119.6(4F, m), \delta_c - 121.6(4F, m). \delta_c - 121$

4.5 Preparation of FSO₂R_fSO₂F 4a-c

In a typical reaction, **3a** (31.00 g, 77.69 mmol) and dry KF (15.00 g, 0.259 mol, 1: 3.33) were added into a 250-mL round-bottomed flask in the dry box. The flask was evacuated and dry CH₃CN (50 mL) was vacuum transferred into the flask. The mixture was stirred at 22 °C for 24 h. ¹⁹F NMR spectroscopy was used to monitor the reaction process. After reaction was complete, the crude product and CH₃CN were transferred to a trap at high vacuum. Water (30 mL) was then added to the CH₃CN mixture. The lower layer was separated and distilled over P₄O₁₀. Purified product 21.34 g of (FSO₂C₂F₄)₂ **4a** (yield 75%) was collected in the flask.

 $\begin{array}{l} \underline{4a} \; (F^{a}SO_{2}CF_{2}{}^{b}CF_{2}{}^{c})_{2} \; \, ^{19}F \; \text{NMR} \; (\text{CD}_{3}\text{CN}, \text{ppm}): \; \delta_{a} \; 47.5 \; (2F, s) \; , \; \delta_{b} \; -106.9 \; (4F, m), \; \delta_{c} \; -119.0 \; (4F, m), \; bp \; (750 \; \text{torr}) \; 120^{o} \; \text{C}. \\ \underline{4b} \; (F^{a}SO_{2}CF_{2}{}^{b}CF_{2}{}^{c}CF_{2}{}^{d})_{2} \; \; (\text{yield}, \; 79\%). \\ {}^{19}F \; \text{NMR} \; (\text{CD}_{3}\text{CN}, \text{ppm}): \; \delta_{a} \; 47.2 \; (2F, s), \; \delta_{b} \; -106.8 \; (4F, m), \; \delta_{c} \; -119.1 \; (4F, m), \; \delta_{d} \; -120.3 \; (4F, m). \\ bp \; (750 \; \text{torr}) \; 140^{o} \; \text{C}. \\ \underline{4c} \; (F^{a}SO_{2}CF_{2}{}^{b}CF_{2}{}^{c})_{2}O \; \; (\text{yield}, \; 73\%). \\ {}^{19}F \; \text{NMR} \; (\text{CD}_{3}\text{CN}, \text{ppm}): \; \delta_{a} \; 46.6 \; (2F, s), \; \delta_{b} \; -80.9 \; (4F, m), \; \delta_{c} \; -111.2 \; (4F, m). \\ bp \; (750 \; \text{torr}) \; 120^{o} \; \text{C}. \end{array}$

4.6 Preparation of p-IPhSO₂N(Cs)SO₂R_fSO₂N(Cs)SO₂PhI-p **5a-c**

In a typical reaction, dry p-iodobenzenesulfonyl amide **1** (5.66 g, 0.02 mol) and $(FSO_2C_2F_4)_2$ **1a** (3.66 g, 0.01 mol) (2:1) were put into a gas tight vessel with 10 mL of dry diisopropyl ethyl amine (DIEA) and 20 mL of dry CH₃CN. The solution was refluxed with good stirring at 80 °C for 2 days. ¹⁹F NMR spectroscopy indicated the reaction was complete by the disappearance of the $-SO_2F$ signal. All the volatile compounds were then removed under vacuum leaving the crude product R₃NH⁺ salt and the inorganic impurities. The mixture was redissolved in 5 mL of acetone and then acidified with 20 mL of 15% dilute hydrochloric acid to pH= 2.5. The crude product was obtained after precipitation with 20 mL of aqueous Cs₂CO₃ solution (0.025 mol). The final product was filtered out and dried under vacuum for 24 hours. The yield was 10.85 g, 80%.

$$\mathbf{5a} \left(\begin{array}{c} \mathbf{Cs} \\ \mathbf{SO}_{2} \mathbf{NSO}_{2} \mathbf{CF}_{2}^{\mathbf{A}} \mathbf{CF}_{2}^{\mathbf{B}} \\ \mathbf{H}^{\mathbf{a}} \\ \mathbf{H}^{\mathbf{b}} \end{array} \right)_{2}$$

¹⁹F NMR (CD₃CN, ppm): AB δ_A –112.2 (4F, t), δ_B -119.3 (4F, t); ¹H NMR (CD₃CN, ppm): ab ¹H NMR δ_a 7.83(4H, d), δ_b 7.60(4H, d), J_{ab} = 10 Hz; IR (cm⁻¹) (KBr pellet, acetone) 2924(vs), 2855(vs), 1650(w), 1572(m), 1460(s), 1385(m), 1325(vs), 1294(s), 1270(m)1314(s), 1196(vs), 1142(vs), 1093(s), 1007(m), 818(m), 761 (m), 719(w).



Yield, 87%; ¹⁹F NMR (CD₃CN, ppm): ABC δ_A –112.4 (4F, t), δ_B -119.7 (4F, m), δ_C –121.1 (4F, t);

¹H NMR (CD₃CN, ppm): ab, δ_a 7.86 (4H, d), δ_b 7.51(4H, d), J_{ab} = 10 Hz; IR (cm⁻¹) (KBr pellet, acetone) 2926 (vs), 2855(vs), 1650(w), 1569(m), 1460(s), 1377(s), 1314(s), 1201(m), 1147(s), 1097(m), 1002(m), 767(m), 722 (m).



Yield, 84%; ¹⁹F NMR (CD₃CN, ppm): AB, δ_A –80.5(4F, t), δ_B –115.3(4F, m); ¹H NMR (CD₃CN, ppm): ab, δ_a 7.83 (4H, d), δ_b 7.60 (4H, d), J_{ab} = 10 Hz; IR (cm⁻¹) (KBr pellet, acetone): 2926(vs), 2855(vs), 1650(m), 1572(m), 1460(s), 1383(s), 1326(s), 1226(s), 1142(vs), 1090(s), 1059(m), 1008(m), 986(m), 819(m), 765(s), 721(m).

4.7 Preparation of BDI-PFSI zwitterions 6a-c

In a typical reaction, (I-PhSO₂N(Cs)SO₂CF₂CF₂)₂ **5a** (2.33 g, 2.0 mmol) was mixed with 30 mL of conc. sulfuric acid in a 50-mL round-bottomed flask, cooled to -30 °C. Potassium persulfate (1.39 g, 8.0 mmol) was added in one portion and the reaction mixture was slowly warmed to -20 °C in an 50% ice-isopropanol bath with good stirring. To the resulting suspension, benzene (0.37 mL, 4.2 mmol, the ratio is 1.4:2.1) was added. The reaction mixture became a dark yellow solution and was warmed to 20°C over 8 h. The mixture was then poured into the ice to quench the reaction. The resulting suspension was filtered and the solid was washed with 30 mL of water. The 1.62 g of dried solid **5a** (the yield is 65%) was obtained with the purity of 95%. The impurity was tentatively identified as the hydrolysis product from **5a**, PhI⁺PhSO₂N⁻SO₂CF₂CF₂CF₂CF₂SO₃H (or SO₃⁻). We were unsuccessful in separating it from **5a** or **6a**. Presumably more rigorous anhydrous conditions would eliminate this impurity.



¹⁹F NMR (DMSO, ppm): $δ_A$ –112.3(4F, t), $δ_B$ -119.6(4F, t); ¹H NMR (DMSO, ppm): ab, $δ_a$ 8.32(4H, d), $δ_b$ 8.23(4H, d), J_{ab} = 8 Hz; (cc'dd'e) $δ_c$ 7.83(4H, d), δ_e 7.66(2H, t), δ_d 7.52(4H, t), $J_{cd} \approx$ 8 Hz, $J_{de} \approx$ 7 Hz; ¹³C NMR (DMSO, ppm): δ 207.1, 148.9, 135.8, 135.8, 132.7, 132.4, 129.7, 128.7, 119.5, 117.2 IR (cm⁻¹) (KBr pellet, acetone) 2927(vs), 2855(vs), 1564(m), 1461(s), 1377(s), 1317(m), 1140(m), 1085(m), 987(m), 725 (m); Td=242 °C.



Yield, 68%, purity 98%; ¹⁹F NMR (DMSO, ppm): δ_A –112.3(4F, t), δ_B -119.7(4F, m), δ_C –121.1(4F, t);

¹H NMR(DMSO, ppm): ab, δ_a 8.33(4H, d), δ_b 8.25(4H, d), J_{ab} =8 Hz; (cc'dd'e)

(cc'dd'e) δ_c 7.84(4H, d), δ_e 7.66(2H, t), δ_d 7.53(4H, t), $J_{cd} \approx 8$ Hz, $J_{de} \approx 7$ Hz;

¹³C NMR (DMSO, ppm): δ 207.1, 148.7, 137.8, 135.8, 132.7, 132.4, 129.7, 128.6, 119.5, 119.4, 117.1;

IR (cm⁻¹) (KBr pellet, acetone) 2919(vs), 2855(vs), 1565(m), 1461(s), 1377(s), 1326(s), 1272(m), 1210(m), 1149(s), 1086(m), 987(m), 821(m), 767 (m), 740(m); Td=243 °C.



Yield, 60%, purity, 94%; ¹⁹F NMR (CD₃CN, ppm): δ_A –115.4 (4F, t), δ_B -80.3 (4F, t); ¹H NMR (CD₃CN, ppm): ab, δ_a 8.32 (4H, d), δ_b 8.23 (4H, d), J_{ab} = 8 Hz; (cc'dd'e) δ_c 7.85 (4H, d), δ_e 7.67(2H, t), δ_d 7.50 (4H, t), $J_{cd} \approx$ 8 Hz, $J_{de} \approx$ 7 Hz;

IR (cm⁻¹) (KBr pellet, acetone) 2927(vs), 2856(vs), 1565(m), 1461(s), 1378(s), 1318(s), 1194(s), 1157(s), 1114(m), 1086(m), 987(m), 822(m), 782(m), 735(m).

Graphical Abstract – Synopsis

Three examples of bis(diaryliodonium) perfluorosulfonimide (BDI-PFSI) zwitterions have been prepared as a potential new class of ionic photo-acid generators for chemically amplified photoresist formulations.



Figure 1. Bis(Diaryliodonium) Perfluorosulfonimide Zwitterions

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Graphical Abstract

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