Synthesis of *N*-(Nitrofluorenylidene)anilines and their Application as Electron Transport Materials in Positive Charge Electrophotography

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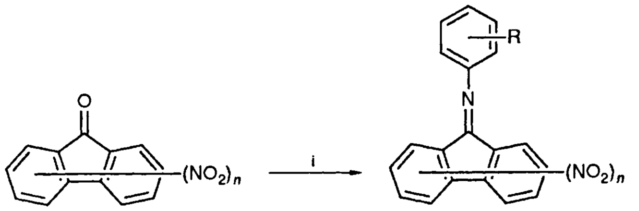
N-(Nitrofluorenylidene)anilines were synthesized by the condensation of nitrofluorenones with substituted anilines in the presence of zinc chloride. 2-Methyl, 2-ethyl, 2-isopropyl and 2-trifluoromethyl derivatives from 2,4,7-trinitrofluorenone showed high compatibility to polycarbonate and good properties as electron transport materials in positive charge electrophotography. The 2-isopropyl and 2-trifluoromethyl derivatives were substantially stable for the repetition test. *N*-(2,4,7-Trinitrofluorenylidene)-2-isopropylaniline was negative for the Ames test.

Much attention has been focused on the functionality of organic compounds.[1] In the field of electrophotography, the use of negative charge organic photoconductor (OPC) is one of the successful examples of the practical application of organic compounds to high technology.[2] The advantage of positive charge OPC consists in both its low ozone generation (70–80% less than the negative one) during the corona discharge process and less decomposition of OPC. Although 2,4,7-trinitrofluorenone (TNF) is known as an electron transport material, it shows poor solubility in organic solvents, poor compatibility to resin, and high toxicity. Therefore, improvement of these properties of TNF is of utility and interest. This paper describes the synthesis, solubility, compatibility, and mutagenicity of *N*-(nitrofluorenylidene)anilines, and their application as electron transport materials in positive charge electrophotography.

Results and Discussion

Synthesis, Solubility and Compatibility of N-*(Nitrofluorenylidene)anilines.*—Scheme 1 shows the synthesis of *N*-(nitrofluorenylidene)anilines **1–3**, which were obtained by heating nitrofluorenones with substituted anilines in the presence of anhydrous zinc chloride followed by purification by column chromatography and recrystallization.



Scheme 1 *Reagents and conditions:* i, $RC_6H_4NH_2$, $ZnCl_2$, 150–200 °C

The yields, solubility and compatibility of *N*-(nitrofluorenylidene)anilines are summarized in Table 1. Di- and tri-nitro derivatives **1** and **2** were prepared in moderate to good yields, and tetranitro derivatives **3** in low yields. The relationship between solubility in chloroform of *N*-(nitrofluorenylidene)anilines and their compatibility to polycarbonate was examined. *N*-(Nitrofluorenylidene)aniline derivatives substituted with fluorine and trifluoromethyl group(s) **2c–g** showed similar solubilities as TNF, while 2-trifluoromethyl derivative **2h** revealed remarkably good solubility. Although 2-alkyl- and 2-perfluorobutylthio-aniline derivatives **2i–k** and **2o** showed extremely good solubility and high compatibility to polycarbonate, *tert*-butyl derivative **2l** showed poor solubility and compatibility. Di- and tetra-nitrofluorenones **1k**, **3h**, **3j** and **3k**, less soluble into chloroform than the corresponding trinitrofluorenones **2k**, **2h** and **2j**, were not compatible enough to polycarbonate for evaluation as electron transport materials. All highly soluble *N*-(nitrofluorenylidene)anilines such as **2h–k** and **2o** also showed high compatibility to polycarbonate.

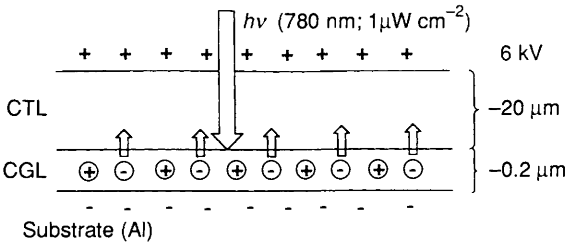


Fig. 1 Construction of an OPC

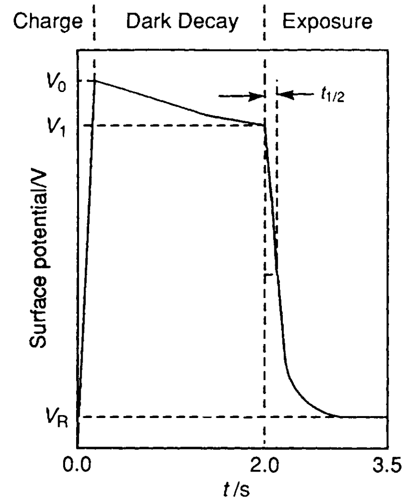


Fig. 2 Photoinduced discharge curve of OPC for test cycle

Application of N-*(Nitrofluorenylidene)anilines as Electron Transport Materials in Electrophotography.*—Prepared OPC is a dual layer type consisting of a charge generation layer (CGL) of metal-free phthalocyanine and a charge transport layer (CTL) of *N*-(nitrofluorenylidene)anilines. The construction is shown in Fig. 1. A typical photoinduced discharge curve of OPC for a test cycle is shown in Fig. 2. The electrical potential of the photoconductor surface reaches a fixed potential by corona discharge (6 kV) followed by dark decay (2 s). Upon irradiation (780 nm, 1 μW cm^{-2}), the potential immediately decreases.

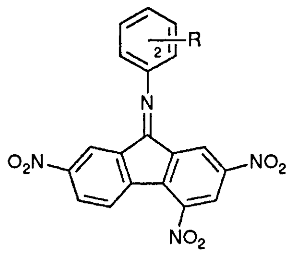
The property of an OPC is evaluated using the following parameters.

Table 1 Yields, solubility and compatibility of *N*-(nitrofluorenylidene)anilines **1**–**3**

Compd.	R	Yield[a] (%)	Solubility[b] (wt%)	Compatibility to PC[c]
1k	2-Pr^i	77	6.37	medium
2a	H	73	2.89	poor
2b	3-Et	59	2.91	poor
2c	4-F	57	1.93	poor
2d	2,3,4,5,6-F_5	29	1.11	poor
2e	4-CF_3	68	2.01	poor
2f	3-CF_3	80	1.16	poor
2g	3,5-$(CF_3)_2$	86	3.38	poor
2h	2-CF_3	28	22.82	high
2i	2-Me	88	12.17	high
2j	2-Et	73	25.29	high
2k	2-Pr^i	87	18.90	high
2l	2-Bu^t	90	3.43	low
2m	2-Br	30	6.57	medium
2n	2-OMe	23	5.51	medium
2o	2-SC_4F_9	87	22.84	high
3h	2-CF_3	10	4.29	medium
3j	2-Et	16	1.96	poor
3k	2-Pr^i	24	0.45	poor

[a] Isolated yield. [b] Determined in $CHCl_3$ at 25 °C, spectroscopically [2,7-dinitrofluorenone = 0.19; 2,4,7-trinitrofluorenone (TNF) = 2.85; 2,4,5,7-tetranitrofluorenone = 0.16]. [c] Polycarbonate.

Table 2 Evaluation of selected *N*-(2,4,7-trinitrofluorenylidene)anilines as electron-transport materials in OPC



Compd.	R	V_0/V	DDR (%)	$E_{\frac{1}{2}}$/μJ cm^{-2}	V_R/V
2h	2-CF_3	665	92	0.52	105
2i	2-Me	567	92	0.55	71
2j	2-Et	675	94	0.47	87
2k	2-Pr^i	586	93	0.31	39
2o	2-SC_4F_9	690	95	0.77	225

(i) Charge acceptance (V_0/V).
(ii) Dark decay ratio (DDR) [$(V_0 - V_t)/V_0 \times 100$ (%)].
(iii) Sensitivity ($E_{\frac{1}{2}}$) [$t_{\frac{1}{2}}$ (s) × light intensity (μW cm^{-2})].
(iv) Residual potential (V_R/V).

For the practical use of the OPC, V_0 should be in the range 600–800 V; DDR > 90%; $E_{\frac{1}{2}} < 0.50$ μJ cm^{-2}; and $V_R < 50$ V.

The results of the evaluation of selected *N*-(nitrofluorenylidene)anilines **2h**–**k** and **2o** as electron transport materials in OPC are summarized in Table 2. All samples showed excellent charge acceptance and DDR. The sensitivity and residual potential of **2k** represented the best result among them.

The drift mobility (μ) of **2i** is shown in Fig. 3. Compound **2i** showed better drift mobility than TNF (*ca.* 5×10^{-7} cm^2 V^{-1} S^{-1} in TNF–polycarbazole system).

The repetition test of **2h**–**k** and **2o** was then examined. The changes in the parameters V_0, $E_{\frac{1}{2}}$ and V_R until 1000 times repetition are shown in Figs. 4, 5 and 6, respectively. In all cases, the values gradually increased, suggesting the decomposition of electron transport materials. Compound **2o** being most unstable could not be used as an electron transport material. For all parameters, compounds **2h** and **2k** showed good results. The oxidation of the C=N moiety of **2h** and **2k** by ozone might be depressed by an electron-withdrawing or a steric substituent at the *ortho*-position.[3]

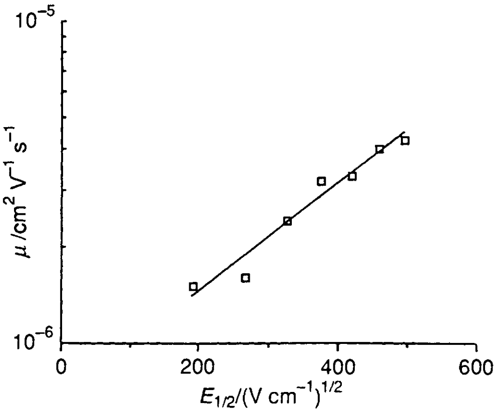


Fig. 3 Drift mobility of CTM

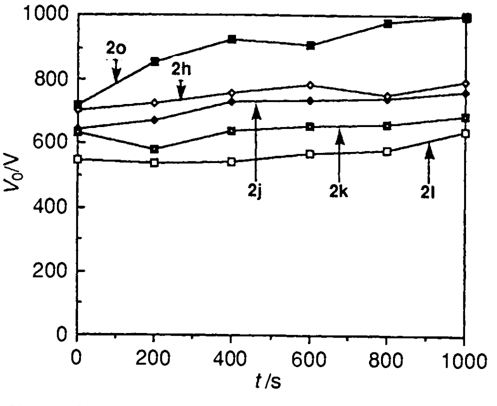


Fig. 4 Change in charge acceptance (V_0)

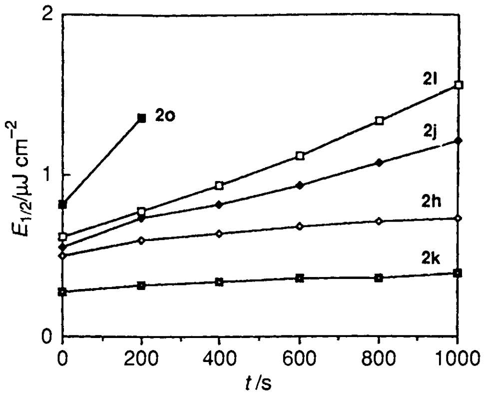


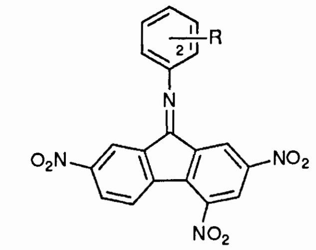
Fig. 5 Change in sensitivity ($E_{\frac{1}{2}}$)

Mutagenicity (*Ames Test*) *of* N-(*Nitrofluorenylidene*)*anilines.*—The results of mutagenicity (Ames test) of TNF and **2h**–**k** are summarized in Table 3. *Salmonella TA98* and *TA100* with (+S9) and without (−S9) liver were used for the test. Not only TNF but also **2h** and **2i** were Ames positive. However, compound **2k**, which showed the good property as an electron transport material in positive charge electrophotography, was Ames negative.

Experimental

Mass spectra (70 eV) were recorded on Shimadzu QP-1000 and 9020-DF spectrometers. NMR spectra ($CDCl_3$ solution) were obtained with a JEOL JNM-270GX FT NMR spectrometer.

Table 3 Ames test of *N*-(2,4,7-trinitrofluorenylidene)anilines



		TA 98		TA 100	
Compd.	R	− S9	+ S9	− S9	+ S9
TNF	H	+ + +	+ + +	+ +	+ +
2h	2-CF_3	+ + +	+ + +	+ +	+ +
2i	2-Me	+	+	−	−
2j	2-Et	−	+	−	−
2k	2-Pr^i	−	±	−	−

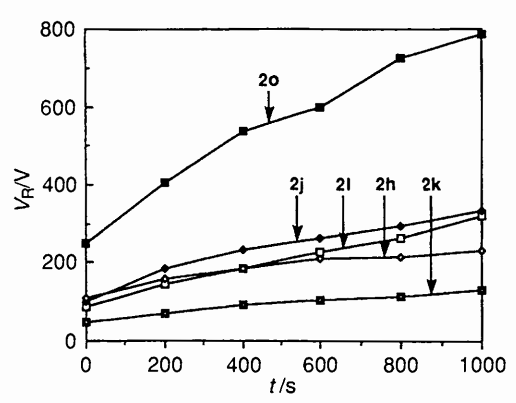


Fig. 6 Change in residual potential (V_R)

J Values are in Hz. M.p.s were measured with a Yanagimoto micro-point apparatus and were uncorrected.

N-(*Nitrofluorenylidene*)*anilines* **1–3**.—*General procedure*. A mixture of an aniline (10 mmol), a nitrofluorenone (5 mmol) and anhydrous zinc chloride (0.1 g) was heated (**1k**: 150–155 °C, 2 h; **2a**: 185–190 °C, 1 h; **2b**: 150–155 °C, 2 h; **2c**: 190–195 °C, 1 h; **2d**: 155–160 °C, 60 h; **2e**: 190–195 °C, 5 h; **2f**: 190–195 °C, 1.5 h; **2g**: 200–205 °C, 2 h; **2h**: 175–180 °C, 6 h; **2i**: 195–200 °C, 6 h; **2j**: 175–180 °C, 6 h; **2k**: 160–165 °C, 4 h; **2l**: 135–140 °C, 1.5 h; **2m**: 205–210 °C, 7 h; **2n**: 175–180 °C, 6 h; **2o**: 160–165 °C, 3 h; **3h**: 175–180 °C, 3 h; **3j**: 180–185 °C, 4 h; **3p**: 150–155 °C, 1.5 h). Afterwards, the product was extracted with chloroform (200 cm^3) and purified by column chromatography (SiO_2, $CHCl_3$).

N-(2,7-*Dinitrofluorenylidene*)-2-*isopropylaniline* **1k**. M.p. 207–208 °C (Found: C, 68.3; H, 4.45; N, 10.8. $C_{22}H_{17}N_3O_4$ requires C, 68.21; H, 4.42; N, 10.85%); δ_H 1.16 (6 H, d, *J* 6.7), 3.06 (1 H, hept, *J* 6.7), 6.78 (1 H, d, *J* 7.6), 7.28 (1 H, t, *J* 7.6), 7.35 (1 H, t, *J* 7.6), 7.49 (1 H, d, *J* 7.6), 7.50 (1 H, d, *J* 1.8), 7.91 (1 H, d, *J* 8.2), 7.92 (1 H, d, *J* 8.2), 8.35 (1 H, dd, *J* 8.2 and 1.8), 8.49 (1 H, dd, *J* 8.2 and 2.4) and 8.89 (1 H, d, *J* 2.4); *m*/*z* 387 (M^+, 100%), 372 (55) and 357 (30); $\lambda_{max}(CHCl_3)$/nm 281 (ε/dm^3 mol^{-1} cm^{-1} 30 000).

N-(2,4,7-*Trinitrofluorenylidene*)*aniline* **2a**. M.p. 227–229 °C (lit.,[4] 224–225 °C).

3-*Ethyl*-N-(2,4,7-*trinitrofluorenylidene*)*aniline* **2b**. M.p. 220–222 °C (Found: C, 60.7; H, 3.3; N, 13.5. $C_{21}H_{14}N_4O_6$ requires C, 60.29; H, 3.37; N, 13.39%); δ_H 1.27 (3 H, t, *J* 7.6), 2.73 (2 H, q, *J* 7.6), 6.86 (2 H, d, *J* 7.2), 7.22 (1 H, s), 7.46 (1 H, t, *J* 7.2), 7.77 (1 H, d, *J* 1.8), 8.30 (1 H, d, *J* 8.5), 8.37 (1 H, dd, *J* 8.5 and 1.8), 8.96 (1 H, d, *J* 1.8) and 9.12 (1 H, d, *J* 1.8); *m*/*z* 418 (M^+, 100%); $\lambda_{max}(CHCl_3)$/nm 275 (ε/dm^3 mol^{-1} cm^{-1} 26 000) and 329 (15 000).

4-*Fluoro*-N-(2,4,7-*trinitrofluorenylidene*)*aniline* **2c**. M.p. 230–232 °C (lit.,[4] 232.5–233.5 °C).

2,3,4,5,6-*Pentafluoro*-N-(2,4,7-*trinitrofluorenylidene*)*aniline* **2d**. M.p. 243–244 °C (Found: C, 47.5; H, 1.0; N, 11.6. $C_{19}H_5F_5N_4O_6$ requires C, 47.52; H, 1.05; N, 11.67%); δ_H 8.03 (1 H, d, *J* 2.1), 8.40 (1 H, d, *J* 8.8), 8.52 (1 H, dd, *J* 8.8 and 1.8), 9.02 (1 H, d, *J* 2.1) and 9.11 (1 H, d, *J* 1.8); *m*/*z* 480 (M^+, 100%), 434 (11), 388 (15), 342 (14) and 323 (29); $\lambda_{max}(CHCl_3)$/nm 280 (ε/dm^3 mol^{-1} cm^{-1} 35 000) and 320 (11 000).

4-*Trifluoromethyl*-N-(2,4,7-*trinitrofluorenylidene*)*aniline* **2e**. M.p. 243–244 °C (Found: C, 52.4; H, 1.9; N, 11.7. $C_{20}H_9F_3N_4O_6$ requires C, 52.41; H, 1.98; N, 12.22%); δ_H 7.13 (2 H, d, *J* 8.5), 7.61 (1 H, d, *J* 1.8), 7.83 (2 H, d, *J* 8.5), 8.33 (1 H, d, *J* 8.7), 8.41 (1 H, dd, *J* 8.7 and 2.2), 8.99 (1 H, d, *J* 1.8) and 9.11 (1 H, d, *J* 2.2); *m*/*z* 458 (M^+, 100%), 412 (12), 366 (19), 320 (33), 319 (17) and 251 (16); $\lambda_{max}(CHCl_3)$/nm 278 (ε/dm^3 mol^{-1} cm^{-1} 27 000) and 323 (5700).

3-*Trifluoromethyl*-N-(2,4,7-*trinitrofluorenylidene*)*aniline* **2f**. M.p. 235–238 °C (Found: C, 52.1; H, 1.7; N, 12.0. $C_{20}H_9F_3N_4O_6$ requires C, 52.41; H, 1.98; N, 12.22%); δ_H 7.24 (3 H, m), 7.66–7.70 (2 H, m), 8.33 (1 H, d, *J* 8.6), 8.41 (1 H, dd, *J* 8.6 and 1.8), 8.98 (1 H, d, *J* 1.8) and 9.10 (1 H, d, *J* 1.8); *m*/*z* 458 (M^+, 100%), 412 (9), 366 (14), 320 (22), 319 (12) and 251 (9); $\lambda_{max}(CHCl_3)$/nm 278 (ε/dm^3 mol^{-1} cm^{-1} 32 000) and 324 (14 000).

3,5-*Bis*(*trifluoromethyl*)-N-(2,4,7-*trinitrofluorenylidene*)*aniline* **2g**. M.p. 217–219 °C (Found: C, 47.7; H, 1.4; N, 10.5. $C_{21}H_8F_6N_4O_6$ requires C, 47.92; H, 1.53; N, 10.65%); δ_H 6.03 (2 H, s), 6.12 (1 H, d, *J* 1.5), 6.34 (1 H, s), 6.70 (1 H, d, *J* 7.1), 6.76 (1 H, dd, *J* 7.1 and 1.5), 7.21 (1 H, d, *J* 1.5) and 7.27 (1 H, d, *J* 1.5); *m*/*z* 526 (M^+, 100%); $\lambda_{max}(CHCl_3)$/nm 278 (ε/dm^3 mol^{-1} cm^{-1} 37 000) and 320 (13 000).

2-*Trifluoromethyl*-N-(2,4,7-*trinitrofluorenylidene*)*aniline* **2h**. M.p. 154–157 °C (Found: C, 52.8; H, 2.0; N, 12.0. $C_{20}H_9F_3N_4O_6$ requires C, 52.41; H, 1.98; N, 12.22%); δ_H 6.98 (1 H, d, *J* 7.8), 7.44 (1 H, d, *J* 1.8), 7.50 (1 H, t, *J* 7.8), 7.70 (1 H, t, *J* 7.8), 7.89 (1 H, d, *J* 7.8), 8.33 (1 H, d, *J* 8.7), 8.40 (1 H, dd, *J* 8.7 and 1.8), 8.99 (1 H, d, *J* 1.8) and 9.10 (1 H, d, *J* 1.8); *m*/*z* 458 (M^+, 100%), 366 (18), 300 (22) and 251 (11); $\lambda_{max}(CHCl_3)$/nm 278 (ε/dm^3 mol^{-1} cm^{-1} 35 000) and 324 (14 000).

2-*Methyl*-N-(2,4,7-*trinitrofluorenylidene*)*aniline* **2i**. M.p. 184–186 °C (Found: C, 59.0; H, 2.95; N, 13.4. $C_{20}H_{12}N_4O_6$ requires C, 59.41; H, 2.99; N, 13.86%); δ_H 2.18 (3 H, s), 6.84 (1 H, d, *J* 7.6), 7.30–7.34 (2 H, m), 7.42 (1 H, d, *J* 7.6), 7.66 (1 H, d, *J* 1.8), 8.31 (1 H, d, *J* 8.6), 8.38 (1 H, dd, *J* 8.6 and 2.1), 8.97 (1 H, d, *J* 1.8) and 9.16 (1 H, d, *J* 2.1); *m*/*z* 404 (M^+, 100%), 357 (21) and 265 (42); $\lambda_{max}(CHCl_3)$/nm 278 (ε/dm^3 mol^{-1} cm^{-1} 28 000) and 327 (14 000).

2-*Ethyl*-N-(2,4,7-*trinitrofluorenylidene*)*aniline* **2j**. M.p. 169–170 °C (Found: C, 60.1; H, 2.9; N, 13.2. $C_{21}H_{14}N_4O_6$ requires C, 60.29; H, 3.37; N, 13.39%); δ_H 1.13 (3 H, t, *J* 7.3), 2.55 (2 H, q, *J* 7.3), 6.78 (1 H, d, *J* 6.7), 7.32–7.36 (2 H, m), 7.45 (1 H, d, *J* 6.7), 7.67 (1 H, d, *J* 1.8), 8.30 (1 H, d, *J* 8.5), 8.37 (1 H, dd, *J* 8.5 and 1.8), 8.97 (1 H, d, *J* 1.8) and 9.14 (1 H, d, *J* 1.8); *m*/*z* 418 (M^+, 100%) and 265 (22); $\lambda_{max}(CHCl_3)$/nm 278 (ε/dm^3 mol^{-1} cm^{-1} 28 000) and 325 (15 000).

2-*Isopropyl*-N-(2,4,7-*trinitrofluorenylidene*)*aniline* **2k**. M.p. 184–186 °C (Found: C, 61.6; H, 3.8; N, 12.7. $C_{22}H_{16}N_4O_6$ requires C, 61.11; H, 3.73; N, 12.96%); δ_H 1.17 (6 H, d, *J* 7.3), 3.06 (1 H, hept, *J* 7.3), 6.74 (1 H, d, *J* 8.2), 7.29 (1 H, t, *J* 8.2), 7.39 (1 H, t, *J* 8.2), 7.52 (1 H, d, *J* 8.2), 7.77 (1 H, d, *J* 1.8), 8.31 (1 H, d, *J* 8.6), 8.37 (1 H, dd, *J* 8.6 and 2.3), 8.97 (1 H, d, *J* 1.8) and 9.14 (1 H, d, *J* 2.3); *m*/*z* 432 (M^+, 100%), 417 (63), 371 (13), 425 (22) and 278 (36); $\lambda_{max}(CHCl_3)$/nm 279 (ε/dm^3 mol^{-1} cm^{-1} 33 000) and 325 (16 000).

2-tert-*Butyl*-N-(2,4,7-*Trinitrofluorenylidene*)*aniline* **2l**. M.p.

242–243 °C (Found: C, 61.5; H, 3.8; N, 12.5. $C_{23}H_{18}N_4O_6$ requires C, 61.88; H, 4.06; N, 12.55%); δ_H 1.36 (9 H, S), 6.69 (1 H, d, *J* 7.3), 7.27 (1 H, t, *J* 7.3), 7.36 (1 H, t, *J* 7.3), 7.63 (1 H, d, *J* 7.3), 7.65 (1 H, d, *J* 1.8), 8.30 (1 H, d, *J* 8.6), 8.39 (1 H, dd, *J* 8.6 and 1.8), 8.97 (1 H, d, *J* 1.8) and 9.10 (1 H, d, *J* 1.8); *m*/*z* 446 (M^+, 56%) and 431 (100); λ_{max}($CHCl_3$)/nm 282 (ε/dm^3 mol^{-1} cm^{-1} 28 000) and 332 (16 000).

2-*Bromo*-N-(2,4,7-*trinitrofluorenylidene*)*aniline* **2m**. M.p. 230–232 °C (Found: C, 48.8; H, 1.7; N, 11.9. $C_{19}H_9BrN_4O_6$ requires C, 48.64; H, 1.93; N, 11.94%); δ_H 7.00 (1 H, d, *J* 8.1), 7.27 (1 H, t, *J* 8.1), 7.50 (1 H, t, *J* 8.1), 7.61 (1 H, d, *J* 2.0), 7.80 (1 H, d, *J* 8.1), 8.33 (1 H, d, *J* 8.7), 8.41 (1 H, dd, *J* 8.7 and 2.1), 8.99 (1 H, d, *J* 2.0) and 9.16 (1 H, d, *J* 2.1); *m*/*z* 468 (M^+, 100%), 422 (12), 376 (17), 330 (14); λ_{max}($CHCl_3$)/nm 278 (ε/dm^3 mol^{-1} cm^{-1} 25 000) and 324 (9800).

2-*Methoxy*-N-(2,4,7-*trinitrofluorenylidene*)*aniline* **2n**: m.p. 188–190 °C (Found: C, 57.0; H, 2.9; N, 13.2. $C_{20}H_{12}N_4O_7$ requires C, 57.15; H, 2.88; N, 13.33%); δ_H 3.76 (3 H, s), 7.00 (1 H, d, *J* 7.7), 7.12 (1 H, d, *J* 7.7), 7.13 (1 H, t, *J* 7.7), 7.36 (1 H, t, *J* 7.7), 7.87 (1 H, d, *J* 2.2), 8.29 (1 H, d, *J* 8.6), 8.37 (1 H, dd, *J* 8.6 and 1.8), 8.94 (1 H, d, *J* 2.2) and 9.16 (1 H, d, *J* 1.8); *m*/*z* 420 (M^+, 100%), 373 (16) and 313 (17); λ_{max}($CHCl_3$)/nm 279 (ε/dm^3 mol^{-1} cm^{-1} 30 000) and 324 (14 000).

2-*Nonafluorobutylthio*-N-(2,4,7-*trinitrofluorenylidene*)*aniline* **2o**. M.p. 144–145 °C (Found: C, 43.3; H, 1.4; N, 8.6. $C_{23}H_9F_9N_4O_6S$ requires C, 43.14; H, 1.42; N, 8.75%); δ_H 7.08 (1 H, d, *J* 7.7), 7.47 (1 H, t, *J* 7.7), 7.67–7.70 (2 H, m), 7.91 (1 H, d, *J* 7.7), 8.35 (1 H, d, *J* 8.8), 8.41 (1 H, d, *J* 8.8), 9.03 (1 H, s) and 9.10 (1 H, s); *m*/*z* 640 (M^+, 100%), 421 (30) and 375 (40); λ_{max}($CHCl_3$)/nm 280 (ε/dm^3 mol^{-1} cm^{-1} 31 000) and 329 (14 000).

2-*Trifluoromethyl*-N-(2,4,5,7-*tetranitrofluorenylidene*)*aniline* **3h**. M.p. 204–206 °C (Found: C, 47.7; H, 1.6; N, 13.8. $C_{20}H_8F_3N_5O_8$ requires C, 47.73; H, 1.60; N, 13.92%); δ_H 7.00 (1 H, d, *J* 7.6), 7.56 (1 H, t, *J* 7.6), 7.65 (1 H, s), 7.73 (1 H, t, *J* 7.6), 7.93 (1 H, d, *J* 7.6), 8.88 (1 H, s), 9.02 (1 H, s) and 9.16 (1 H, s); *m*/*z* 503 (M^+, 100%); λ_{max}($CHCl_3$)/nm 339 (ε/dm^3 mol^{-1} cm^{-1} 11 000).

2-*Ethyl*-N-(2,4,5,7-*tetranitrofluorenylidene*)*aniline* **3j**. M.p. 169–170 °C (Found: C, 53.7; H, 2.65; N, 14.6. $C_{21}H_{13}N_5O_8$ requires C, 54.43; H, 2.83; N, 15.11%); δ_H 1.16 (3 H, t, *J* 7.6), 2.60 (2 H, q, *J* 7.6), 6.81 (1 H, d, *J* 8.1), 7.35 (1 H, t, *J* 8.1), 7.41 (1 H, t, *J* 8.1), 7.49 (1 H, d, *J* 8.1), 7.93 (1 H, d, *J* 1.8), 8.86 (1 H, d, *J* 1.8), 9.01 (1 H, d, *J* 1.8) and 9.20 (1 H, d, *J* 1.8); *m*/*z* 463 (M^+, 100%), 340 (17); λ_{max}($CHCl_3$)/nm 342 (ε/dm^3 mol^{-1} cm^{-1} 14 000).

2-*Isopropyl*-N-(2,4,5,7-*tetranitrofluorenylidene*)*aniline* **3k**. M.p. 268–270 °C (Found: C, 54.3; H, 2.9; N, 14.3. $C_{22}H_{15}N_5O_8$ requires C, 55.35; H, 3.17; N, 14.67%); δ_H 1.20 (6 H, d, *J* 7.3), 3.09 (1 H, hept., *J* 7.3), 6.77 (1 H, d, *J* 7.6), 7.33 (1 H, t, *J* 7.6), 7.45 (1 H, t, *J* 7.6), 7.56 (1 H, d, *J* 7.6), 7.93 (1 H, d, *J* 2.4), 8.87 (1 H, d, *J* 1.8), 9.02 (1 H, d, *J* 2.4) and 9.20 (1 H, d, *J* 1.8); *m*/*z* 477 (M^+, 100%) and 462 (46); λ_{max}($CHCl_3$)/nm 340 (ε/dm^3 mol^{-1} cm^{-1} 15 000).

Preparation of an OPC.—To the aluminized polyester film was coated a thin charge generation layer (CGL) of metal-free phthalocyanine by the drawbar technique. *N*-(Nitrofluorenylidene)aniline (5.0 g) was mixed with a chloroform–chlorobenzene (7 : 3) solution (45 cm^3) of polycarbonate (5.0 g) and stirred for 1 h. On the CGL was coated a thin layer of the mixture. The resultant film was dried.

Evaluation of N-(*Nitrofluorenylidene*)*anilines as Electron Transport Materials in Positive Charge Electrophotography.*—Kawaguchi electrostatic paper analyser model SP428 was used to measure surface potentials of synthesized OPC materials.

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