Novel Hydrazone and Azine Based Hole Transport Materials

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Abstract

Thirteen novel hole transport materials were prepared in our labs either as polymeric structures (Compounds (1) – (7)) or as dimeric structures (Compounds (8)-(13)) and several were evaluated for electrophotography. These hole transport materials contain either hydrazone or azine moieties as part of the electrophotographically functional chromophore. The chemical structure of these compounds was confirmed by proton NMR, infrared and ultraviolet spectroscopy. The ionization potential and hole mobility (determined via a xerographic time of flight method) are reported for some of these compounds. The presence of hydroxyl groups on some of these materials improves adhesion and compatibility with traditional polycarbonate (PC) and polyvinylbutyral (PVB) binder materials. In addition, these dimeric or polymeric hole TM can be chemically cross-linked in the photoconductive layer, for example, by reaction of the hydroxyl groups with polyisocyanates, to increase the layer stability to bending, stretching and abrasion, as well as the effects of abrasion. The synthesized TM and compositions with binder exhibit good hole transporting properties and high mobility making them useful for preparation of high sensitivity electro-photographic photoconductors.

Introduction

Organic charge-transporting materials are used in electrophotographic photoreceptors, light-emitting diodes, photovoltaic devices and other optoelectronic devices.[1,2] Rapid charge transporting ability, high photosensitivity, simple synthesis and low price are a few of the advantages of the hydrazones and azines charge TM.[3] Low molecular weight TM-containing hydrazone moieties are usually crystalline materials, are not capable of forming thin, neat homogenous layers, and must be used in combination with polymeric binders. The presence of a large proportion of polymer binder in the compositions, usually 50% of the total composition mass, leads to considerable decrease of carrier mobility. Even in such compositions, the possibility of the TM crystallization remains; this causes problems during electrophotographic layer (EPL) preparation and extended printing. From this consideration, low-molecular weight materials that form stable amorphous glasses having glass-transition temperatures above room temperature or photoconducting polymers are more desirable as compared to crystalline TM materials. Among the great number of studies devoted to low-molar-mass aromatic hydrazones, only a few glass-forming compounds[4-7] and polymers[9-11] with hydrazone moiety are reported.

In this paper, we report on the synthesis, characterization, and photoconductive properties of a representative group of novel hydrazone-based and azine-based hole TMs in dimeric and polymeric structural forms. The ionization potential (I_p) and hole mobility (using xerographic time of flight technique) are reported for some of these compounds. The presence of hydroxyl groups improves adhesion and compatibility with traditional PC and PVB binders used in commercial photoconductors. The synthesized TM and compositions with binder exhibit good hole transporting properties and high mobility making them useful for preparation of high sensitivity electro-photographic photoconductors.

Experimental

Representative Synthesis of Polymeric HTM

Preparation of Compound (1)

A mixture of poly[9-(2,3-epoxypropyl)-3-formylcarbazole] (1.5 g), N-methyl-N-phenylhydrazone (1.5 g) and tetrahydrofuran (5 ml) was reacted in a 25 ml, 3-neck round bottom flask under reflux conditions for approximately 2 hours and then cooled to room temperature. The mixture was filtered through a layer of silica gel (grade 62, 60-200 mesh, 150 Å) having a thickness of 3-4 cm and the silica gel was washed with tetrahydrofuran. A tetrahydrofuran solution was collected, concentrated to 5 ml by evaporation, and then poured into 20-fold excess of hexane with intensive stirring. The resulting precipitate was filtered, washed repeatedly with 2-propanol, and dried in a vacuum oven at 50°C for 5 hours. The yield of Compound (1) was 1.2 g (80%). The IR spectrum of Compound (1) in a KBr salt window displayed the following characteristic vibrational frequencies, ν (cm^{-1}): 3590-3280 (OH), 3050 (aromatic CH); and 2930, 2874, 2810 (aliphatic CH); 902, 802, 748, and 692 (carbazole and monosubstituted benzene). The UV spectrum of Compound (1) in tetrahydrofuran was characterized by the following absorption wavelengths (nm, logε): 208 (4.31); 242 (4.40); 310 (4.20); and 343 (4.37).

Preparation of Compound (3)

A mixture of 4,4'-bis(diethylamino)benzophenone 2,4-bis(1,2-epoxypro-poxy)benzaldehyde azine (1.61 g, 2.83 mmol), 4,4'-thiobisbenzenethiol (0.709 g, 2.8 mmol) and diethylamide (0.2 ml, 1.415 mmol) was refluxed in 20 ml of tetrahydrofuran (THF) under argon for 60 hours. The reaction mixture was cooled to room temperature, filtered through a layer of silica gel (3-4 cm thick, grade 62, 60-200 mesh, 150 Å) and then the silica gel was washed with THF. The THF solution was concentrated to 15-20 ml by evaporation and then poured into 20-fold excess of methanol with intensive stirring. The resulting precipitate was filtered off, washed repeatedly with methanol, and dried in a vacuum oven at 50°C for 5 hours. The yield of the product was 1.4 g (60.4%).

Representative Synthesis of Dimeric HTM

Preparation of Compound (8)

Carbazole (120 g, 0.72 mole), 1,10-dibromodecane (100 g, 0.33 mole), benzyltriethyl ammonium chloride (12 g) and 400 ml of tetrahydrofuran (THF) were added to a 2-liter 3-neck round bottom flask. A concentrated solution of sodium hydroxide (120 g) in water (120 ml) was added to the solution. The mixture was heated at reflux with strong mechanical stirring for 4 hours, cooled to room temperature, and poured into an excess of water. The solid that precipitated was filtered off and the THF layer was dried over magnesium sulfate and concentrated to dryness. The combined organic solids were recrystallized from THF/water and dried at 50°C for 6 hours. The yield was 116.5 g (69%). The product had a melting point of 130°C.

Dimethylformamide (200 ml) was added to 1-liter 3-neck round bottom flask and cooled in ice bath. Phosphorous oxychloride (70 ml, 115 g, 0.75 mole) was added gradually. 1,10-bis(9-carbazolyl)decane (100 g, 0.22 mole) was introduced and the resulting mixture was heated on steam bath with stirring for 1.5 hours. A viscous, dark brown liquid was generated from which a yellow solid precipitated upon cooling. The entire mixture was added to water (400 ml). The crude product was filtered off, washed with water (200 ml) and then with ethanol (70 ml) and then recrystallization from THF/water to afforded 1,10-bis (3-formyl-9-carbazolyl)decane as light brown crystals. The yield was 92.3 g (83%) and the product had a melting point of 122°C.

1,10-bis(3-formyl-9-carbazolyl)decane (10.0 g, 0.019 mole) and 150 ml of tetrahydrofuran (THF) were added to a 500 ml, 3-neck round bottom flask and heated to dissolve the solids. A solution of the 9-fluorenone-4-n-butylcarboxylate hydrazone (11.23 g, 0.0381 mole) in 50 ml of tetrahydrofuran and 10 drops of 37% aqueous hydrochloric acid were added to the flask. The flask was refluxed for 5 hours. The solution was filtered hot into a beaker that contained 500 ml of ethyl alcohol. The product was isolated and recrystallized from THF/ethyl alcohol with activated charcoal. The product was isolated and dried at 50°C oven vacuum for 6 hours. The yield of Compound (8) was 7.85 g (40%).

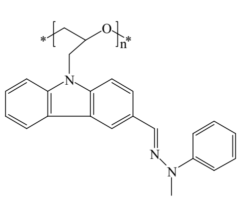
Preparation of Compound (10)

A 10.0 g quantity of 9-fluorenone-4-carbonyl chloride (0.04 mole) and 100 ml of tetrahydrofuran were added to a 250 ml, 3-neck round bottom flask followed by 5.16 g of 4,4'-thiobisbenzenethiol (0.02 mole) in 50 ml of tetrahydrofuran and 4.17 g of triethylamine (0.04 mole). The solution was refluxed for 6 hours, filtered hot to remove triethylamine hydrochloride salt byproduct, and evaporated to dryness. The dimeric fluorenone derivative was then recrystallized from tetrahydrofuran / methanol with activated charcoal and dried at 60°C vacuum oven for 6 hours to yield a yellow solid (6.85 g, 50% yield).

The dimeric fluorenone derivative (10.00 g, 0.0151 mole, prepared in previous step) and 200 ml tetrahydrofuran (THF) were added to a 500 ml, 3-neck round bottom flask and heated to dissolve the solids. A solution of 3,5-di-tert-butyl-4-hydroxybenzaldehyde hydrazone (3.75 g, 0.0151 mole) in 50 ml of tetrahydrofuran was added to the flask, followed by the addition of 20 drops of 37% aqueous hydrochloric acid. The solution was refluxed for 5 hours and the solution was filtered hot into a beaker that contained 500 ml of ethyl alcohol. The product was isolated and recrystallized from THF/ethyl alcohol with activated charcoal. The product was isolated and dried at 50°C in a vacuum oven for 6 hours. The yield of product was 5.76 g (53%).

Using the preceding preparation, the following thirteen compounds were made:

Polymeric Hole Transport Materials



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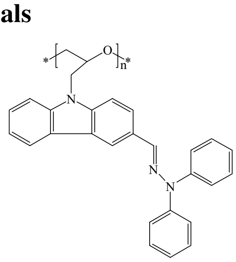

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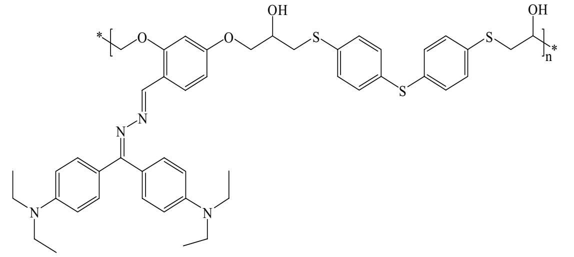

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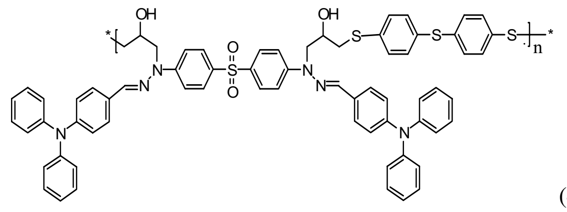

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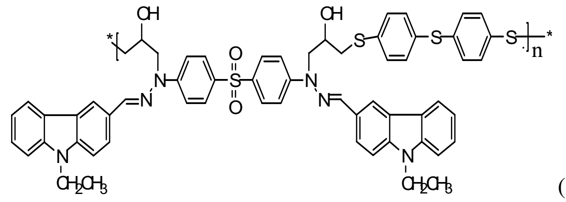

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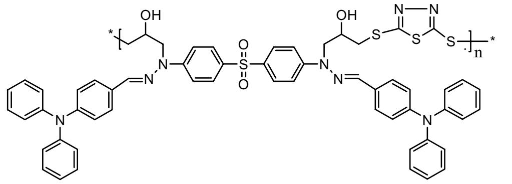

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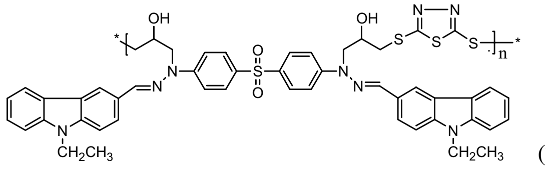

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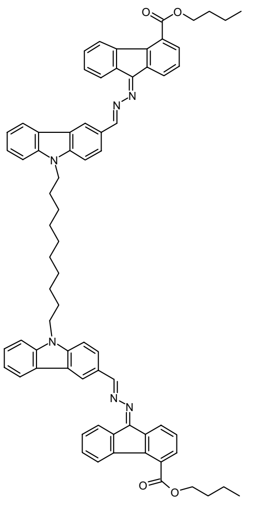
Dimeric Hole Transport Materials



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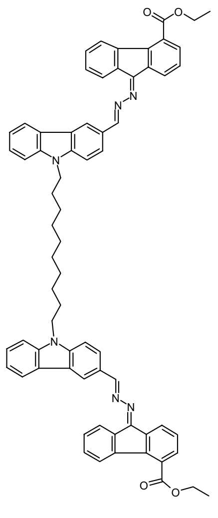

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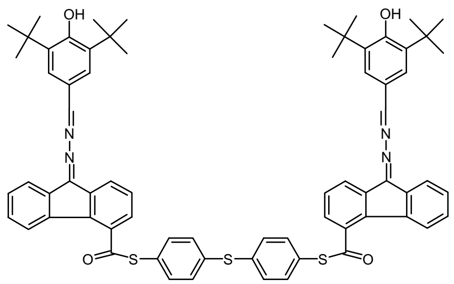

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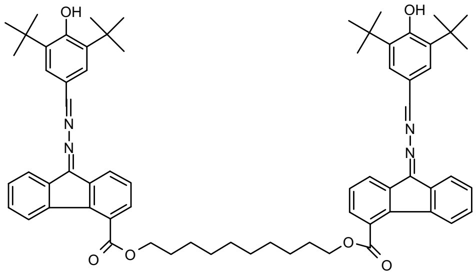

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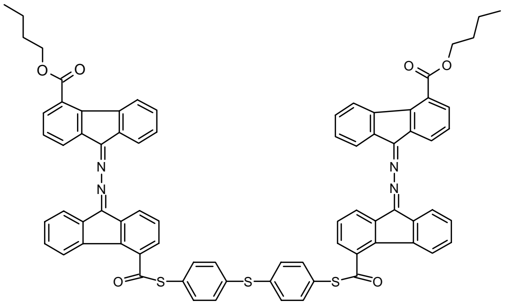

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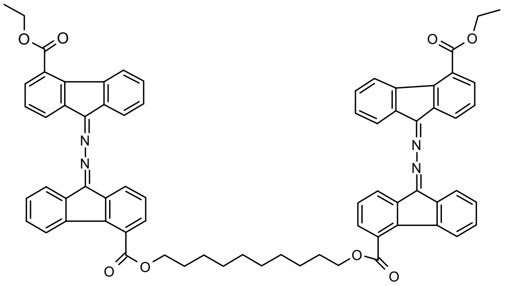

(13)

Hole Mobility Measurements

Sample Preparation:

A mixture of 0.1 g of Compound (2) and 0.1 g of polycarbonate Z binder was dissolved in 2 ml of tetrahydrofuran. The solution was coated on a polyester film containing a conductive aluminum layer by a dip roller method. The coating was dried for 1 hour at 80°C to produce a transparent, 10 µm thick layer. Sample preparation for measuring hole mobility of Compounds (3), (4) and (6) was similar to Compound (2) except without binder.

Table 1 lists the hole mobility values, measured by a xerographic time of flight technique (XTOF),[12] for Compounds 2, 3, 4, and 6. Positive corona charging creates an electric field inside the hole transport layer and the charge carriers were generated at the layer surface by illuminating the sample with a pulse from a nitrogen laser (pulse duration was 2 ns, wavelength 337 nm). As a result of the pulse illumination, the surface potential of the layer decreased by 1-5% of its initial potential. A capacitance probe connected to the wide frequency band electrometer measured the surface potential reduction rate, $\mathrm{d}U/\mathrm{d}t$. The transit time t_t was determined by the kink in the curve of the $\mathrm{d}U/\mathrm{d}t$ transient in double logarithmic scale. Figure 1 illustrates typical xerographic time of flight transients obtained using Compound (3).

The drift mobility was calculated by the formula $\mu = d^2/U_0 \cdot t_t$, where d is the layer thickness and U_0 is the surface potential at the moment of illumination. The curves in Figure 1 were used to calculate the drift mobility values for each of the initial surface potentials, U_0 ranging from 98 V to 388 V, and these mobility values were plotted against the square root of the initial field strength. Figure 2 illustrates the hole mobility dependence on the initial field strength of the samples investigated.

Ionization Potential Measurements

Sample Preparation

A thin layer of charge transport material, ca. 0.5 µm thick, was coated from a solution of 2 mg of charge transport material in 0.2 ml of tetrahydrofuran onto a 20 cm^2 substrate surface. The substrate was an aluminized polyester film coated with a 0.4 µm thick methylcellulose sub-layer. Table 1 presents the ionization potentials for the investigated samples.

Ionization potential was measured as described in Grigalevicius et al., "3,6-Di(N-diphenylamino)-9-phenylcarbazole and its methyl-substituted derivative as novel hole-transporting amorphous molecular materials," Synthetic Metals **128** (2002), p. 127-131. In particular, each sample was illuminated with monochromatic light from the quartz monochromator with a deuterium lamp source. The power of the incident light beam was $2\text{-}5 \cdot 10^{-8}$ W. A negative voltage of –300 V was supplied to the sample substrate. A counter-electrode, with the 4.5×15 mm^2 slit for illumination, was placed 8 mm from the sample surface. The counter-electrode was connected to the input of a BK2-16 type electrometer, working in the open input regime, for the photocurrent measurement. A 10^{-15}– 10^{-12} amp photocurrent was flowing in the circuit under illumination. The photocurrent, I, was strongly dependent on the incident light photon energy hν. The $I^{0.5}=f(h\nu)$ dependence was plotted. Usually, the dependence of the square root of photocurrent on incident light quanta energy is well described by linear relationship near the threshold (see references "Ionization Potential of Organic Pigment Film by Atmospheric Photoelectron Emission Analysis," Electrophotography, 28, Nr. 4, p. 364 (1989) by E. Miyamoto, Y. Yamaguchi, and M. Yokoyama; and "Photoemission in Solids," Topics in Applied Physics, **26**, 1-103 (1978) by M. Cordona and L. Ley). The linear part of this dependence was extrapolated to the hν axis, and the Ip value was determined as the photon energy at the interception point. The ionization potential measurement has an error of ±0.03 eV.

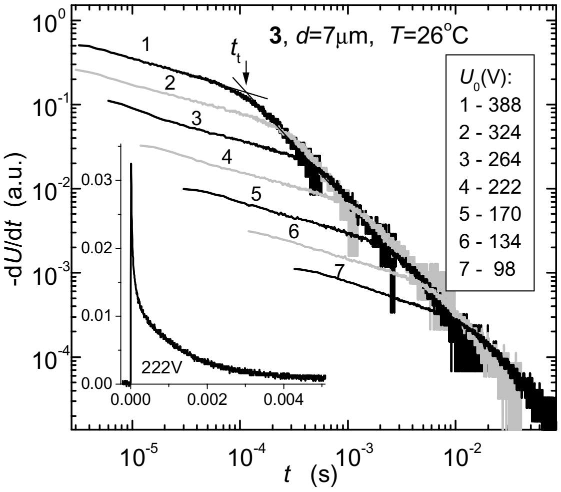

Figure 1. Xerographic time of flight transients for Compound 3

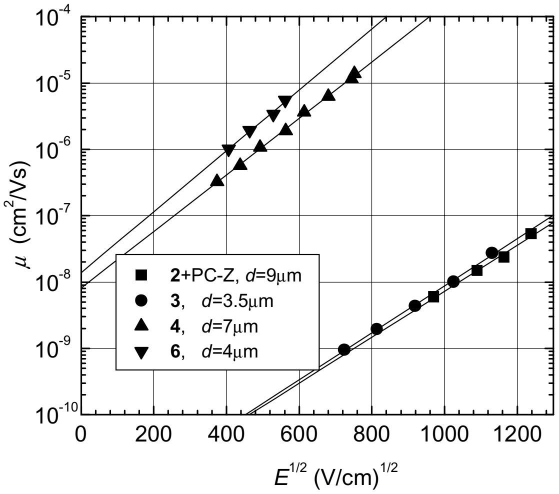

Figure 2. Hole mobility field dependencies for the Compounds investigated

Results and Discussion

Table 1 presents a summary of the electrostatic characterization values determined for four of the hole transport materials in this paper. In general, the hole mobility value for samples prepared without binder is expected to be at least an order of magnitude larger than the value for the same sample prepared with a binder matrix.

The binder material decreases hole mobility due to chromophore dilution, increased positional or energetic disorder, etc. Taking the binder effect into consideration, the hole mobility for polymeric Compounds (4) and (6) is still more than three orders of magnitude larger than that for polymeric Compounds (2) and (3). Figure 2 illustrates the magnitude of hole drift mobility values and their strong mobility dependence on the electric field strength for the four polymeric hole transporting materials. The huge difference in mobility values could be explained either by structural differences, (triphenylamine versus carbazole moieties or hydrazone versus azine based) or by electrostatic factors, such as deep charge trapping that may exist in Compounds (2) and (3).

Table 1. Hole Mobility and Ionization Potential

Cpd	μ_0 (cm^2/V.s)	μ (cm^2/V.s) at 6.4x10^{5}V/cm	*A* (cm/V)$^{0.5}$	*Ip* *(ev)*
2	2.6 x 10^{-12}	1.5 x 10^{-9}	~0.008	5.49
3	3.0 x 10^{-12}	1.7 x 10^{-9}	~0.0079	5.42
4	8.0 x 10^{-9}	2.0 x 10^{-5}	0.0098	5.49
6	~1.0 x 10^{-9}	~6.0 x 10^{-5}	~0.011	5.49

Conclusion

Dimeric and polymeric hydrazone and azine based hole transport compounds were prepared and investigated as potential new materials for electrophotography. Their chemical structures were confirmed by proton NMR and hole drift mobility determined by a xerographic time of flight method. The hole drift mobility was found to be highest for polymeric compounds containing triphenylamine hydrazone pendent groups and lowest for polymeric compounds containing azine or carbazole based pendent groups.

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Biography

Dr. Nusrallah Jubran received his Ph.D. in Chemistry from Ben-Gurion University at Beer-Sheva, Israel in 1985. In 1988 he joined 3M Company after spending two and half years of post doctoral research with Prof. Daryl H. Busch at the Ohio State University. He is currently working as a staff chemist with Samsung Electronics, Digital Printing Solutions Laboratory in Woodbury, MN. His research activities focus on the development and scale up of novel organic photoconductor materials for electrophotography. He is a member of the IS&T. njubran@mn.sisa.samsung.com