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Electroactive oxetanyl-functionalized aromatic hydrazones and enamine

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Various oxetanyl-functionalized aromatic hydrazones and enamine have been synthesized by the multi-step reaction procedures. Full characterization of their structure is presented. The synthesized materials were examined by various techniques including differential scanning calorimetry, UV spectrometry, electron photoemission and time of flight techniques. The electron photoemission spectra of the layers showed the ionisation potentials of 5.46-5.61 eV. Room temperature hole drift mobility of some derivatives molecularly dispersed in bisphenol Z polycarbonate ranged from 10^{-6} to 4×10^{-5} cm^2/Vs.

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1. Introduction

Electroactive and photoactive organic materials are known for various optoelectronic and electronic applications such as electrophotographic photoreceptors [i], displays [ii,iii], photovoltaic cells [iv], photorefractive materials [v], organic transistors [vi]. Among the low-molar-mass amorphous derivatives, triphenylamine and carbazole based compounds are the most extensively used as hole transport materials because they are easily oxidized to form stable radical cations [vii-xi]. However, the latter compounds have some problems such as the lack of the morphological stability of their glasses as well as rather high ionization potentials [xii,xiii].

In this work, we have designed and synthesised new aromatic amines having hydrazone or enamine fragments, which were expected to enhance hole injection and transport properties of the latter materials. On the other hand, the compounds contain reactive oxetane moieties and could be (photo)polymerized/cross-linked directly in thin films, which could be applied in manifold ways for organic optoelectronics [xiv-xvi]. Recently photocross-linking is a common strategy of protecting thin organic systems against solvents [xvii-xix].

2. Experimental

2.1. Instrumentation

^{1}H NMR spectra were recorded using Bruker AC 250 (250 MHz) and JOEL FX 100 (100 MHz) apparatuses. Mass spectra were obtained on a Waters ZQ 2000 spectrometer. FTIR spectra were recorded using Bio-Rad Digilab FTS-40 and Perkin Elmer Spectrum GX spectrophotometers. Ultraviolet (UV) spectra were measured with Spectronic Unicam Genesys^{TM} 8 spectrophotometer and Specord M-40 spectrometer. Fluorescence (FL) spectra were recorded with Hitachi MPF-4 spectrometer. Thermogravimetric analysis (TGA) was performed on Perkin-Elmer thermal analysis system 409. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin Elmer Pyris Diamond calorimeter. The TGA and DSC curves were recorded in a nitrogen atmosphere at a heating rate of 10^o C/min.

The ionisation potentials of the layers of the compounds synthesized were measured by the electron photoemission method in air, which we have described earlier [xx]. The measurement method was, in principle, similar to that demonstrated by Miyamoto et al. [xxi].

The hole drift mobility was measured by the time of flight technique in electrophotographic regime [xxii]. The samples for the charge carrier mobility measurements were prepared by casting molecular mixtures of the materials with bisphenol Z polycarbonate (PC-Z) on polyester films with Al layer. The thickness of the transporting layer varied in the range of 6-10 μm.

2.2. Materials

Triphenylamine (**1**), 9-ethylcarbazole (**2**), N-phenylhidrazine, diphenylacetaldehyde (**10**), diphenylamine (**11**) and 3-(bromomethyl)-3-methyl oxetane were purchased from Aldrich and used as received.

4-Formyltriphenylamine (**3**) and 3-formyl-9-ethylcarbazole (**4**) were prepared from the aromatic amines **1** and **2**, respectively, by the Vilsmeier procedure [xxiii].

Triphenylamine 4-carbaldehyde N-phenylhydrazone (**5**) was synthesized according to our earlier reported procedure [xxiv]. 4-Formyltriphenylamine (11.0g, 0.04 mol) was dissolved in 300 ml of methanol under mild heating. Then, a solution of 6.52g (0.06 mol) of

N-phenylhydrazine in 5 ml of methanol was added. The reaction mixture was refluxed for 0.5h until no starting materials were observed (TLC control). After cooling and crystallisation, yellowish crystals were filtered, washed with a large amount of methanol and dried. The yield of **5** was 85 % (12.3 g), mp 168-169°C. ^{1}H NMR (100 MHz, CDCl$_3$, δ, ppm): 6.55-7.64 (m, 21H, Ar, =CH, -NH). MS: m/z=364 (100%, (M+H)$^+$), 314, 223, 159. IR (in cm^{-1}): ν(N-H) 3294, ν(C-H in Ar) 3026, ν(C=C in Ar) 1595; 1489, ν(C-N) 1282; 1257, γ(Ar) 750; 731.

9-Ethylcarbazole-3-carbaldehyde-N-phenylhydrazone (**6**) was prepared using similar procedure as described for **5**. 10 g (0.045 mol) of 9-ethylcarbazole-3-carbaldehyde was dissolved in 300 ml of methanol under mild heating. Then a solution of 7.25g (0.067 mol) of N-phenyl hydrazine in methanol was added. The reaction mixture was refluxed for 2h and stopped when no starting materials were left (TLC control). The product was filtered, washed with a large mount of methanol and dried. The product was obtained as yellow-grey crystals in the yield of 13.12 g (92 %), mp 136-137^{o}C. ^{1}H NMR (100 MHz, CDCl$_3$): δ=1.34 (t, J=7.0 Hz, 3H, CH$_3$); 4.23 (q, J=7.0 Hz, 2H, CH$_2$); 6.90-7.64 (m, 8H, Ar); 7.60 (s, 1H, Ar); 7.81 (d, 1H, Ar); 8.08 (d, 2H, Ar); 8.15(d, 1H, =CH). MS m/z=314 (90%, M+1), 222. IR (in cm^{-1}): ν(N-H) 3306, ν(C-H) 2972, ν(C-H in Ar) 3051, ν(C=C, C-N in Ar) 1602; 1494; 1475; 1237, ν(C-N) 1256, γ(Ar) 815; 747; 731.

Triphenylamine 4-carbaldehyde N-(3-methyl-3-oxetanylmethyl)-N-phenylhydrazone (**7**). 3 g (0.0076 mol) of material **5** was dissolved in 50 ml of methyl ethyl ketone, and then 1.3 g (0.023 mol) of KOH and 1.05 g (0.0076 mol) of K$_2$CO$_3$ were added to the solution. Then 2.5 g (0.015 mol) of 3-(bromomethyl)-3-methyl oxetane was added into the reaction mixture. The mixture was refluxed for 48 h. After cooling the inorganic components were filtered off and the solvent was evaporated. The product was purified by column chromatography using an eluent mixture of ethylacetate and hexane in a volume ratio of 1:4. The yield was 59 % (2 g of yellow amorphous material). ^{1}H NMR (250 MHz, CDCl$_3$): δ= 1.57 (s, 3H, CH$_3$), 3.93 (s, 2H, =N-$\underline{CH_2}$-C-), 4.33 (d, J=2.5 Hz, 2H, -C-$\underline{CH_2}$-O), 4.74 (d, J= 5 Hz, 2H, -C-$\underline{CH_2}$-O), 7.07-7.51 (m, 20H, Ar, –$\underline{CH}$-N). MS: m/z=448 (100%, (M+H)$^+$), 374, 271. IR (in cm^{-1}): ν(C-H in Ar) 3057, 3025; ν(C-H) 2925, 2963, 2857; ν(C=C, C-N in Ar) 1590, 1488, 1449; ν(C-N) 1281; 1269; ν(C-O-C) 1127, 989; ν(cyclic ether) 975; γ(Ar) 752; 698.

9-Ethylcarbazole-3-carbaldehyde-N-(3-methyl-3-oxetanylmethyl)-N-phenylhydrazone (**8**). 4.1 g (0.013 mol) of hydrazone **6** was dissolved in 50 ml of methyl ethyl ketone, and 2.4g (0.04 mol) of KOH and 1.79 g (0.013 mol) of K$_2$CO$_3$ were added to the solution. Then 4.3 g (0.026 mol) of 3-(brom methyl)-3-methyl oxetane was added into the reaction mixture. The mixture was refluxed for 24 h. After cooling the inorganic components were filtered off and the solvent was evaporated. The product was purified by column chromatography using an eluent mixture of ethyl acetate and hexane in a volume ratio of 1:4. The product was crystallized from eluent, filtered and dried. The yield was 78 % (4 g of yellow crystals), mp 118-120 ^{o}C. ^{1}H NMR (250 MHz, CDCl$_3$): δ=1.34 (t, J=7.0 Hz, 3H, CH$_3$); 1.57 (s, 3H, CH$_3$); 3.93 (s, 2H, =N-$\underline{CH_2}$-C-); 4.23 (q, J=7.0 Hz, 2H, CH$_2$); 4.33 (d, J=6.25 Hz, 2H, -C-$\underline{CH_2}$-O); 4.74 (d, J= 5 Hz, 2H, -C-$\underline{CH_2}$-O); 7.07-7.51 (m, 13H, Ar, –$\underline{CH}$-N). MS: m/z=398 (100%, (M+H)$^+$). IR (in cm^{-1}): ν(C-H in Ar) 3018, 3050, ν(C-H) 2958, 2941, 2866, ν(C=N) 1590, ν(C=C, C-N in Ar) 1492, 1476, ν(C-N) 1333, 1258, νC-O-C) 1129, 984, ν(cyclic ether) 973, γ(Ar) 808, 747, 733.

Di(4-[{N-(3-ethyl-3-oxetanylmethyl)-N-phenylamino}iminomethyl]phenyl)phenylamine (**9**) was prepared from 4,4′-diformyltriphenylamine using the same procedures as described for mono functionalized derivative **7**. The product **9** was purified by column chromatography using an eluent mixture of hexane and ethyl acetate in a volume ratio of 5:1. The yield was 29 % (1 g of yellow amorphous material). ^{1}H NMR (250 MHz, CDCl$_3$): δ= 1.35 (s, 6H, CH$_3$); 3.54 (s, 4H, N-$\underline{CH_2}$-C); 4.37 (d, J=4.75 Hz, 4H, C-$\underline{CH_2\text{-}O}$); 4.54 (d, J=4.75 Hz, 4H, C-$\underline{CH_2\text{-}O}$); 7.02-7.59 (m, 25H, Ar, -$\underline{CH}$=N). MS m/z=650 (80%, (M+H)$^+$), 448, 298. IR (in cm^{-1}): ν(C-H in Ar) 3057, 3025; ν(C-H) 2925, 2963, 2857; ν(C=C, C-N in Ar) 1590, 1488, 1449; ν(C-N) 1281; 1269; ν(C-O-C) 1127, 989; ν(cyclic ether) 975; γ(Ar) 752; 698.

(2,2-Diphenylvinyl)diphenylamine (**12**). Diphenylamine (12.9 g, 0.076 mol) was dissolved in 50 ml of toluene, and catalytic amount of 10-camphorsulfonic acid was added. The solution was refluxed for 20 minutes and 4.46 ml (0.026 mol, d=1.096) of diphenylacetaldehyde was added in the reaction mixture. After refluxing for 5 hours, part of solvent was distilled, and the rest was precipitated into methanol. The crude product was purified by precipitation into methanol twice to obtain white powder in 73 % (6.45 g) yield, mp 154 ^{o}C. ^{1}H NMR (250 MHz, CDCl$_{3,}$ ppm): δ= 6.78-7.34 (m, 21H, Ar, CH=). MS: m/z = 348 (100 %,(M+H)$^+$), 170. IR (in cm^{-1}): ν(C-H in Ar) 3067, 3055, 3026, ν(C=C) 1588, 1489, 1442, 1390, 1343, (C-N) 1261, 1156, 1111, γ(Ar) 871, 755, 694.

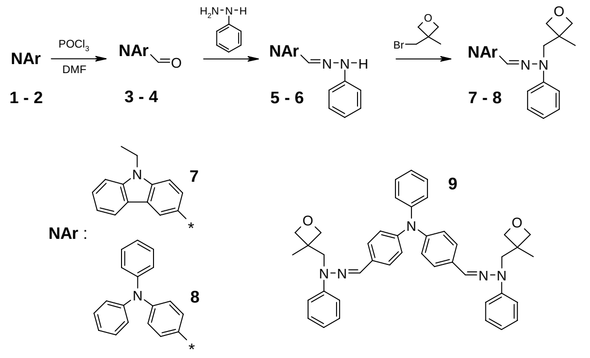
(2,2-Diphenylvinyl)-(4-formylphenyl)phenylamine (**13**). POCl$_3$ (5.44 g, 0.035 mol) was added drop wise to 8.23 g (0.113 mol) of dry DMF at 0^{o}C under nitrogen atmosphere. The solution was warmed up slowly to room temperature and 4.1 g (0.012 mol) of derivative **11** in 20 ml of dry DMF was added drop wise. The reaction mixture was heated at 80^{o}C for 24h and then poured into ice water. The mixture obtained was neutralized with 10% solution of potassium hydroxide, and the product was extracted with chloroform. The material was purified by column chromatography using an eluent mixture of ethyl acetate and hexane in a volume ratio of 1:5. The yield was 59 % (2.63 g). ^{1}H NMR (250 MHz, CDCl$_3$): δ= 6.78-7.84 (m, 20H, Ar, =CH); 9.67 (s, 1H, -CHO). MS: m/z = 376 (100 %, (M+H)$^+$). IR (in cm^{-1}): ν(C-H in Ar) 3067, 3055, 3026, ν(C=O) 1699, ν(C=C) 1588, 1489, 1442, 1390, 1343, (C-N) 1261, 1156, 1111, γ(Ar) 871, 755, 694.

(2,2-Diphenylvinyl)-(4-hydroxyphenyl)phenylamine (**14**). 2.35 g (0.006 mol) of (2,2-diphenylvinyl)-(4-formylphenyl)phenylamine (**13**) were dissolved in 100 ml of methanol, and 0.3 g (0.008 mol) of sodium borohydride was added to the solution. After refluxing for 1 h, 50 ml of 10% NaOH solution was added to the mixture, and product was extracted with ether. Purification of the product was achieved through column chromatography using an eluent mixture of ethyl acetate and hexane in a volume ratio of 4:1. The yield was 81 % (1.91 g of brown amorphous material). ^{1}H NMR (250 MHz, CDCl$_3$): δ= 1.61 (s, 1H, OH); 4.53 (s, 2H, -$\underline{\mathrm{CH_2}}$OH); 6.75-7.37 (m, 20H, Ar, =CH). MS: m/z = 378 (45 %, $(M+H)^+$), 360. IR (in cm^{-1}): ν(OH) 3340, ν(C-H in Ar) 3054, 3024, ν(C-H) 2927, 2862, ν(C=C) 1590, 1508, 1419, (C-N) 1262, 1107, γ(Ar) 861, 758, 694.

(2,2-Diphenylvinyl)-[4-(3-methyl-3-oxetanylmethoxy)phenyl]phenylamine (**15**). To a three-neck flask equipped with a magnetic stirrer and a condenser 100 ml of ethyl methyl ketone, 0.75 g (0.002 mol) of hydroxyl compound **14,** 0.49 g (0.003 mol) of 3-(bromomethyl)-3-methyl oxetane, 0.34g (0.006 mol) of KOH and 0.26 g (0.002 mol) of K_2CO_3 were added and refluxed for 24 h. After filtration and evaporation of the solvent, the crude product **15** was purified by silica gel column chromatography using an eluent mixture of ethyl acetate and hexane in a volume ratio of 1:4. The yield was 33 % (0.3 g), mp 96 °C. ^{1}H NMR (250 MHz, CDCl$_3$): δ= 1.36 (s, 3H, CH$_3$); 3.46 (s, 2H, Ar-$\underline{\mathrm{CH_2}}$-O); 4.41 (d, J=4.75 Hz, 2H, -C-$\underline{\mathrm{CH_2}}$-O); 4.55 (d, J= 4.95 Hz, 2H, -C-$\underline{\mathrm{CH_2}}$-O); 4.47 (s, 2H, O-$\underline{\mathrm{CH_2}}$-C); 6.75-7.3 (m, 20H, Ar, =CH). MS: m/z = 462 (43 %, $(M+H)^+$), 360. IR (in cm^{-1}): ν(C-H in Ar) 3056, 3027, ν(C-H) 2961, 2930, 2867, ν(C=C) 1591, 1509, (C-N) 1264, ν (C-O-C) 1092, (cyclic ether) 980, γ(Ar) 863, 759, 696.

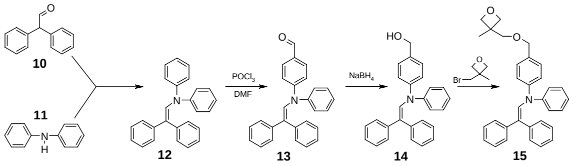
3. Results and discussion

The synthetic route to oxetanyl-functionalized aromatic hydrazones (**7**-**9**) is illustrated in Scheme 1. The key starting aromatic aldehydes (**3** and **4**) were synthesized by Vilsmeier formylation [xxiii] of triphenylamine (**1**) or 9-ethylcarbazole (**2**), respectively. The second step was condensation of the dialdehydes with N-phenylhidrazine to afford aromatic hydrazones (**5** and **6**), which were converted to oxetanyl-functionalized derivatives (**7** and **8**) using 3-(bromomethyl)-3-methyl oxetane under basic conditions. Cross-linkable bis-functionalized derivative (**9**) was prepared from 4,4′-diformyltriphenylamine using the same procedures as described for mono functionalized compound **7**.



Scheme 1

(2,2-Diphenylvinyl)diphenylamine based compound with polymerizeable oxetane moiety (**15**) was synthesized by multi-step procedure as described in Scheme 2. Reaction of diphenylacetaldehyde (**10**) with diphenylamine (**11**) under acidic conditions afforded an aromatic enamine **12**, which was converted to corresponding aldehide **13** by Vilsmeier formylation [xxiii]. Hydroxyl group having compound (**14**) was synthesised by reduction of the aldehide **13** with sodium borohydride. Reaction of the latter derivate **14** with an excess of 3-(bromomethyl)-3-methyl oxetane under basic conditions afforded the oxetanyl-functionalized aromatic enamine **15**.



Scheme 2

All the newly synthesized compounds were identified by mass spectrometry, IR and ^{1}H NMR spectroscopy. The data were found to be in good agreement with the proposed structures. All the oxetanyl-functionalized compounds (**7** – **9** and **15**) were soluble in common organic solvents, such as tetrachloroethane, chloroform, THF and acetone at room temperature.

The behaviour under heating of the new materials (**7** – **9** and **15**) was studied by TGA and DSC under a nitrogen atmosphere. All the derivatives demonstrate sufficient thermal stability for their application in optoelectronic devices. The mass loss occurs at the temperatures in the range from 253 to 290 °C, as confirmed by TGA with a heating rate of 10° C/min. It should be mentioned that thermal stability of the compounds synthesized is slightly lower than that of earlier reported carbazole/triarylamine-based derivatives [xi]. The hydrazone or enamine moiety apparently degrades in the first stage, while aromatic amines demonstrate higher thermal stability.

Compounds **7** and **8** were obtained as polycrystals by crystallisation from solutions, however they readily formed glasses when the melt samples were cooled on standing in air or with liquid nitrogen. As an example, the DSC thermograms of **8** are shown in Fig. 1. When the crystalline sample was heated, the endothermic peak due to melting was observed at 112 °C. When the melt sample was cooled down and heated again, the glass-transition phenomenon was observed at 25 °C and on further heating no peaks due to crystallisation and melting appeared. The crystalline sample of compound **7** demonstrates the similar behaviour. It melts on first heating at 124 °C and forms a glass (T_g = 33 °C) upon cooling.

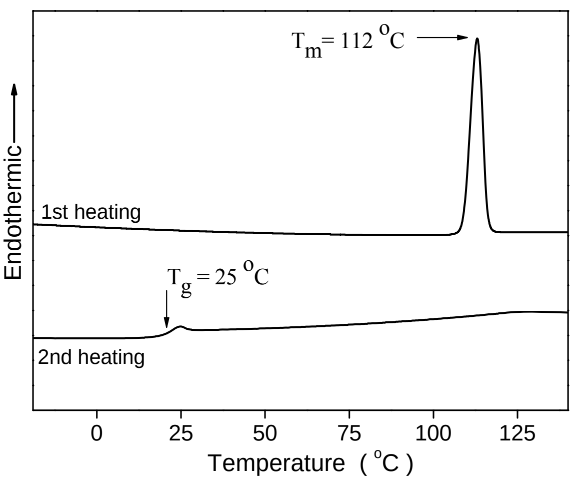
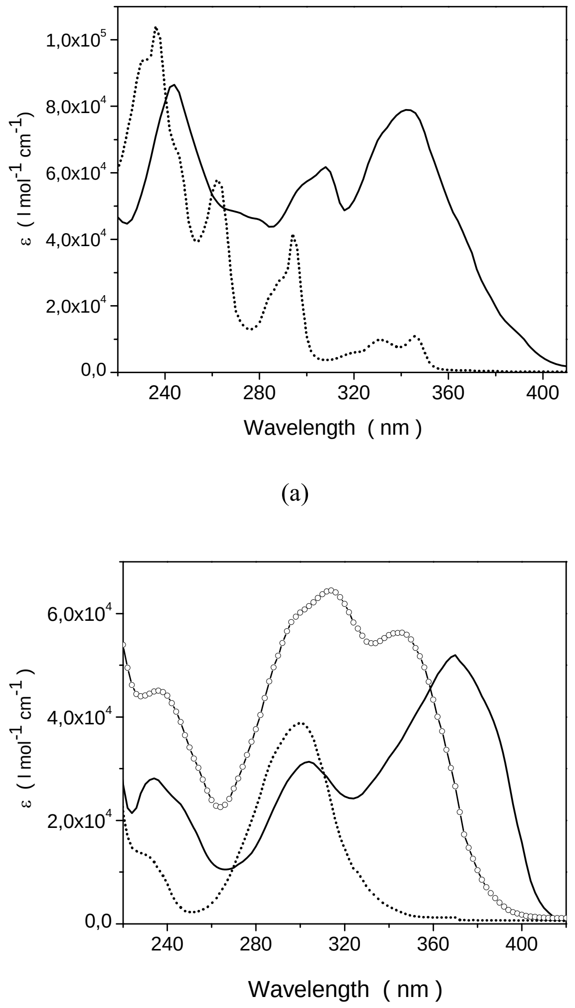


Fig. 1. DSC curves of the material 8. Heating rate: 10 °C/min.

The derivatives **9** and **15** were obtained as viscous amorphous materials after purification by column chromatography. All the attempts to crystallise the compounds in different solvents failed. The materials with functional groups and low T_gs have some advantages. They can be (photo)polymerized or cross-linked directly in thin films at rather low temperatures without using organic solvents. The method is useful for protecting charge transporting organic films against solvents [xvi,xvii] UV absorption spectra of dilute solutions of the compounds synthesized were recorded. The selected data are presented in Fig. 2. For the comparison the corresponding spectrum of 9-ethylcarbazole (EtCz) as well as triphenylamine are given. The electronic absorbtion energies of the synthesized compounds are rather close, and the λ_{max} values are in the range of 220- 400 nm.

Comparison of the UV absorption spectra of the carbazole based hydrazone (**7**) with that of EtCz (Figure 2a) shows that the spectra of compounds synthesized exhibit considerable bathochromic shift with respect of the spectrum of EtCz. In the UV spectra of **7** B and R bands are submerged by the bathochromically and hyperchromically shifted K bands attributed to $\pi \rightarrow \pi^*$ transitions [xxv]. Comparison of the corresponding spectrum of triphenylamine based derivatives **8** and **15** with that of triphenylamine (Fig. 2b) demonstrate the similar phenomenon. This observation shows that the new molecules are conjugated through the aromatic units and the lone electron pairs at the nitrogen atoms and that π-electrons are de-localised over these molecules. In the same manner with the red shift of UV absorption, which is interpreted as the extended conjugation, stabilizing the oxidized state of the compounds, they are expected to demonstrate lower values of ionization potentials (I_p) than compounds containing unsubstituted carbazole or triphenylamine moieties.



(a)

(b)

Fig. 2. UV absorption spectra of dilute THF solutions of (a) 5 (—) and EtCz (---), and of (b) 8 (—), 15 (-○-) and triphenylamine (---).

The photoemission spectra of compounds **7**-**8** and **15** are presented in Fig. 3. For the comparison the spectrum of poly(vinylcarbazole) (PVK) containing unsubstituted carbazole rings as chromophores is shown. The values of I_p in eV are 5.45 for **7**, ca. 5.5 for **8** and 5.61 for **15**. As it could be expected, the values of I_p of the newly synthesized aromatic hydrazones (**7**-**9**) are lower than those of the derivatives having unsubstituted triphenylamine [xxvi] or carbazolyl groups (cf. photoemission spectrum of PVC in Fig. 3). I_p of the material **15** is close to that of unsubstituted triphenylamine. This observation is can be explained by the similar electronic absorption energies of **15** and of triphenylamine. (Fig. 2b).

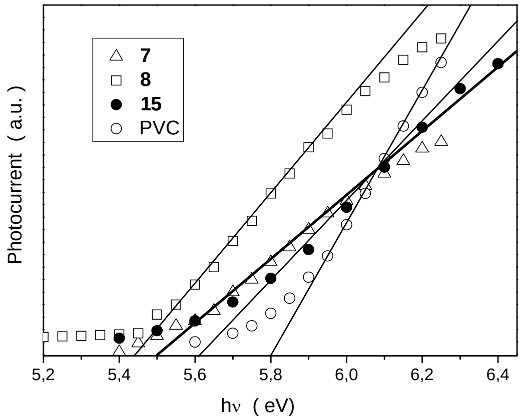


Fig. 3. The electron photoemission spectrum of the new materials and PVK.

Positive charges would be easily injected into the layers of the compounds synthesized from a conductive anode or charge generation layer with a work function or I_p close to 5.45-5.6 eV. It should be mention that the I_p values for widely used in electrophotography charge generation materials, such as titanyl phthalocyanines [xxvii,xxviii], perylene pigments [xxix] and bisazo pigments [xxx] are in the range of 5.1-5.6 eV.

The selected compounds (**8**, **12** and **15)** having the best solubility in PC-Z solutions were used for preliminary charge carrier mobility studies. Time of flight measurements were applied to characterise the magnitude of the hole drift mobility (μ_h) for the materials molecularly dispersed in the latter polymer host (Fig. 4).

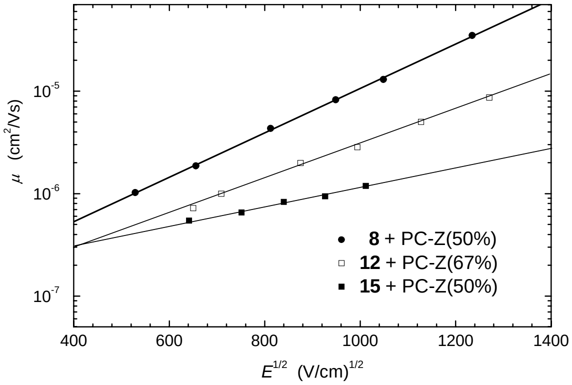


Fig. 4. The electric field dependencies of the hole drift mobility in charge transport layers of the materials 8, 12 and 15 molecularly dispersed in PC-Z.

The room temperature hole mobilities show linear dependencies on the square root of the electric field for the solid solutions in PC-Z of all the materials studied. Such characteristic dependencies are observed for the majority of non-crystalline organic systems and can be attributed to the effects of disorder on charge transport [i]. The compositions with aromatic hydrazone **8** demonstrated the highest μ_h values exceeding 10^{-5} cm^2/Vs at high electric fields at room temperature. The charge mobility values for the solid solution of the same concentration of aromatic enamine **15** were by ca. one order of magnitude lower. The different charge transporting properties could be determined by the conjugation length and ionisation potential. For the comparison μ_h of an intermediate material **12** was studied. The material forms amorphous layers only when higher ratio (1:3) of the polymeric host is used. The composition with **12** demonstrates still better charge transport properties than those of similar oxetanyl-functionalized derivative **15**, apparently due to higher concentration of electrophores or more favourable distribution of the molecules in the polymer host.

In conclusion, we have synthesized various oxetanyl-functionalized aromatic hydrazones and enamine, which exhibit sufficient thermal stability and form amorphous films with low glass transition temperatures. The values of ionisation potentials of the materials and hole drift mobility studies showed that these compounds are potential materials for the application in electrophotographic photoreceptors. The synthesis and properties of polymers prepared from the newly synthesized monomers will be included in a future publication.

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