Supporting information

"Click-chemistry" inspired synthesis of hydrazone-based molecular glasses

Artiom Magomedov^a, Simona. Urnikaite^a, Osvaldas Paliulis^a, Vygintas Jankauskas^b and Vytautas Getautis^{*, a}

^aDepartment of Organic Chemistry, Kaunas University of Technology, Radvilėnų st. 19, Kaunas 50254, Lithuania ^bDepartment of Solid State Electronics, Vilnius University, Saulėtekio st. 9, Vilnius 10222, Lithuania

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General information (materials and methods)

Chemicals were purchased from Sigma-Aldrich and TCI Europe and used as received without 4-(diethylamino)benzaldehyde N-phenylhydrazone (Ha) and further purification. 4-(4methyldiphenylamino)benzaldehyde N-phenylhydrazone (**Hb**) were synthesized according to an earlier reported procedure^{1,2}. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) with ALUGRAM SIL G/UV254 plates and developed with I₂ or UV light. Silica gel (grade 9385, 230-400 mesh, 60 Å, Aldrich) was used for column chromatography. ¹H NMR (300 or 700 MHz field strength) spectra and ¹³C NMR (75 or 176 MHz field strength) were recorded with a Varian Unity Inova or Bruker Avance III 700. The chemical shifts, expressed in ppm, are reported relative to tetramethylsilane (TMS). UV-Vis spectra were recorded on Perkin Elmer Lambda 35 UV/Vis spectrometer. Melting points were determined for the crystalline materials on an electrothermal MEL-TEMP capillary melting point apparatus and are uncorrected. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyzer, Model 440 C/H/N/. Differential scanning calorimetry (DSC) was performed on a Q10 calorimeter (TA Instruments) at a scan rate of 10 K min⁻¹ in the nitrogen atmosphere. The glass transition temperatures for the investigated compounds were determined during the second heating scan.

Ionization potential measurements

The solid state ionization potential (I_p) of the layers of the synthesized compounds was measured by the electron photoemission in air method^{3,4,5}. The samples for the ionization potential measurement were prepared by dissolving materials in CHCl₃ and were coated on Al plates precoated with ~0.5 µm thick methylmethacrylate and methacrylic acid copolymer adhesive layer. The thickness of the transporting material layer was 0.5-1 µm. Usually photoemission experiments are carried out in vacuum and high vacuum is one of the main requirements for these measurements. If vacuum is not high enough the sample surface oxidation and gas adsorption are influencing the measurement results. In our case, however, the organic materials investigated are stable enough to oxygen and the measurements may be carried out in the air. The samples were illuminated with monochromatic light from the quartz monochromator with deuterium lamp. The power of the incident light beam was $(2-5)\cdot 10^{-8}$ W. The negative voltage of -300 V was supplied to the sample substrate. The counter-electrode 3 with the 4.5×15 mm² slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of the BK2-16 type electrometer, working in the open input regime, for the photocurrent measurement. The $10^{-15} - 10^{-12}$ A strong photocurrent was flowing in the circuit under illumination. The photocurrent *I* is strongly dependent on the incident light photon energy hv. The $I^{0.5} = f(hv)$ dependence was plotted. Usually the dependence of the photocurrent on incident light quanta energy is well described by linear relationship between $I^{0.5}$ and hv near the threshold^{4,5}. The linear part of this dependence was extrapolated to the hv axis and I_p value was determined as the photon energy at the interception point.

Hole drift mobility measurements

The samples for the hole mobility measurements were prepared by spin-coating the solutions of the synthesized compounds on the polyester films with conductive Al layer. The layer thickness was in the range of 5-10 μ m. The hole drift mobility was measured by xerographic time of flight

technique (XTOF)^{6,7,8}. Electric field was created by positive corona charging. The charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 2 ns, wavelength 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1-5 % of initial potential before illumination. The capacitance probe that was connected to the wide frequency band electrometer measured the speed of the surface potential decrease dU/dt. The transit time t_t was determined by the kink on the curve of the dU/dt transient in double logarithmic scale. The drift mobility was calculated by the formula $\mu = d^2/U_0 t_t$, where *d* is the layer thickness, U_0 – the surface potential at the moment of illumination.

Synthesis of dihydrazones 2Ha and 2Hb

General procedure:

To a solution of 1,3-bis(bromomethyl)benzene (1 eq.) in acetone (12ml/mmol) 2.5 eq of <u>HYDRAZONE</u> was added. The mixture was stirred at reflux for 1 h, followed by addition of 5.8 eq. powdered KOH. Completeness of the reaction was controlled by <u>TLC</u>. Product purification <u>PROCEDURE</u> is specified in more details for each compound.

2Ha: *1,3-bis*{*1-phenyl-2-[4-(diethylamino)benziliden]hydrazinmethyl}benzene*



HYDRAZONE: 4-(diethylamino)benzaldehyde N-phenylhydrazone (2 g 7.5 mmol)

TLC: acetone:n-hexane:diethyl ether, 4:19:2 v:v:v

<u>PROCEDURE</u>: the reaction mixture was treated with ethyl acetate and washed with distilled H_2O . The organic layer was dried over anhydrous Na_2SO_4 , filtered and the solvents were removed. Obtained solid was washed with 2-propanole.

The yield was 1.14 g (79 %); m.p. 167°C (recrystallized from THF:2-propanole 1:2 v:v)

¹H NMR (300 MHz, CDCl₃) δ 7.49 – 7.06 (m, 18H), 6.92 – 6.84 (m, 2H), 6.62 (d, *J* = 8.9 Hz, 4H), 5.08 (s, 4H), 3.35 (q, *J* = 7.0 Hz, 8H), 1.15 (t, *J* = 7.0 Hz, 12H).

¹³C NMR (75 MHz, CDCl₃) δ 148.28, 147.81, 137.38, 133.99, 129.69, 129.19, 127.77, 125.11, 123.99, 123.94, 119.87, 114.38, 111.66, 50.40, 44.54, 12.75.

Anal. calcd for C₄₂H₄₈N₆: C, 79.21; H, 7.60; N,13.20; found: C, 79.02; H, 7.67; N, 13.14.



<u>HYDRAZONE</u>: 4-(4-methyldiphenylamino)benzaldehyde N-phenylhydrazone (2.5g 6.6mmol)

<u>TLC</u>: acetone:*n*-hexane; 5:20 v:v

<u>PROCEDURE</u>: obtained solid was filtered and washed with water (until neutral reaction) and 2-propanole.

Yield - 1.73 g (78 %); m.p. 134-135 °C (recrystallized from toluene:acetone, 1:1 v:v).

¹H NMR (700 MHz, CDCl₃) δ 7.46 – 6.86 (m, 42H), 5.11 (s, 4H), 2.30 (s, 6H).

¹³C NMR (176 MHz, CDCl₃) δ 147.86, 147.84, 147.63, 144.88, 136.87, 133.02, 132.51, 130.24, 129.96, 129.75, 129.16, 129.14, 127.00, 125.11, 125.05, 123.94, 123.81, 123.00, 122.60, 120.49, 114.63, 50.30, 20.83.

Anal. calcd for C₆₀H₅₂N₆: C, 84.08; H, 6.12; N, 9.81; found: C, 83.99; H, 6.09; N, 9.72 .

Synthesis of tetrahydrazones 4Ha and 4Hb

General procedure:

To a solution of 1,2,4,5-tetrakis(bromomethyl)benzene (1 eq.) in acetone (34ml/mmol) 4.5 eq of <u>HYDRAZONE</u> was added. The mixture was stirred at reflux for 1.5 h, followed by addition of 10.4 eq. powdered KOH. Completeness of the reaction was controlled by <u>TLC</u>. Product purification <u>PROCEDURE</u> is specified in more details after each compound.

4Ha: *1,2,4,5-tetrakis*{*1-phenyl-2-*[*4-(diethylamino)benziliden*]*hidrazinmethyl*}*benzene*



HYDRAZONE: 4-(diethylamino)benzaldehyde N-phenyl-hydrazone (3 g 11.2mmol)

TLC: acetone:n-hexane, 8:17 v:v

<u>PROCEDURE</u>: obtained solid was filtered and washed with water (until neutral reaction) and 2-propanole

The yield was 2.23g (75%); m.p. 141-142°C (recrystallized from toluene)

¹H NMR (300 MHz, CDCl₃) δ 7.33 – 7.09 (m, 28H), 6.97 (s, 2H), 6.87 – 6.75 (m, 4H), 6.57 (d, J = 8.8 Hz, 8H), 4.99 (s, 8H), 3.37 (q, J = 7.0 Hz, 16H), 1.17 (t, J = 7.0 Hz, 24H).

¹³C NMR (75 MHz, CDCl₃) δ 147.78, 147.75, 134.96, 133.05, 129.09, 127.99, 127.71, 124.02, 120.30, 115.62, 111.59, 49.17, 44.57, 12.81.

Anal. calcd for C₇₈H₉₀N₁₂: C, 78.35; H, 7.59; N, 14.06; found: C, 78.14; H, 7.73; N, 13.85.

4Hb: *1,2,4,5-tetrakis{1-phenyl-2-[4-(4-methyldiphenylamino)benziliden]hidrazinmethyl}benzene*



HYDRAZONE: 4-(4-methyldiphenylamino)benzaldehyde N-phenylhydrazone (3g 7.9mmol)

TLC: ethyl acetate:diethyl ether:*n*-hexane, 1:1:20 v:v:v

<u>PROCEDURE</u>: obtained solid was filtered and washed with water (until neutral reaction) and 2-propanole.

The yield was 2.16g (75%); m.p. 191-192°C (recrystallized from toluene:2-propanole, 3:1 v:v)

¹H NMR (300 MHz, DMSO) δ 7.28 – 6.68 (m, 78H), 5.11 (s, 8H), 2.28 (s, 12H).

¹³C NMR (75 MHz, DMSO) δ 146.91, 146.63, 144.15, 132.31, 131.62, 129.60, 129.50, 128.70, 128.47, 128.41, 127.71, 126.61, 124.81, 124.38, 123.14, 122.18, 122.14, 120.02, 114.78, 46.83, 20.31.

Anal. calcd for $C_{114}H_{98}N_{12}$: C, 83.69; H, 6.04; N, 10.27; found: C, 83.51; H, 6.15; N, 10.19.

Synthesis of trihydrazones 3Ha and 3Hb

General procedure:

To a solution of 2,4,6-tris(bromomethyl)mesitylene (1 eq.) in acetone (20ml/mmol) 3.5 eq of <u>HYDRAZONE</u> was added. The mixture was stirred at reflux for 1.5 h, followed by addition of 8 eq. powdered KOH. Completeness of the reaction was controlled by <u>TLC</u>. Product purification <u>PROCEDURE</u> is specified in more details after each compound.

3Ha: 2,4,6-tris{1-phenyl-2-[4-(diethylamino)benziliden]hidrazinmethyl}-1,3,5-trimethylbenzene



HYDRAZONE: 4-(diethylamino)benzaldehyde N-phenyl-hydrazone (2 g 7.5 mmol)

TLC: acetone:n-hexane, 5:20 v:v

<u>PROCEDURE</u>: the reaction mixture was treated with ethyl acetate and washed with distilled H₂O. The organic layer was dried over anhydrous Na₂SO₄, filtered and the solvents were removed. The residue was purified by column chromatography (eluent acetone:*n*-hexane, 3:22 v:v) with the following precipitation in a great excess of *n*-hexane. The yield was 1.75 g (85 %).

¹H NMR (300 MHz, CDCl₃) δ 7.41 – 7.34 (m, 9H), 7.20 – 7.13 (m, 6H), 7.05 – 6.92 (m, 9H), 6.57 (d, J = 9.0 Hz, 6H), 4.71 (s, 6H), 3.37 (s, J = 7.0 Hz, 12H), 2.25 (s, 9H), 1.17 – 1.09 (m, J = 7.0 Hz, 18H).

¹³C NMR (75 MHz, CDCl₃) δ 148.54, 148.03, 140.99, 137.50, 132.47, 128.83, 127.96, 123.69, 123.01, 121.91, 111.60, 52.73, 44.52, 16.68, 12.74.

Anal. calcd for C₆₃H₇₅N₉: C, 78.96; H, 7.89; N, 13.15; found: C, 78.88; H, 7.95; N, 13.09.

3Hb: 2,4,6-tris{1-phenyl-2-[4-(4-methyldiphenylamino)benziliden]hidrazinmethyl}-1,3,5-trimethylbenzene



HYDRAZONE: 4-(4-methyldiphenylamino)benzaldehyde N-phenylhydrazone (3g 7.9mmol)

TLC: ethyl acetate:diethyl ether:n-hexane, 1:1:20 v:v:v

<u>PROCEDURE</u>: the reaction mixture was treated with chloroform and washed with distilled H_2O . The organic layer was dried over anhydrous Na₂SO₄, filtered and the solvents were removed. The residue was purified by column chromatography (eluent toluene:n-hexane, 5:20 v:v) with the following precipitation in a great excess of *n*-hexane.

The yield was 2.26 g (77%).

¹H NMR (300 MHz, CDCl₃) δ 7.34 – 6.89 (m, 57H), 4.78 (s, 6H), 2.29 (s, 9H), 2.24 (s, 9H).

¹³C NMR (75 MHz, CDCl₃) δ 147.81, 147.76, 147.21, 145.06, 137.43, 136.00, 133.04, 132.35, 130.50, 130.06, 129.26, 129.04, 127.01, 125.15, 124.23, 124.00, 123.28, 123.14, 122.62, 52.97, 20.98, 16.81.

Anal. calcd for C₉₀H₈₁N₉: C, 83.88; H, 6.34; N, 9.78; found: C, 83.69; H, 6.26; N, 9.81.



Figure S2. ¹³C NMR spectrum of 2Ha.



Figure S4. ¹³C NMR spectrum of 2Hb.



Figure S6. ¹³C NMR spectrum of 4Ha.



Figure S7. ¹H NMR spectrum of 4Hb.



Figure S8. ¹³C NMR spectrum of **4Hb**.











Thermal properties of the synthesized compounds

Figure S13. DSC first heating/cooling and second heating curves of 2Ha, 2Hb, 3Hb and 4Hb

18-14 16 2Ha 12 2Hb 14 10 12 8 10 .0.5 1 .0.5 1 8 -6 6 4 4 2 2 · 0 0 -5.6 5.8 6.0 6.2 5.8 6.0 6.2 6.4 4.8 5.0 5.2 5.4 6.4 5.0 5.2 5.4 5.6 4.6 hv(eV) hv(eV)18-12 -16 3Ha 14 10 3Hb 12 -8 10 $l^{0.5}$ l.0.5 6 8 6 4 4 2 2 · . 0 -0. 4.8 5.2 5.4 5.6 5.8 6.0 6.2 6.4 5.2 5.4 5.6 5.8 6.0 6.2 6.4 4.6 5.0 5.0 hv(eV)hv(eV)٦ 16 10 14 4Ha • 4Hb 12 -8 10 6 8 .0.5 1 1 6-4 4 2 2

Photoemission in air spectra of the synthesized compounds

Figure S14. Photoemission in air spectra of the (2-4)H(a,b)

0 -

5.0

5.2

5.4

5.6

5.8

 $h\nu({\rm eV})$

6.0

6.2

6.4

0 -

4.6 4.8 5.0 5.2

5.4 5.6

hv(eV)

5.8

6.0 6.2

6.4

Proposed reaction mechanism



Figure S15. Proposed reaction mechanism for the synthesis of the twin molecules 2H(a,b)

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