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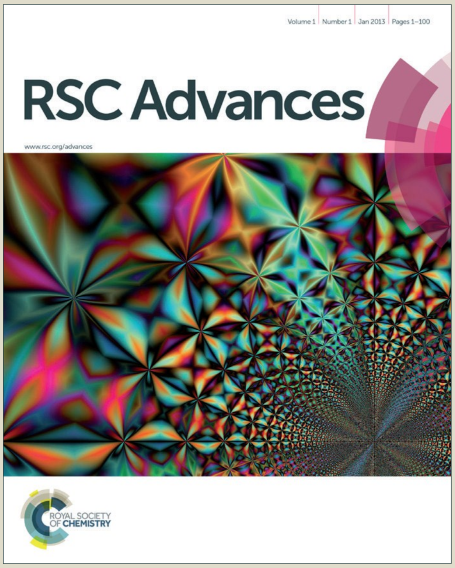

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COMMUNICATION

“Click-chemistry” inspired synthesis of hydrazone-based molecular glasses

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Fast and simple synthesis of hole transporting materials inspired by “click-chemistry” was performed. By employing hydrazone chromophores high hole drift mobility (up to 0.0013 cm^{2}V^{-1}s^{-1}) and controllable morphology was achieved.

Introduction

Materials with hydrazone (>C=N–N<) functional group are widely used in different areas, e.g., medicine[1,2], organic synthesis[3,4], and as molecular switches[5-8]. One of the important application fields for these molecules is hole transporting materials (HTM) in different electronic devices[9,10]. Suitable hole drift mobilities in a combination with a relatively simple synthesis makes them attractive for industrial uses. On the other hand, high crystallinity is often a limiting factor because of the poor long-term stability of amorphous HTM layers[11,12]. Therefore, materials dispersed in polymer binder[9] or attached to the polymer chain as a side group[13] are used. Inactive components reduce concentration of hydrazone moieties and consequently decrease overall performance[11]. That is why new material structures are needed. Usual strategies are synthesis of dendrimeric or branched structures. These methods afford better photophysical and morphological properties. However, they have two main disadvantages: complicated synthesis process with low yields[14] and high environmental impact[15,16].

In the beginning of the 21st century, novel trend appeared in the synthetic chemistry called “click chemistry”[17]. The main idea is to adopt simple reactions for fast and versatile search of novel materials. To match this approach a reaction should be modular, result in very high yields, generate non-toxic by-products, reaction conditions and product isolation have to be simple[18].

Over the years, a huge amount of aromatic and heteroaromatic hydrazones have been synthesized. Triphenylamine[11], carbazole[19,20], phenothiazine[21,22] etc. can be easily functionalized with hydrazone group. If phenylhydrazine is used for the synthesis, the resulting product has an active hydrogen atom attached to the nitrogen[23]. It gives a great variety of readily available starting materials for further structure modification.

In this communication, we report on the “click-chemistry” inspired synthesis of the novel photoconductive molecular glasses with varying number of hydrazone sidearms. These hole transporting organic semiconductors are obtained in one step synthesis procedure, can be solution processed, handled in air, require no high temperature annealing steps, and possess comparatively high charge drift mobility (up to 0.0013 cm^{2}V^{-1}s^{-1}). To achieve hole-transporting properties two well-known and routinely employed chromophores were used: N,N-diethylaniline[24] and 4-methyltriphenylamine[24,25].

Results and discussion

The detailed procedures for the synthesis of the products are described in the ESI.

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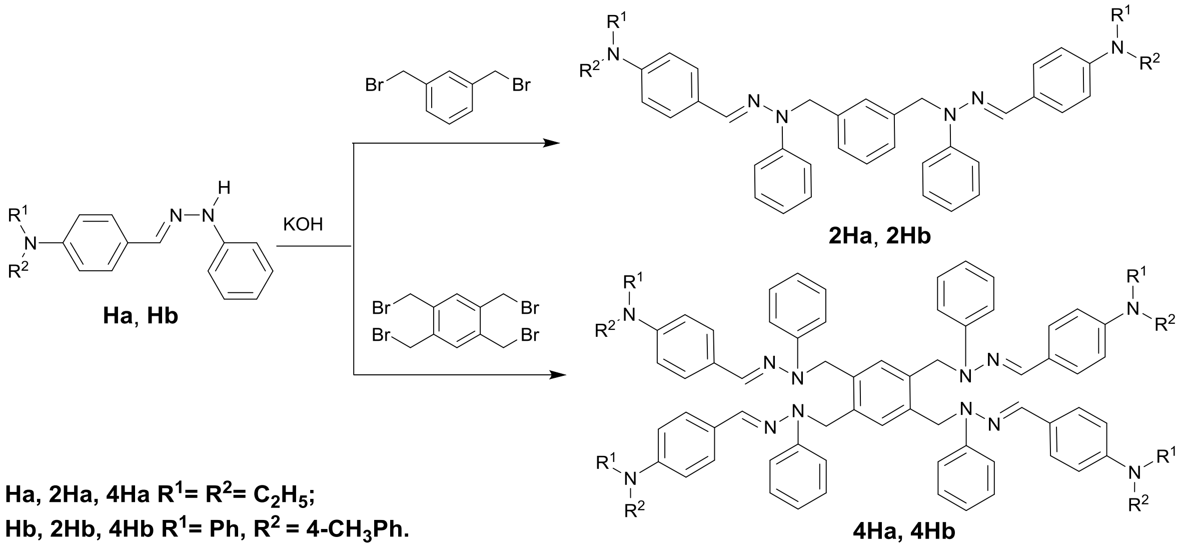
† Electronic Supplementary Information (ESI) available: Synthesis details and characterization data, ^{1}H and ^{13}C NMR spectra, DSC profiles, I_p, mobilities plots. See DOI: 10.1039/x0xx00000x



Scheme 1 Synthesis of molecular glasses **2Ha**, **2Hb**, **4Ha**, and **4Hb** with two or four hydrazone sidearms

Briefly, N-phenyl hydrazones **Ha** and **Hb** were deprotonated of the N-H bond with KOH in acetone (Scheme 1, Figure S15). Thus formed anions immediately reacted with appropriate halogen compound (1,3-bis(bromomethyl)benzene or 1,2,4,5-tetrakis(bromomethyl)benzene) in a nucleophilic substitution to give twin molecules **2Ha** and **2Hb**, or tetramers **4Ha** and **4Hb**, possessing photoconductive hydrazone moieties. Starting precursors **Ha** and **Hb** were freshly prepared by a simple reaction of corresponding aromatic aldehyde with phenylhydrazine[15] and were directly used for the subsequent synthesis just after filtration and washing with hexane. In all cases, the processes proceeded rapidly and the twins **2Ha**, **2Hb**, as well as the tetrahydrazones **4Ha**, **4Hb** crystallized during the reaction. The products were purified by non-chromatographic methods with yields in the range of 75-85% what is a good value for high molecular weight molecules. All compounds were characterized by ^{1}H NMR, ^{13}C NMR and elemental analysis. (For more details see ESI).

The formation of the glassy state in the hydrazone-based molecules was confirmed by differential scanning calorimetry (DSC) (Figure 1; Figure S13). The melting points (T_m) and glass transition temperatures (T_g) of the synthesized derivatives are presented in Table 1. These investigations had revealed, that during the first heating cycle the twins **2Ha**, **2Hb**, as well as compounds with four hydrazone sidearms (**4Ha**, **4Hb**) showed melting process. Furthermore, at the first heating the tetrahydrazone **4Ha** revealed several endothermic peaks, corresponding to four eutectic melting points at 141ºC, 222ºC, 231ºC, and 240ºC. Thus, tetrahydrazone with diethylamino groups is distinguished by polymorphism with the predominant second crystalline phase at 222ºC. No crystallization took place during cooling or second heating scans, only glass transition was observed (Table 1, Figure 1a). T_g values increased while going from twin molecules to tetrahydrazones (14ºC for **2Ha** to **4Ha**, 7ºC for **2Hb** to **4Hb**) and when replacing the diethyl aniline chromophore by 4-methyltriphenylamine (~30ºC).

Table 1. Thermal properties of (**2-4**)**H**(**a**,**b**)

Compound	T_m[a], ºC	T_g[b], ºC
2Ha	171	61
2Hb	131	97
3Ha	-	63
3Hb	-	72
4Ha	144, 222, 231, 240[c]	75
4Hb	186	104

[a] Determined by DSC: scan rate=10°C•min^{-1}; only during the first heating.

[b] Determined by DSC: scan rate=10°C•min^{-1}; second heating.

[c] Several endothermic peaks were observed during the first heating.

In general, the organic compounds employed for application in optoelectronics should ideally be amorphous, exhibit high glass transition and thermal decomposition temperatures (T_{dec})[12,26]. The DSC investigation results presented above have revealed that the obtained hydrazone-based molecules **2Ha**, **2Hb** and **4Ha**, **4Hb** can exist both in crystalline and amorphous state.

We next set out to test the viability of our synthesis strategy on the related completely amorphous photoconductors. 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene was chosen as a connecting fragment of the hydrazone branches (Scheme 2). The presence of aliphatic groups and ability to form three sidearms should prevent easy packing of resultant molecules

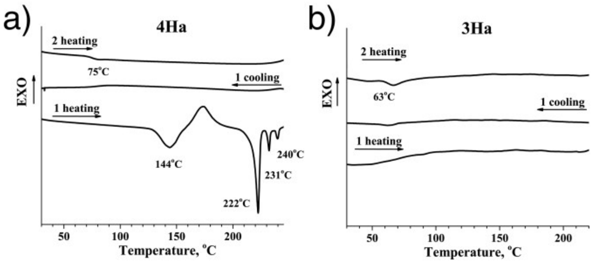
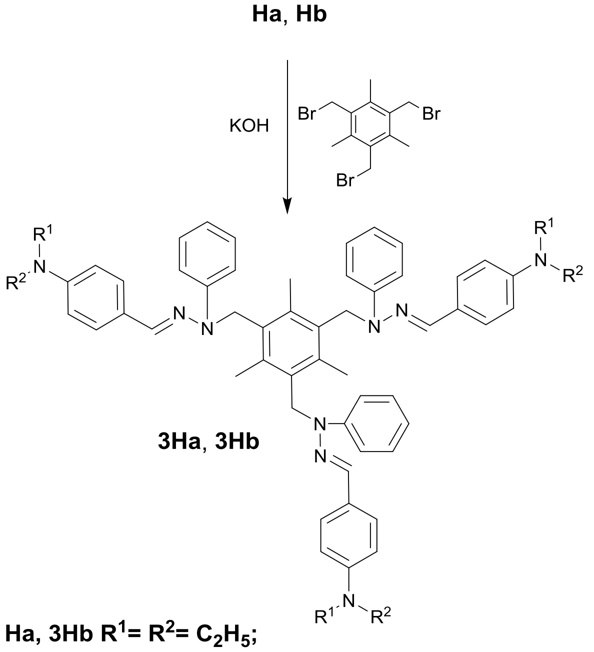


Figure 1. DSC first heating/cooling and second heating curves of: a) **4Ha**; b) **3Ha** (heating rate 10 °C•min^{-1})

and hence hinder crystallization. The target products **3Ha** and **3Hb** were obtained rapidly and in high yields from **Ha** and **Hb** under reaction conditions mentioned above.



Ha, 3Hb $R^1 = R^2 = C_2H_5$;

Ha, 3Hb R^1= Ph, R^2 = 4-CH_3Ph.

Scheme 2. Synthesis of molecular glasses **3Ha** and **3Hb** with three hydrazone sidearms

The hydrazone trimers **3Ha** and **3Hb** were isolated by column chromatography with the subsequent precipitation in a great excess of *n*-hexane. **3Ha** and **3Hb** isolated by such a procedure are amorphocus compounds. All our attempts to crystallize them were unsuccessful. The DSC investigations had revealed that **3Ha** and **3Hb** were found only in amorphous state (Table 1, Figure 1b, Figure S13). Moreover, X-ray diffraction patterns of these compounds show only broad halos.

Since π-electrons are very important for the charge transporting process in the structures of photoconductors, the absorption spectra of compounds with different chromophores **Ha** and **Hb** were recorded and are presented in Figure 2a. The bathochromic shift of the absorption of **2Hb** and **4Hb**, compared to that of **2Ha** and **4Ha**, respectively, is attributed to the extension of the π-conjugated system of chromophore **Hb** compared to **Ha**. The comparison of UV spectra of compounds with two (**2Ha**), three (**3Ha**), and four (**4Ha**) hydrazone sidearms had shown that increasing number of chromophores led to a noticeable hyperchromic shift (Figure 2b). It is in a good agreement with the structure of the investigated compounds. The spectrum of twin hydrazone **2Ha** is very similar to the sum of the spectra of the separate components (**Ha** and 1,3-bis(bromomethyl)benzene), what indicates that there is no interaction at the ground state between the hydrazone and the central core of the molecule (Figure 2c).

When considering the use of an organic material for hole-transport applications it is important to have an understanding of its solid state ionization energies (I_p). This understanding can help in identifying suitable partner for organic transport materials and inorganic electrode materials. The ionization potential was measured by photoelectron spectroscopy in air (PESA) method[27] and the results are presented in Table 2 and Figure S14. The measurement error is evaluated as 0.03 eV. Values are almost the same in a series of the compounds with the same hydrazone chromophore and differ for the ones with different hydrazone chromophore (5.0-5.02 eV for **2Ha**, **3Ha**, and **4Ha**; 5.33-5.35 eV for **2Hb**, **3Hb**, and **4Hb**).

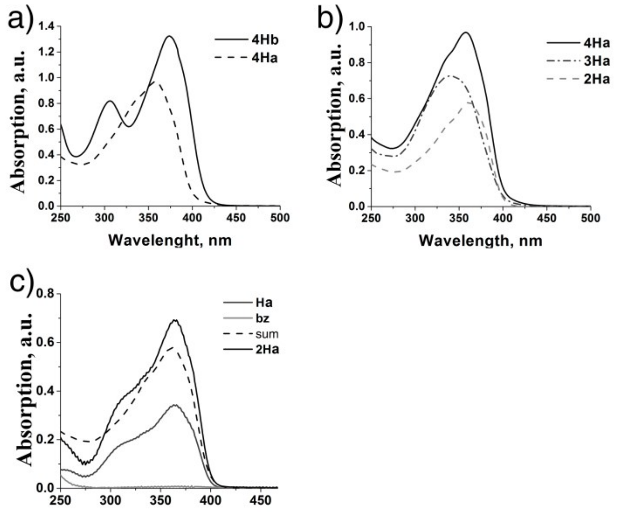


Figure 2. UV/Vis spectra of: a) **4Ha** and **4Hb**; b) **2Ha**, **3Ha** and **4Ha** c) separate fragments **Ha** and **bz** (1,3-bis(bromomethyl)-benzene), **2Ha** and calculated sum of the fragment spectra (**sum** = **bz**+2x**Ha**).

Table 2. I_p and and hole mobility data for (**2-4**)**H**(**a,b**).

Compound	I_p[a], eV	μ_0[b], (cm^2/V•s)	μ[c], (cm^2/V•s)	α, (cm/V)$^{1/2}$
2Ha	5.02	$3x10^{-7}$	$8x10^{-5}$	0.0069
2Hb	5.35	$7.4x10^{-5}$	$1.3x10^{-3}$	0.0036
3Ha	5.00	$3.5x10^{-8}$	$2.2x10^{-5}$	0.0081
3Hb	5.33	$4.6x10^{-6}$	$2.0x10^{-4}$	0.0047
4Ha[d]	5.00	-	$\sim 1x10^{-5}$	-
4Hb[d]	5.35	-	$\sim 6.7x10^{-4}$	-

[a] Ionization potential was measured by the photoemission-in-air method from films

[b] Mobility value at zero field strength

[c] Mobility value at 6.4×10^5 V•cm^{-1} field strength

[d] Due to the high dispersity the mobilities were measured only at the strong electrical fields

Charge transport properties of the synthesized hydrazone-based molecular glasses were studied by the xerographic time-of-flight (XTOF) technique[28] (Figure 3). The values of charge mobility defining parameters: zero field mobility (μ_0), Poole–Frenkel parameter (α), and the mobility at the electric field of 6.4×10^5 V•cm^{-1} for the compounds with a varying number of hydrazone sidearms **2H**, **3H**, and **4H** are given in the Table 2. As expected, the room temperature hole-drift mobility of compounds with 4-methyltriphenylamine chromophore was by ca. one order of magnitude higher than that of the corresponding 4-diethylaniline-based compounds. This is in good agreement with the data for the photoconductors possessing these hydrazone chromophores[24]. The highest hole-drift mobility in amorphous films of **2Hb** exceeds 10^{-3} cm^2/V•s at an electric field of 10^5 V•cm^{-1}. This is a really high mobility for amorphous photoconductor.

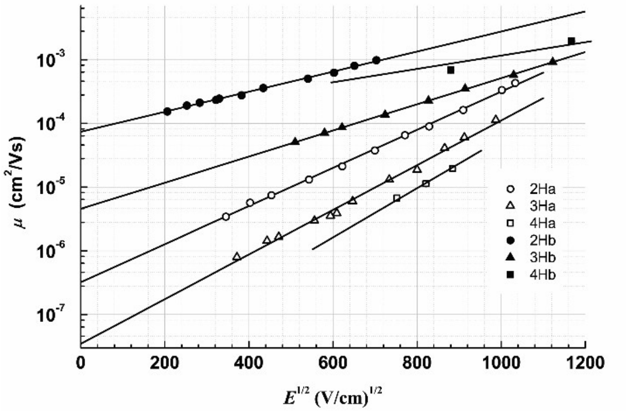


Figure 3. Electric-field dependencies of the hole drift mobilities (μ) in charge-transport layers of (**2-4**)**H**(**a**,**b**).

Conclusions

We have demonstrated "click chemistry" inspired synthesis method to obtain photoconductive molecular glasses with a varying number of hydrazone sidearms from well-known and relatively inexpensive precursors. The morphology and photoconductive properties could be easy controlled and we strongly believe that numerous promising photoconductors could be easily constructed by following the proposed synthesis protocol.

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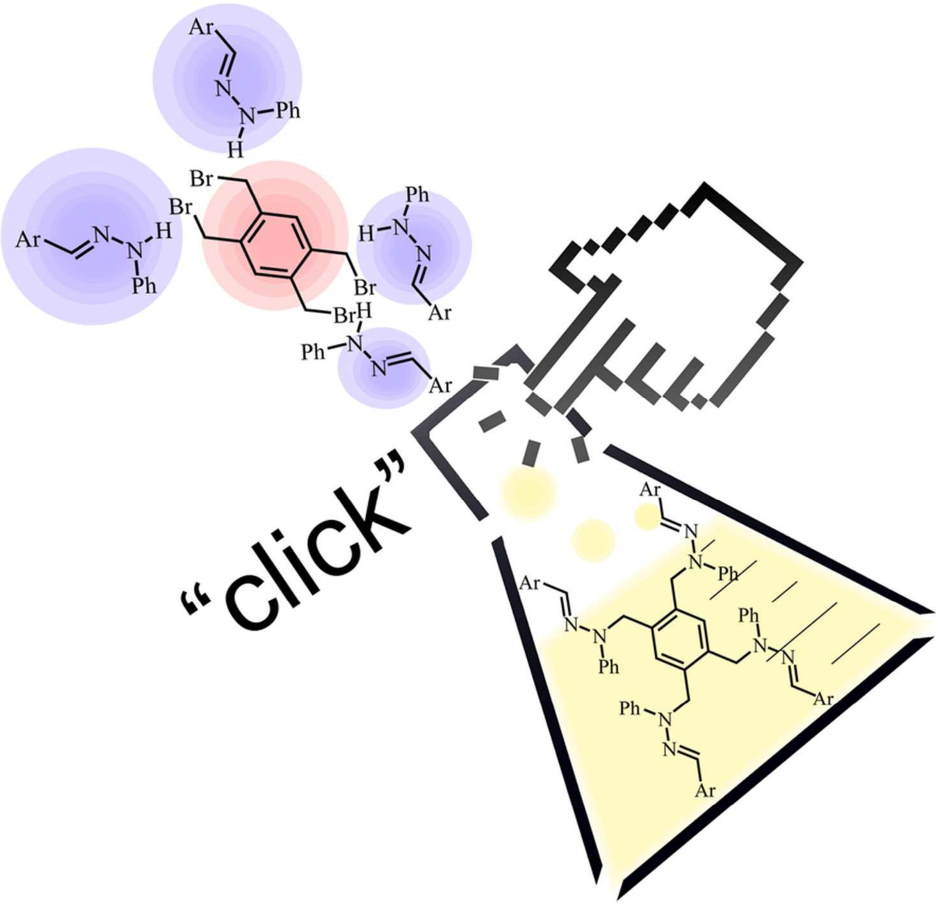

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