

Versatile Synthesis of Small NLO-Active Molecules Forming Amorphous Materials with Spontaneous Second-Order NLO Response

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Low-molecular-weight organic glasses have gained an increasing interest in optoelectronics during the last 5 years.¹ Compared to polymers, they offer well-defined molecular structure, ensuring reproducible properties as well as reduced time aging. Such materials have been involved in electroluminescent devices,² photorefractivity,³ and holographic data storage⁴ where triarylamino derivatives play an essential role due to their remarkable electron-donor capability. On the contrary, very few papers deal with second-order nonlinear optically (NLO) active materials based on small organic molecules giving efficient and orientationally stable non-centrosymmetric materials for electrooptic modulators and frequency converters applications.⁵ We report in this contribution a versatile synthesis of push-pull compounds comprising a bulky electron-donating triarylamino group linked to varied electron-withdrawing groups. Moreover, to the best of our knowledge, these molecules are the first example of compounds forming amorphous materials with spontaneous NLO activity without requiring any external poling process.

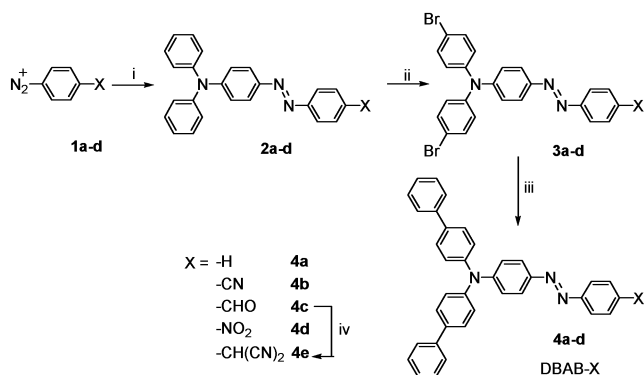
Classical synthesis of substituted triarylamines involves phase-transfer Ullman or Hartwig coupling conditions which require aromatic halides and electron-rich amino compounds.^{6,7} This limitation prohibited us from using aminoazobenzene derivatives while synthesis of bromo- or iodoazobenzene substituted by an electron-deficient group encounters low-yield reactions. We adopted the following three-step synthetic pathway which permitted varying the nature of the electron-withdrawing group and the introduction of the bulky substituents at the very final stage; hence, compounds with various thermal properties can be synthesized (Scheme 1).

The corresponding freshly prepared 4-substituted phenyldiazonium salt⁸ was reacted with 1 equiv of triphenylamine under phase-transfer conditions at room temperature over 1 day to afford the azobenzene derivative **2**.⁹

Bromination of **2** by 2 equiv of *N*-bromosuccinimide in refluxing CHCl₃ for 4 h gave the sole dibromo compound **3**. Subsequent Suzuki cross-coupling between 2 equiv of phenylboronic acid and **3** was carried out in toluene overnight in the presence of a 1 mol·L⁻¹ Na₂CO₃ aqueous solution and Pd(Ph₃)₄ as catalyst, and yielded DBAB-X **4** in 50–70% yield. Compared to the initial synthesis of DBAB-H (4-[di(biphenyl-4-yl)amino]azobenzene)^{4b} following an Ullman phase-transfer coupling at 190 °C, this mild three-step sequence avoids deleterious high temperatures and can be extended to less chemically inert electron-accepting groups.

Thermal analyses were carried out at a 20 °C·min⁻¹ scan rate under a nitrogen flow and involved two heating cycles from 25 to 300 °C (Table 1). For all of the compounds **4a–e**, the first temperature sweep showed a sharp endothermic peak featuring product melting (*T*_m) around 200 °C without any material loss. After cooling to room temperature and heating again, a slope change was clearly detected around 80 °C, and no melting peak was observed

Scheme 1. General Synthesis of DBAB-X^a



^a Conditions: i) triphenylamine, NaDBS, CH₂Cl₂/H₂O, rt, 18 h. ii) NBS, CH₂Cl₂ reflux, 4 h. iii) Pd(PPh₃)₄, PhB(OH)₂, 1 mol·L⁻¹ Na₂CO₃, toluene, 80 °C. iv) Malononitrile, pyridine.

above 200 °C. This thermal behavior as well as the absence of X-ray diffraction peaks in the melt product signifies amorphous properties. The ability of compounds **4a–e** to form stable glassy materials compared to their analogous *N,N*-diphenylamino-substituted compounds undoubtedly originates from the biphenyl moieties which prevent close packing of the molecules and efficiently reduce their tendency to crystallization.

Elaboration of thin films with a high optical quality plainly benefits from this amorphous property. Vacuum evaporation of compounds around 200 °C at a pressure of 5 × 10⁻⁵ mbar onto a glass substrate led to transparent films with a rms roughness of less than 0.7 nm from AFM topographic measurements. Such a deposition process offers the great advantage to discard any solvent pollution and subsequent time-consuming drying steps. Moreover, it suits need of multilayer materials for which the spin-coating technique requires elaborate insoluble polymers.¹⁰

UV–vis absorption spectra of both evaporated films and compounds in various solvents exhibit two bands (Table 1). The first one, centered around 335 nm, is insensitive to the nature of the electron-withdrawing group and the solvent polarity, contrarily to the second band which appears in the visible range and is strongly red-shifted when going from the less to the most polar compounds (**4a** to **4e**). The visible absorption maximum of evaporated films made from polar DBAB-X compounds undergoes a slight bathochromic shift, compared to that of films in DMSO solutions; this expresses the actual polar influence exerted on each chromophore by the neighboring molecules.

From comparison with *N,N*-diphenylamino model compounds, the visible and UV bands have been reasonably assigned to azobenzene-centered charge transfer and biphenyl-centered π–π* transitions, respectively.¹¹ In addition, semiempirical AM1 computations show an extended electron density from the biphenyl ends to the azo core for the HOMO, and from the azo core to the

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Table 1. Thermal, UV–Visible Absorption, and Second-Order NLO Properties of DBAB-X Compounds

compound	λ_{\max} (nm) in toluene	λ_{\max} (nm) in DMSO	λ_{\max} (nm) in film ^d	T_g (°C)	T_m (°C)	$\mu\beta_{1907}$ (10^{-48} esu) ^{b,c}	$\mu\beta_0$ (10^{-48} esu) ^c	d_{33} (pm/V) ^d
4a	435, 335	438, 330	335, 435	74	225	170	126	<0.1
4b	475, 328	481, 326	483, 328	85	239	484	337	1.3
4c	475, 329	482, 329	485, 330	91	197	430	302	2.1
4d	493, 331	501, 329	509, 333	76	227	828	555	3
4e	524, 341	544, 345	541, 345	96	216	1073	667	17

^a Absorbance of 500 nm-thick evaporated films. ^b CHCl₃ solution. ^c Accuracy $\pm 10\%$. ^d 1.5 μm -thick evaporated films.

electron-attracting group for the LUMO. Consequently, the resulting charge-transfer transition presents a bathochromic shift compared to that of the phenyl-substituted analogues. Finally, some occupied and vacant MOs close in energy to the HOMO and LUMO are located on biphenyl groups, and should be responsible for the UV transition.

The second-order NLO properties of DBAB-X compounds were investigated in CHCl₃ solutions and in solid state (powder and evaporated thin films) by second harmonic generation (SHG) at 1907 nm where resonance and second-harmonic reabsorption effects are ruled out. From electric field-induced second harmonic (EFISH) measurements and using the two-level model¹² for extrapolated first-order hyperpolarizability to zero-frequency β_0 , the product $\mu\beta_0$ (μ describing the dipole moment) was obtained. This value increases with the electron-accepting strength of X, being the highest one for the strongest electron-withdrawing dicyanovinylene moiety (Table 1).¹³ Contrarily to previous studies on polymers, introduction of the dicyanovinylene group substantially raises the NLO activity and the glass transition temperature without generating lower thermal stability.¹¹

Whereas the crystallized powder exhibited no spontaneous SHG activity when probing at 1907 nm, vacuum-deposited films formed from polar compounds **4b–e** unexpectedly gave a significant spontaneous signal whose intensity remains stable up to one year. The NLO coefficient d_{33} ranged from 1.3 to 17 pm/V, scaling with the strength of the electron-withdrawing group (Table 1). Formation of acentric crystallites has been ruled out as no X-ray diffraction peak was detected and no roughness feature was evidenced by surface AFM imaging. Bulk homogeneity was checked through the linear dependence found between absorbance and film thickness. As the SHG intensity $I_{2\omega}$ showed remarkable quadratic variation with the film thickness, we can reasonably discard any nonlinear contribution from the asymmetric organic layer–glass substrate interface and put forward a molecular auto-organization. Indeed, the SHG intensity at normal incidence has been measured to be zero so that molecules seem to orient around a symmetry axis normal to the film surface. Heating films above T_g led to an abrupt and irreversible disappearance of the SHG activity. These last results confirm the glassy character of the evaporated films where constructive dipole–dipole interactions due to strongly dipolar molecules might induce local ordering stable up to the glass transition temperature.^{14,15}

Such an assumption agrees with the large solvatochromic shift of the charge-transfer transition observed in the amorphous films. Molecules tend then to align following the direction of their main charge-transfer axis. To gain insight into the molecular assemblies, evaporated films are currently subjected to polarized UV–visible and IR absorption spectroscopic studies.

In summary, a novel mild and modular synthetic approach to bulky triarylamine compounds substituted by strong electron-

withdrawing groups has been developed which allows an easy tuning of their thermal (T_g above 80 °C) and NLO properties. Upon vacuum deposition, they form auto-organized amorphous glasses with high optical quality and spontaneous second-order NLO activity stable over one year. This unexpected result offers new developments for orientationally stable noncentrosymmetric organic materials based on the clean and reproducible vacuum deposition process.

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Supporting Information Available: Experimental procedures for **4b–e**, characterizations, and SHG equipment (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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