Cite this: Chem. Commun., 2011, 47, 7770–7772

www.rsc.org/chemcomm

COMMUNICATION

One small step in synthesis, a big leap in charge mobility: diphenylethenyl substituted triphenylamines[†]

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Received 7th May 2011, Accepted 25th May 2011 DOI: 10.1039/c1cc12700d

Star-shaped charge transporting materials with a triphenylamine core and a varying number of diphenylethenyl sidearms, obtained using a one step synthesis procedure from commercially available and relatively inexpensive starting materials and possessing comparatively high hole drift mobility (up to 0.017 cm² V⁻¹ s⁻¹), are reported.

Electronic and optoelectronic devices using organic materials as active elements involve charge transport as an essential operation process and hence, require charge-transporting materials. Therefore, development of high-performance, charge-transporting materials is a key issue for the fabrication of high-performance devices.

Realization of organic electronics potential for simple processing requires the ability to form devices by solution deposition methods, preferably using simple, inexpensive, easily purified materials.¹

In this communication, we report star-shaped charge transporting materials with a triphenylamine core and a varying number of diphenylethenyl sidearms. These hole transporting organic semiconductors are obtained in a 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 0.017 cm² V⁻¹ s⁻¹).

Similar compounds, bearing phenylethenyl or diphenylethenyl fragments, have been reported in the literature. However, they are obtained using either a multistep synthesis procedure, involving the McMurry cross-coupling reaction,^{2a} or by palladium-catalyzed cross-coupling, facilitated by a tailor-made ligand^{2b} or employing quite high loading of the catalyst.^{2c} For the synthesis of the herein reported compounds we have employed a different approach. The reported method utilizes commercially available and relatively inexpensive precursors

and the catalyst, the reaction isn't oxygen sensitive and the final product could be obtained in one step.

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

Briefly, condensation of the appropriate triphenylamine (TPA) derivatives with diphenylacetaldehyde in toluene (water generated during the course of the reaction was removed with a Dean–Stark trap), at a reflux temperature, in the presence of (+/-)-camphor-10-sulfonic acid (CSA), results in the formation of corresponding diphenylethenyl substituted triphenylamines 1–3 (Scheme 1). Although compound 3 has been already reported in the literature,³ it was included in this communication as a reference material and a demonstration of the method's scope and potential.

Both derivatives **1**, **2** are soluble in common organic solvents such as THF, toluene, chloroform. Their thermal properties were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements (Table 1). TGA shows that both compounds exhibit high thermal stability.

The DSC and TGA measurements indicate that additional bulky diphenylethenyl fragments increase both glass transition temperature and thermal stability.

The absorption bands of compounds 1-3 measured in tetrahydrofuran (THF) are shown in Fig. 1. The bathochromic shift of the absorption of 2 and 3 compared to that of TPA is attributed to the extension of the core π -conjugated system by



Scheme 1 Synthesis of diphenylethenyl substituted triphenylamines 1-3.

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[†] Electronic supplementary information (ESI) available: Detailed experimental procedures, measurement details, spectroscopic characterization, CV. See DOI: 10.1039/c1cc12700d

Table 1 Optical and thermal characteristics of the synthesized derivatives

Compound	$T_{\rm g}^{\ a}/^{\circ}{ m C}$	$T_{\rm m}^{\ \ b}/^{\circ}{\rm C}$	$T_{\rm dec}{}^c/{}^{\circ}{ m C}$	$\lambda_{\max}^{abs} d/nm$	$\epsilon/M^{-1} \text{ cm}^{-1}$
1 2 2	98 73	$\frac{201}{-126}$	465 374 254	392 390 270	6.97×10^4 4.45×10^4 4.25×10^4
3	_	130	354	370	4.23×10^{-5}

^{*a*} Determined by DSC: scan rate, 10 K min⁻¹; N₂ atmosphere; second run. ^{*b*} Melting point was only detected during the first heating; the compound vitrified on cooling to room temperature with 10 K min⁻¹. ^{*c*} Onset of decomposition determined by TGA: heating rate, 10 K min⁻¹; N₂ atmosphere. ^{*d*} UV-Vis spectra measured in 10⁻⁴ M THF solution.

one and two diphenylethenyl units, respectively. The maximum of the absorption spectra of **3** is shifted by about 71 nm with respect to the TPA and is located at 370 nm. In line with expectations the absorption of **2** is shifted even more bathochromically by about 91 nm compared with TPA. An additional diphenylethenyl fragment in **1** has a very limited effect on the overall π -conjugated system of the molecule, the bathochromic shift going from the di- to tri-substituted TPA derivative is very small (~2 nm). However, absorption intensity increases quite noticeably. This fact indicates that the probability of interaction between the radiation energy and the electronic system is substantially higher, and the transition is accompanied by a larger charge in the electronic charge distribution occurring during excitation.

Charge transport properties of the synthesized TPA derivatives **1–3** were studied by the xerographic time-of-flight (XTOF) technique (see ESI†, Fig. S1). The values of charge mobility defining parameters: zero field mobility (μ_0), the Poole–Frenkel parameter (α), and the mobility at the electric field of 6.4 × 10⁵ V cm⁻¹ for compounds **1–3**, are given in Table 2.



Fig. 1 Absorption spectra of 10^{-4} M THF solutions of the TPA derivatives **1–3**. The absorption spectrum of triphenylamine is shown for comparison.

The room temperature hole-drift mobility of the as-spun film of the tri-substituted TPA derivative 1 was $0.017 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at strong electric fields and it is approximately four times higher than that of the mono-substituted analogue 3. Compound 2 demonstrated similar performance and μ_{h} of 0.014 cm² V⁻¹ s⁻¹ was reached.

It has been recognized that solution-processable materials offer a better ease of processing compared to vacuum deposited ones, but generally have lower carrier mobility. The lower mobility is generally attributed to the lower structural order that reduces intermolecular π -orbital overlap. However, compared with other low molecular weight triarylamines,⁴ diphenylethenyl substituted TPA derivatives **1** and **2** demonstrate relatively high hole drift mobility (an order of magnitude higher than a very well-known hole transporting material TPD). It has to be noted that these results were obtained from solution processed films and a majority of the best performing low molecular weight triarylamines were vacuum deposited.

The electronic properties of molecular transport materials depend on the manner in which the molecules are organized in the solid state.^{5a,b} In particular, π -stacking, although not a guarantee of good wavefunction overlap, 5c is a feature of many high mobility materials.^{5d,e} To investigate possible $\pi - \pi$ stacking and aggregate formation, absorption spectra of the drop-cast thin films (as is and annealed) of 1 and 2 were recorded (Fig. 2). The films for absorption spectra measurements need to be sufficiently thin, as a consequence the solvent evaporates very quickly and molecules of the investigated compound become essentially "frozen". In order to allow them to organize, the samples for UV-Vis measurements were heated above glass transition temperature and cooled slowly to room temperature. The annealing stage wasn't required during the layer preparation for the mobility measurements as the solvent evaporation rate (during a spin-coating process) is slower and the molecules have sufficient time to organize themselves. From the absorption spectra, a small (~ 10 nm) red shift of the absorption edge of TPA derivative 1 from solution $(10^{-4} \text{ M in THF})$ to the solid state is observed (Fig. 2a), suggesting some degree of intermolecular interactions in the solid state and formation of the J-aggregates. Annealing (at 110 °C) of the film leads to the blue shift of the short-wavelength slope of the $\pi \to \pi^*$ transition band, indicating formation of the H-aggregates. A similar picture is observed in the case of derivative 2 (Fig. 2b). However, thermal annealing (at 100 °C) yields much more profound effects, the intermolecular interactions are much stronger, and changed $\pi \rightarrow \pi^*$ transition band's shape

Table 2 HOMO, LUMO, E_{I} , band gap energies, and hole mobility data for $1-3^{a}$

Compound	$E_{\rm g}^{{\rm opt}b}/{ m eV}$	$E_{\rm HOMO}^{c}/{\rm eV}$	$E_{\rm LUMO}^{d}/{\rm eV}$	$E_{\rm I}{}^{e}/{ m eV}$	$D/\mu { m m}$	$\mu_0^f/\mathrm{cm}^2 \mathrm{V}^{-1} \mathrm{s}^{-1}$	$\mu_{\rm h}{}^g/{\rm cm}^2~{\rm V}^{-1}~{\rm s}^{-1}$	$\alpha/cm^{1/2}\ V^{-1/2}$
1	2.76	-5.09	-2.33	5.41	6.3	3×10^{-3}	0.017	0.0022
2	2.78	-5.09	-2.31	5.35	2.9	2×10^{-3}	0.014	0.0025
3	2.88	-5.11	-2.23	5.43	4.9	5.6×10^{-4}	0.0045	0.0045

^{*a*} The CV measurements were carried out at a glassy carbon electrode in dichloromethane solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte and Ag/AgNO₃ as the reference electrode. Each measurement was calibrated with ferrocene (Fc). ^{*b*} The optical band gaps E_g^{opt} estimated from the edges of electronic absorption spectra. ^{*c*} $E_{HOMO} = 4.8 + (E_{1/2} - E_{1/2}^{FC})$. ^{*d*} $E_{LUMO} = E_{HOMO} - E_g^{opt}$. ^{*e*} Ionization energy was measured by the photoemission in air method from films. ^{*f*} Mobility value at zero field strength. ^{*g*} Mobility value at 6.4 × 10⁵ V cm⁻¹ field strength.



Fig. 2 Normalized absorptions of the films drop-cast from the THF solutions of **1** (a) and **2** (b).

indicates that both types of aggregates are formed, but H-aggregates predominate.

Development of some ordering was also evident in AFM height images (Fig. 3). The surface of as-cast compound **2** revealed the presence of distinct, rod-shaped features, most likely corresponding to microcrystallines.

To elucidate the energetic conditions for energy and electron transfer in dilute solutions, the HOMO/LUMO values were also determined using cyclic voltammetry (CV) (Table 2). These E_{HOMO} values do not represent any absolute solid-state or gas-phase ionization energies, but can be used to compare different compounds relative to one another. The cyclic voltammograms of the synthesized compounds in dichloromethane show one quasi-reversible and one irreversible oxidation couples and no reduction waves (Fig. S2 and S3, ESI†). The electrochemical data are summarized in Table S1 (ESI†).



Fig. 3 Intermittent contact mode AFM image of the spin-cast 2 film.

The tri- and di-substituted derivatives 1, 2 exhibit the first oxidation wave half-wave potentials corresponding to 0.29 V vs. Fc, which results in a $E_{\rm HOMO}$ value of -5.09 eV (on the basis of the $E_{\rm HOMO}$ energy level of ferrocene as 4.8 eV). These results are quite similar to those demonstrated by mono-substituted TPA 3, only a very slight increase in $E_{\rm HOMO}$ is observed. Additional diphenylethenyl groups have a more substantial effect on $E_{\rm LUMO}$, which increases by approximately 0.1 eV.

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 (E_I). This understanding can help in identifying suitable partner organic transport materials and inorganic electrode materials. The ionization energy was measured by the electron photoemission in air method (Fig. S4, ESI†) and results are presented in Table 2, the measurement error is evaluated as 0.03 eV. The measured E_I values are about 0.3 eV higher as compared with the HOMO levels found in the CV experiments. The difference may be caused by different states of the materials investigated (solution in CV and solid film in a photoemission method) and measurement methods.

In conclusion, we have demonstrated a simple one step synthesis method to obtain solution processable star-shaped charge transporting materials with a triphenylamine core and a varying number of diphenylethenyl sidearms from commercially available and relatively inexpensive starting materials. Tris(4-(2,2-diphenylethenyl)phenyl)amine **1** is an especially promising candidate because it can be handled in air, requires no high temperature annealing steps, can be solution deposited, possesses comparatively high mobility, and could be synthesized in one step from commercially available and cheap triphenylamine.

This research was funded by a grant (VP1-3.1-ŠMM-07-K 01-078) from the Research Council of Lithuania.

Notes and references

- (a) S. Allard, M. Forster, B. Souharce, H. Thiem and U. Scherf, Angew. Chem., Int. Ed., 2008, 47, 4070; (b) Y. Shirota and H. Kageyama, Chem. Rev., 2007, 107, 953.
- 2 (a) J. M. Plater and T. Jackson, *Tetrahedron*, 2003, **59**, 4673;
 (b) M. V. Nandakumar and J. G. Verkade, *Angew. Chem., Int. Ed.*, 2005, **44**, 3115; (c) K. Itami, K. Tonogaki, Y. Onashi and J. Yoshida, *Org. Lett.*, 2004, **6**, 4093.
- 3 M. Sasaki, (Ricoh Company Ltd.), US Patent US 4859556, 1989.
- 4 (a) P. M. Borsenberger, L. Pautmeier, R. Richert and H. Bässler, J. Chem. Phys., 1991, 94, 8276; (b) Y. Shirota, K. Okumoto and H. Inada, Synth. Met., 2000, 111–112, 387; (c) A. Higuchi, K. Ohnishi, S. Nomura, H. Inada and Y. Shirota, J. Mater. Chem., 1992, 2, 1109; (d) M. Sonntag, K. Kreger, D. Hanft, P. Strohriegl, S. Setayesh and D. de Leeuw, Chem. Mater., 2005, 17, 3031; (e) Q.-X. Tong, S.-L. Lai, M.-Y. Chan, K.-H. Lai, J.-X. Tang, H.-L. Kwong, C.-S. Lee and S.-T. Lee, Chem. Mater., 2007, 19, 5851.
- 5 (a) H. E. Katz and Z. Bao, J. Phys. Chem. B, 2000, 104, 671; (b) R. C. Haddon, X. Chi, M. E. Itkis, J. E. Anthony, D. L. Eaton, T. Siegrist, C. C. Mattheus and T. T. M. Palstra, J. Phys. Chem. B, 2002, 106, 8288; (c) Y. Olivier, V. Lemaur, J. L. Bredas and J. Cornil, J. Phys. Chem. A, 2006, 110, 6356; (d) A. M. van de Craats, N. Stutzmann, O. Bunk, M. M. Nielsen, M. Watson, K. Müllen, H. D. Chanzy, H. Sirringhaus and R. H. Friend, Adv. Mater., 2003, 15, 495; (e) K. O. Sylvester-Hvid, J. Phys. Chem. B, 2006, 110, 2618.