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An electron-deficient tris(triazole)-based discotic liquid crystal that exhibits fast electron transport[†]

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In this study, a C_3 -symmetric star-shaped discotic mesogen has been reported based on an electron-deficient tris(triazole) central rigid core functionalized with three peripheral trialkoxyphenyl units. The mesogen exhibits an enantiotropic columnar hexagonal (Col_n) phase that can sustain over a significant temperature range. When used in space-charge limited current (SCLC) devices, it showed ambipolar charge transport behavior with high electron mobility (μ_e) of 1.61×10^{-2} cm² V⁻¹ s⁻¹ at ambient temperature. The finding is sufficiently significant to warrant their use in organic electronic devices.

Organic semiconducting materials (OSCs) provide an alternate solution to inorganic semiconductors as electron and holetransporting materials in various (opto)-electronic devices due to their low cost, less sophisticated, and low-temperature fabrication processes.^{1,2} The simple processing of OSC materials with liquid crystalline (LC) phases can be regarded as a new generation of OSCs3 because of the organization of discotic molecules into supramolecular columnar (Col) structures having charge carrier migration properties in one-dimension.^{4,5} Discotic liquid crystals (DLCs) based on electron-rich systems (p-type semiconductors) have been widely studied in comparison to electron-deficient (n-type) ones.⁶ The few reported electron-deficient cores are designed from their electron-rich counterparts by substituting aromatic CH groups with nitrogen atoms⁷ or by the introduction of electron-withdrawing groups⁸ like carboxyl, imide and amide. It has been seen that n-type discotics with low bandgap are excellent candidates for transportation of both positive and negative charges in organic

semiconductors.^{3,9} The charge transport values depend highly on the structural ordering of molecules and intracolumnar orbital coupling to ensure a uniaxial pathway for charge migration.¹⁰ The n-type aromatic systems,^{11,12} possessing nitrogen-rich cores, improve structural ordering because of their excellent π - π stacking ability.^{13,14} This type of design has been contrived to place the HOMO (LUMO) in the central position of the molecules to increase the overlap of atomic orbitals that will improve the hole (electron) transport property. HATNA (5,6,11,12,17,18-hexaazatrinaphthylene), formed after substituting six nitrogen atoms in a triphenylene core, showed an electron mobility of 10^{-3} cm² V⁻¹ s⁻¹.¹⁵ The electron mobility of anthraquinone, an electron-deficient core was found to be 3.2 \times 10 $^{-4}$ cm 2 V $^{-1}$ s $^{-1}.^{16}$ Truxenone and triazatruxene are electron-deficient cores derived from truxene that show high electron mobility.¹⁷ Introduction of boronic esters in the triphenylene core makes it electron-deficient, however, it showed only hole mobility.¹⁸ A heterocoronene core, an extension of the coronene core using four electron-withdrawing carboxaimide groups, shows an ambipolar charge transport.¹⁹ Apart from these, discotic systems bearing nitrogen moieties with ambipolar charge transport are still rather scarce, in respect to the present context. In this regard, tristriazolotriazines are new tetracyclic, nitrogen-rich electron-deficient cores for DLCs, but to date, extensive research has been done on compounds based on 1,2,4-triazole and 1,3,5-triazine.²⁰ Besides, Muzik et al. first laid the foundation for the synthesis of tris(triazole)-based molecules.²¹

Motivated by this, the present work demonstrated the synthesis of a C_3 -symmetrical star-shaped DLC material (Compound 1, Scheme 1), with an electron-deficient tris(triazole) central rigid core attached to which were electron-rich alkoxy units at the periphery. Tait *et al.* reported a non-LC analogue that was shown to grow into highly ordered structures.²² The mesogen reported in this paper shows excellent homeotropic Col alignment^{23,24} (the director is perpendicular to the substrate surface) at room temperature over a macroscopic area which is highly warranted for semiconducting devices. In addition to

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Scheme 1 Molecular design of tris(triazole)-based ambipolar DLCs with planar aromatic structure.

this, the introduction of peripheral flexible alkyl chains elegantly empowers the devices with a solution or melt processability. When mesogen **1** is fabricated in SCLC devices to determine charge carrier mobility, the electron and hole mobilities extracted from an average of at least five devices were $1.85 \pm 0.72 \times 10^{-3}$ cm² V⁻¹ s⁻¹ (1.61×10^{-2} cm² V⁻¹ s⁻¹ for champion device) and $1.38 \pm 0.50 \times 10^{-6}$ cm² V⁻¹ s⁻¹, respectively.

The threefold symmetric target compound was readily prepared by the reaction sequence depicted in Scheme 2. In basic conditions, the azo-coupling reactions^{22,25} on all three bare positions of 1,3,5-triaminobenzene with the diazotization product derived from 3,4,5-tridodecyloxyaniline followed by its cyclization reaction afforded the requisite product as a beige solid in reasonably good yield (*i.e.* 72%). It was then purified and fully characterized by ¹H NMR, ¹³C NMR, and HRMS (Fig. S1–S14, ESI†) techniques.

To determine the phase behavior of the synthesized compound **1**, differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction at variable



Scheme 2 Synthesis of tris(triazole) derivative **1** (R: $C_{12}H_{25}$). Reagents and conditions: (i) K_2CO_3 , dodecylbromide, DMF, 80 °C, 48 h, yield = 75%; (ii) NaNO₂, Conc. HNO₃, DCM, RT, 12 h, yield = 65%; (iii) Pd–C, dry THF, H₂ atm, 12 h, yield = 90%; (iv) DPPA, triethylamine, toluene, *tert*-butanol, 80 °C, 4 h, followed by 110 °C, 2 h, yield = 68%; (v) Conc. HCl, ethanol, RT, 12 h, yield = 75%; (vi) TFA, *tert*-butyl nitrite, K_2CO_3 , DCM, 0 °C, 12 h, yield = 79%; (vii) Cu(OAc)₂·H₂O, pyridine, 80 °C, 1 h, yield = 72%.

temperature studies were performed. Under POM, the compound displayed characteristic Col textures with rectilinear defects. A striking fan-like growth pattern (Fig. S15, ESI[†]) was observed that gradually blends into a mosaic texture having dispersed bright and dark regions as shown in Fig. 1a. This shearable texture that persists to room temperature indicates that compound 1 is a room temperature LC. The outcomes corresponding to the phase transitions observed in DSC thermograms (Fig. S16 and Table S1, ESI⁺) were similar to those of the observations in POM. In the heating cycle of DSC from -50 °C, one endothermic peak was observed at 50.4 °C ($\Delta H =$ 56.4 kJ mol⁻¹) *i.e.*, melting temperature, which corresponds to crystalline to mesophase transition and another endothermic peak at 163.3 °C (ΔH = 5.8 kJ mol⁻¹) *i.e.*, clearing temperature, which corresponds to the mesophase to isotropic transition. In addition, a crystal to crystal transition was observed at 28.5 °C (ΔH = 24.7 kJ mol⁻¹). In the cooling cycle of DSC down to -50 °C, the mesophase appeared at 159.5 °C ($\Delta H =$ 4.6 kJ mol⁻¹) and notably, the optical texture remained stable down to ambient temperature and at 16.0 °C ($\Delta H = 27.1 \text{ kJ mol}^{-1}$), it was finally changed to a solid crystalline state. The Col phase was present over a wide temperature range including room temperature. It was observed that the change in phase and their corresponding phase transition temperatures in both optical (POM) and calorimetric (DSC) studies can be replicable for several heating/cooling cycles suggesting its high thermal stability. The thermal stability was also confirmed by thermogravimetric analysis (TGA) (Fig. S17, ESI[†]). Detert and co-workers^{20b} reported a structural isomer of 1 with trialkoxy phenyl substituents in the tangential positions. The isomer exhibits short-range hightemperature columnar disorder mesophase (Cr 128 °C Colhd 153 °C Iso). Interestingly, in the present tris(N-phenyl)triazole derivative with trialkoxy phenyl substituents in the radial positions, the mesomorphic range tremendously widens down to room temperature.

To deduce the detailed structure of the assembly of compound 1, wide-angle X-ray scattering experiments have been performed. The compound exhibits a columnar hexagonal (Col_b) phase where the cross-section of the columns is arranged on two-dimensional hexagonal lattices. The pattern in X-ray diffraction of the compound in the mesophase temperature range exhibited four peaks in the small-angle region with a *d*-spacing in a ratio $1/1: 1/\sqrt{3}: 1/\sqrt{4}: 1/\sqrt{9}$ corresponding to reflection from the (10), (11), (20), and (30) planes of the hexagonal lattice (Fig. 1b). Moreover, there is one broad peak, $h_{\rm a}$, in a wide-angle region of spacing 4.93 Å, which appears due to fluid alkyl chain-chain correlation and one broad hump h_c , with spacing 3.69 Å, indicative of the π - π interactions between the cores. The calculated value of the lattice parameter at temperature 60 °C is found to be a = 37.04 Å (Fig. 1c and Table S2, ESI[†]). The structure remains Col_b in the mesophase regime and the lattice parameter is found to be more or less constant with temperature. Furthermore, to have a better understanding of the arrangement of molecules in the hexagonal phase, electron density maps (EDMs)²⁶ have been constructed by using the information of the peak indexes and intensities. It is clear



Fig. 1 Photomicrograph of the texture observed under POM for the Col phase of **1** kept between a glass slide and coverslip at (a) 59.1 °C, in the cooling cycle. (b) XRD pattern of **1** at 60 °C exhibiting Col_n phase. The inset showed the zoomed area of the pattern. (c) Electron density map in the Col_n phase of compound **1** at temperature 60 °C (a = b = 37.04 Å). The highest electron density is represented by red and the lowest electron density by deep blue.

from the EDM (Fig. 1c) that higher electron density regions exhibit regular hexagonal lattices.

Due to the several chromophores and potential π conjugations present between the peripheral area and the central core, interesting photophysical properties are exhibited by compound 1. In the solution state (Fig. S18a, ESI⁺), UV-vis spectra (dark grey trace) revealed two peaks assigned at 234 and 342 nm corresponding to π - π * and n- π * transitions, respectively, with a small shoulder at 300 nm. Irradiating the solution with absorption maxima, viz., 342 nm, generated the blue emission maxima at 447 nm (red traces). No change in the emission spectra was observed by changing the excitation wavelength (λ_{ex}) at 234, 300 and 342 nm (Fig. S19, ESI[†]). Compound 1 was found to be extremely blue fluorescent in the solution state with the corresponding quantum yield of 0.72 (Table S3 and Fig. S20, ESI⁺). On the other hand, in the solid-state, compound 1 showed the absorption maxima at 339 nm while the emission maxima were observed at 445 nm (Fig. S18b, ESI[†]).

Knowledge of the redox potentials of the material is important to further our understanding of conduction in these systems. For compound **1**, in the oxidation cycle, two wellresolved peaks were observed, whereas one reduction peak was observed (Fig. S21, ESI†). The energy levels of the LUMO and HOMO were estimated at -3.36 eV and -5.71 eV, based on the reduction and first oxidation onsets, respectively (Table S4, ESI†). The electrochemical bandgap value for compound **1** was calculated to be 2.35 eV. Moreover, the HOMO and LUMO distribution of the molecular orbitals obtained by DFT (B3LYP/ 6-31G(d,p) level) suggested the efficient overlap of the orbitals throughout the molecules, prerequisites for high charge transport behavior (Fig. S22, ESI†).

To evaluate the potential application of compound **1** in organic devices, charge carrier transport studies were carried out using the SCLC technique.²⁷ Charge carrier mobility (hole/ electron) is considered as one of the performance parameters to fabricate efficient devices. In the SCLC technique, compound **1** was sandwiched between two electrodes with one being an Ohmic contact with the HOMO (for hole mobility extraction) and with the LUMO (for electron mobility extraction) and the

other being non-ohmic, to ensure efficient charge injection. A non-ohmic counter electrode ensures minimal or no contribution to the overall current measured during J-V characteristics, from the opposite nature of the charge (for example hole in case of electron mobility extraction). Briefly, in the SCLC technique, during J-V characteristics, at lower applied voltages, current behaves linearly at applied voltages. This linear behavior is mainly because at lower applied voltages injected charges are much less than that of the intrinsic carrier concentration of the material. However, at higher applied voltages, due to sufficient charge injection from ohmic contact, charge build up takes place in the sample and the measured current is no more governed by the intrinsic charges of the material, leading to quadratic dependence of the current with applied voltages. Considering the material to be trap free, this SCLC behavior of *I-V* characteristics can be modeled by the Mott Gurney equation:28

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_{\rm r} \mu \frac{V^2}{d^3}$$

where *J* is the current density measured at applied voltage *V*, ε_0 is the permittivity of free space, ε_r is the dielectric constant (4.18) of the material, μ is the charge mobility of the material, and *d* is the thickness of the sample used for SCLC measurements.

For electron mobility cells, Cs_2CO_3 (work function ~ -2.9 to -3.1 eV) coated ITO was chosen, both injecting and noninjecting electrodes to fabricate electron-only cells. Cs_2CO_3 was chosen because its work function matches well with the LUMO of the compound 1.²⁹ For hole-only devices gold (Au) (work function ~ -5.1 eV) was chosen as the injecting electrode with UV ozone treated ITO as a non-injecting electrode to fabricate SCLC devices. A typical *J*–*V* characteristic obtained for compound 1 for electron and hole mobility devices is shown in Fig. 2e and f, respectively, where one can clearly distinguish linear as well as the quadratic regime.

The average SCLC electron and hole mobilities extracted from five devices were 1.85 \pm 0.72 \times 10⁻³ cm² V⁻¹ s⁻¹ and 1.38 \pm 0.50 \times 10⁻⁶ cm² V⁻¹ s⁻¹, respectively (Table S5, ESI†). However, the electron mobility of 1.61 \times 10⁻² cm² V⁻¹ s⁻¹ was



Fig. 2 Cross polarized optical microscopic images of the SCLC cell taken for electron mobility at an angle of (a) 90° and (b) 45° and for hole mobility at an angle of (c) 90° and (d) 45° of compound **1**. *J*–*V* curve for **1** (at 25 °C) showing ideal ohmic (slope 1, green line) and SCLC regimes (slope 2, red line) for the (e) electron mobility and (f) hole mobility cell.

determined for the champion device which is one order of magnitude higher than the average electron mobility. Higher electron mobility (~three orders of magnitude) over hole mobility for **1** is obvious since the core of **1** is designed by utilizing a central tris(triazole) core (electron-deficient) along with flexible trialkoxy units (electron-rich) at the periphery to enhance their ability to increase the ordering of molecules bearing π rings in donor-acceptor arrangement. Structural ordering is one of the fundamental requirements to achieve higher charge carrier mobility in π -stacked molecules.³⁰

The mobility in the SCLC technique is highly dependent on the homeotropic alignment of the material in their respective hole-only or electron-only cells. It can vary from three to four orders of magnitude within the same cell having different devices.³¹ Approximately, one order of higher electron mobility for the champion device over the average value observed can be attributed to its higher degree of homeotropic alignment as compared to other samples. In DLCs, generally, the homeotropic alignment can be achieved by introducing a suitable surface anchoring layer,^{23,32} using various temperature treatments,^{33,34} roughness and surface energy of the substrate^{35,36} and so on. However, in the present case, the homeotropic alignment is obtained spontaneously during the slow filling of the SCLC cells through capillary action from the isotropic melt followed by slow cooling of the samples up to room temperature.

To analyze the disparity in calculated electron and hole mobility values in compound **1**, POM textures of the sample in the SCLC cell have been closely studied in various regions of the cell. The photomicrograph of textures in the SCLC cells under crossed polarizers (at 90° angle) showed that both the hole-only SCLC cell and electron-only SCLC cell display birefringent regions along with homeotropic domains. Moreover, nearly uniform homeotropic alignment was found to exist over a wide region of electron-only cells suggesting better mobility (Fig. 2a and Fig. S23, ESI†). Whereas, no such uniform homeotropic alignment was observed for hole-only cells (Fig. 2c and Fig. S24, ESI†). Besides, the existence of grain boundaries was visualized after rotation of the polarizer to 45° angle (Fig. 2b and d). The uniform homeotropic background was observed for electron-only cells. In contrast, partial or no homeotropic alignment in the case of the hole-only cell further explains its lower mobility values.

Conclusion

We have presented trialkoxy-substituted triazoloarene DLC that shows a stable Col_h phase at room temperature. The charge transport studies reveal fast electron transport of the order of 10^{-2} cm² V⁻¹ s⁻¹ as measured using the SCLC technique. The finding is expected to guide the development of new highperformance n-type materials for semiconducting devices.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- T. Wöhrle, I. Wurzbach, J. Kirres, A. Kostidou, N. Kapernaum,
 J. Litterscheidt, J. C. Haenle, P. Staffeld, A. Baro,
 F. Giesselmann and S. Laschat, *Chem. Rev.*, 2016, **116**, 1139.
- 2 C. Reese, M. Roberts, M. M. Ling and Z. Bao, *Mater. Today*, 2004, 7, 20.
- 3 S. Sergeyev, W. Pisula and Y. H. Geerts, *Chem. Soc. Rev.*, 2007, **36**, 1902.
- 4 R. J. Bushby and K. Kawata, Liq. Cryst., 2011, 38, 1415.
- 5 (a) S. Kumar, *Chem. Soc. Rev.*, 2006, **35**, 83; (b) B. R. Kaafarani, *Chem. Mater.*, 2011, **23**, 378.
- 6 (a) S. Kumar, *Liq. Cryst.*, 2004, 31, 1037; (b) I. Bala, H. Singh,
 V. R. Battula, S. P. Gupta, J. De, S. Kumar, K. Kailasam and
 S. K. Pal, *Chem. Eur. J.*, 2017, 23, 14718; (c) I. Bala, J. De,
 S. P. Gupta, H. Singh, U. K. Pandey and S. K. Pal, *Chem. Commun.*, 2020, 56, 5629.
- 7 N. Boden, R. J. Bushby, K. Donovan, Q. Liu, Z. Lu, T. Kreouzis and A. Wood, *Liq. Cryst.*, 2001, 28, 1739.
- 8 I. Seguy, P. Jolinat, P. Destruel, R. Mamy, H. Allouchi, C. Courseille, M. Cotrait and H. Bock, *ChemPhysChem*, 2001, 2, 448.

- 9 J. L. Brusso, O. D. Hirst, A. Dadvand, S. Ganesan, F. Cicoira, C. M. Robertson, R. T. Oakley, F. Rosei and D. F. Perepichka, *Chem. Mater.*, 2008, **20**, 2484.
- V. Lemaur, D. A. da Silva Filho, V. Coropceanu, M. Lehmann,
 Y. Geerts, J. Piris, M. G. Debije, A. M. van de Craats,
 K. Senthilkumar, L. D. A. Siebbeles, J. M. Warman, J.-L. Brédas and J. Cornil, *J. Am. Chem. Soc.*, 2004, **126**, 3271.
- M. Lehmann, G. Kestemont, R. Gómez Aspe, C. Buess-Herman, M. H. J. Koch, M. J. Debije, J. Piris, M. P. de Haas, J. M. Warman, M. D. Watson, V. Lemaur, J. Cornil, Y. H. Geerts, R. Gearba and D. A. Ivanov, *Chem. – Eur. J.*, 2005, **11**, 3349.
- 12 S. Ellinger, K. R. Graham, P. Shi, R. T. Farley, T. T. Steckler, R. N. Brookins, P. Taranekar, J. Mei, L. A. Padilha, T. R. Ensley, H. Hu, S. Webster, D. J. Hagan, E. W. Van Stryland, K. S. Schanze and J. R. Reynolds, *Chem. Mater.*, 2011, 23, 3805.
- 13 J. De, S. P. Gupta, I. Bala, S. Kumar and S. K. Pal, *Langmuir*, 2017, 33, 13849.
- 14 V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J. L. Brédas, *Chem. Rev.*, 2007, **107**, 926.
- 15 (a) B. Eistert, H. Fink and H. K. Werner, *Liebigs Ann.*, 1962, 657, 131; (b) X.-Y. Liu, T. Usui and J. Hanna, *Chem. Eur. J.*, 2014, 20, 14207.
- 16 H. Zhao, Z. He, M. Xu, C. Liang and S. Kumar, *Phys. Chem. Chem. Phys.*, 2016, **18**, 8554.
- S. Gómez-Esteban, A. Benito-Hernandez, R. Termine, G. Hennrich, J. T. L. Navarrete, M. C. Ruiz Delgado, A. Golemme and B. Gómez-Lor, *Chem. – Eur. J.*, 2018, 24, 3576.
- 18 L. A. Tatum, C. J. Johnson, A. A. Fernando, B. C. Ruch, K. K. Barakoti, M. A. Alpuche-Aviles and B. T. King, *Chem. Sci.*, 2012, 3, 3261.
- 19 J. De, I. Bala, S. P. Gupta, U. K. Pandey and S. K. Pal, *J. Am. Chem. Soc.*, 2019, **141**, 18799.
- 20 (a) R. Cristiano, H. Gallardo, A. J. Bertoluzzi, I. H. Bechtold,
 C. E. M. Campos and R. L. Longo, *Chem. Commun.*, 2008, 5134; (b) T. Rieth, N. Tober, D. Limbach, T. Haspel,
 M. Sperner, N. Schupp, P. Wicker, S. Glang, M. Lehmann and H. Detert, *Molecules*, 2020, 25, 5761.
- 21 V. Chmatal, Z. J. Allan and F. Muzik, *Collect. Czech. Chem. Commun.*, 1959, 24, 484.

- 22 D. L. Wisman, S. Kim, T. W. Morris, J. Choi, C. D. Tempas, C. Q. Trainor, D. Lee and S. L. Tait, *Langmuir*, 2019, **35**, 6304.
- 23 T. S. Perova and J. K. Vij, Adv. Mater., 1995, 7, 919.
- 24 J. K. Vij, A. Kocot and T. S. Perova, *Mol. Cryst. Liq. Cryst.*, 2003, **397**, 531.
- 25 C. Ratto, E. Westphal, C. E. M. de Campos and H. Gallardo, *Mol. Cryst. Liq. Cryst.*, 2017, 657, 147.
- 26 S. P. Gupta, M. Gupta and S. K. Pal, *ChemistrySelect*, 2017, 2, 6070.
- 27 (a) A. Benito-Hernandez, U. K. Pandey, E. Cavero, R. Termine, E. M. García-Frutos, J. L. Serrano, A. Golemme and B. Gomez-Lor, *Chem. Mater.*, 2013, 25, 117; (b) M. Talarico, R. Termine, E. M. GarcíFrutos, A. Omenat, J. L. Serrano, B. Gómez-Lor and A. Golemme, *Chem. Mater.*, 2008, 20, 6589.
- 28 N. F. Mott and D. Gurney, *Electronic Processes in Ionic Crystals*, Academic Press, New York, 1970, p. 45.
- 29 (a) Y. Chen, X. Wei, Z. Li, Y. Liu, J. Liu, R. Wang, P. Wang, Y. Yamada-Takamura and Y. Wang, *J. Mater. Chem. C*, 2017, 5, 8400; (b) L. M. Chen, Z. Xu, Z. Hong and Y. Yang, *J. Mater. Chem.*, 2010, 20, 2575.
- 30 (a) V. Cuesta, M. Vartanian, P. Malhotra, S. Biswas, P. de la Cruz, G. D. Sharma and F. Langa, J. Mater. Chem. A, 2019, 7, 11886; (b) R. Volpi, A. C. S. Camilo, D. A. da Silva Filho, J. T. L. Navarrete, B. Gómez-Lor, M. C. R. Delgado and M. Linares, Phys. Chem. Chem. Phys., 2017, 19, 24202.
- 31 E. M. Garcia-Frutos, U. K. Pandey, R. Termine, A. Omenat, J. Barberá, J. L. Serrano, A. Golemme and B. Gómez-Lor, *Angew. Chem., Int. Ed.*, 2011, **50**, 7399.
- 32 T. S. Perova, J. K. Vij and A. Kocot, *Europhys. Lett.*, 1998, 44, 198.
- 33 J. Eccher, G. C. Faria, H. Bock, H. von Seggern and I. H. Bechtold, *ACS Appl. Mater. Interfaces*, 2013, 5, 11935.
- 34 R. Chico, E. de Domingo, C. Domínguez, B. Donnio, B. Heinrich, R. Termine, A. Golemme, S. Coco and P. Espinet, *Chem. Mater.*, 2017, 29, 7587.
- 35 C. Ruiz, U. K. Pandey, R. Termine, E. M. García-Frutos, G. Lopez-Espezo, R. P. Ortiz, W. Huang, T. J. Marks, A. Fachetti, M. C. R. Delgado, A. Golemme and B. Gómez-Lor, ACS Appl. Mater. Interfaces, 2016, 8, 26964.
- 36 K. S. Haber and A. C. Albrecht, J. Phys. Chem., 1984, 88, 6025.