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A simple, high yield method for the synthesis of organic wires from aromatic molecules using nitric acid as the solvent†

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Using concentrated nitric acid as the solvent, and water as the non-solvent, one-dimensional (1D) organic nanowires can be synthesized in a simple, one-pot process with high yield. The method has broad validity to a wide range of aromatic molecules for the synthesis of derivatized organic wires.

1D organic semiconductor wires are currently emerging as building blocks for various electronic and optical applications such as field effect transistors, light emitting diodes, photo-switches, vapor sensors and optical waveguides.¹ Conventional fabrication methods for 1D organic nanowires are broadly categorized as either solution-based or surface-supported self-assembly.² Solution-based self-assembly of 1D materials generally uses either a solvent-exchange or a non-solvent nucleation method, where the molecules are transferred from a saturated solution into a relatively poor solvent to induce supersaturation. Large anisotropy in surface free energy leads to the growth of ribbons or rods.

Studies have shown that self-assembly of aromatic molecules through π - π stacking can lead to the formation of 1D nanostructures.³ However, non-functionalized oligoacenes, such as tetracene (TCN) and pentacene, usually adopt an edge-to-face herringbone arrangement in the solid state in which the π -overlap is not maximized. The π -stacking can be maximized using functionalized oligoacenes and transistors fabricated from these films exhibit high carrier mobilities.^{4,5} There are very few reports on 1D nanostructures (*e.g.*, nanowires) synthesized from pentacene and TCN.^{5,6} To date, π -stacked TCN derivatives are relatively uncommon.^{4,5}

In this work, we discover that the so-called dilution method, in which a solution containing monomers is mixed with a miscible non-solvent, can be used to synthesize π - π stacked organic nanowires aided by ultrasound. What is surprising is that the reaction uses nitric acid as the solvent, and water as the miscible non-solvent. Nitric acid is known to be a strong acid with strong oxidizing ability, thus it is surprising that 1D

organic nanostructures can be self-assembled in these highly acidic media. Compared with the conventional methods, our synthetic route produces bulk quantities of functionalized TCN wires possessing structures and properties markedly different from the TCN precursor.

TCN is readily dissolved in 70% diluted fuming nitric acid. In contrast, TCN is not readily soluble in most organic solvents, so obtaining a saturated solution in an organic solvent takes a long time even with heating and stirring.

As shown in Fig. 1a, the TCN–acid mixture is a transparent solution. Intriguingly, after adding a small amount of water to the mixture, a colloidal suspension appears immediately. Subsequent analysis shows that the TCN molecules become functionalized in the presence of concentrated nitric acid, a strong oxidizing/nitrating agent. The functionalized TCN molecule possesses nitro and carbonyl groups which allows it to be protonated and solvated in an acid.⁷ A loosely-bonded molecular network may exist in nitric acid maintained by hydrogen bonding, and the presence of ionic groups in the functionalized TCN may resist aggregation. The addition of water, a miscible non-solvent, creates local supersaturation and results in face-to-face π aggregation of the molecular species.⁸

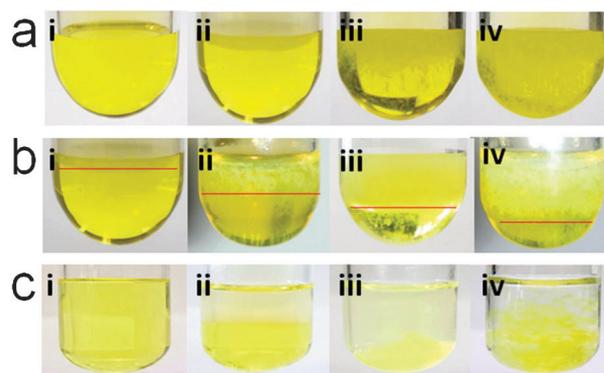


Fig. 1 (a) Time effect of addition of water to TCN/HNO₃ solution: (i) original TCN/HNO₃ solution, (ii) 30 s, (iii) 15 min, (iv) 30 min after adding 10 μ L water into 1 mL original solution. (b) Effect of addition of different amounts of water: (i) 10 μ L, (ii) 50 μ L, (iii) 100 μ L, (iv) 150 μ L. (c) Dilution effect by adding other solvents to TCN/HNO₃: (i) dimethylformamide (DMF), miscible solvent, no aggregation, (ii) hexane, immiscible non-solvent, layered, (iii) methanol, miscible non-solvent, aggregation, (iv) water, miscible non-solvent, aggregation.

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On the other hand, water can also increase the local pH to counteract the protonation process, thus the molecules become electrically neutral and tend towards aggregation. As shown in Fig. 1a, the addition of water creates nucleated monomers, and with time, these assemble into wires. Fig. 1b shows that with increasing amount of water, the extent of aggregation increases.

Besides water, we have tested the dilution effect of other polar and non-polar non-solvents on the assembly of the derivatized TCN wires, as shown in Fig. 1c. It is observed that the ease of aggregation of the wire follows the polarity of the solvent. DMF is a polar solvent which is miscible with an acid but can dissolve the product; and hexane is a non-polar, non-miscible solvent with nitric acid, therefore they have no dilution effect and there is consequently no aggregation. Methanol and water are all polar miscible non-solvents so they can induce the assembly of the wires. Fig. 1c(iv) shows the appearance of a colloidal suspension when the non-solvent is added. In the conventional solvent-exchange method, a small amount of concentrated TCN/DMF solution is added to an excess of poor solvent, which results in high nucleation density and the subsequent growth of the thin wire. In contrast, the acid-sonication and non-solvent dilution method allows a lower nucleation density and thicker wires to be grown.

Compared to the FTIR spectrum of TCN (Fig. 2a), there are several new peaks in the sonicated product which suggests that functionalization of the TCN wire occurs. A characteristic band present at 1680 cm^{-1} is assigned to the carbonyl stretching vibration. Fingerprint groups such as O–H stretching (broad and strong peak, $3300\text{--}2500\text{ cm}^{-1}$), OC–H stretching ($2830\text{--}2695\text{ cm}^{-1}$) and C–O–C stretching ($1240\text{--}1160\text{ cm}^{-1}$ and $1160\text{--}1050\text{ cm}^{-1}$) relating to the carboxyl, aldehyde or ester group are absent, thus the carbonyl vibration is due to ketone groups. It is also noted that there are two bands at 1525 cm^{-1} and 1325 cm^{-1} which are attributed to the asymmetric and symmetric stretching of N–O, respectively. This suggests that the TCN is oxidized as well as nitrated during the nitric acid sonication process. The elemental analysis results show that the mass ratio is C : H : O : N = 18 : 9 : 4 : 1 (Fig. S1, ESI[†]). We have also analyzed the chemical composition of the dissolved wire using MALDI-TOF. One probable structure

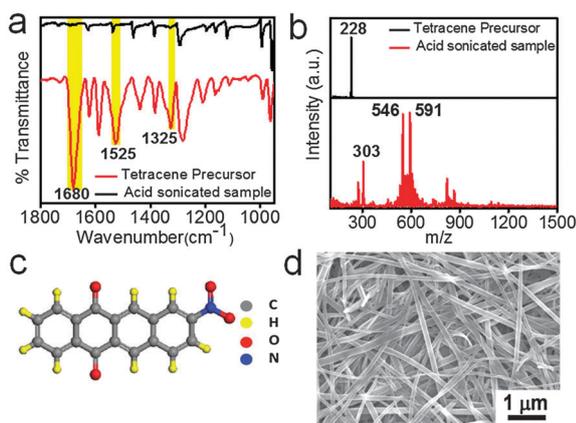


Fig. 2 (a) FTIR and (b) MALDI-TOF MS spectra of the starting tetracene and nitric acid sonicated nanowires. (c) Proposed structure corresponding to $m/z = 303$ peak. (d) SEM images showing a network of nitric acid-sonicated nanowires.

of the m/z peak at 303 in the MALDI-TOF spectrum (Fig. 2b) is a derivatized form of the TCN molecule that contains one nitro group and two ketone groups, which can be the building block of the wire. Based on structure and energetics optimization by the VAMP method using Materials Studio (Table S1, ESI[†]), a suggested structure is 8-nitrotetracene-5,12-dione, as shown in Fig. 2c. The molecular structure of the m/z peak at 546 and 591 may be due to the dimeric form of the TCN, with the difference of 45 corresponding to substitution of a hydrogen atom with a nitro group. However, the sonication process produced a range of products where it is difficult to isolate individual species. Fig. 2d shows the scanning electron microscopy (SEM) image of a network of nanowires generated by nitric acid sonication followed by water dilution, the typical lengths are in the range of micrometre, while the widths are in the range of fifty to several hundred nanometres.

To shed light on the structure of the nitric acid sonicated wires, X-ray diffraction analysis (XRD) and selected area electron diffraction (SAED) were performed on the wires. The crystallographic system of the parent TCN crystal is triclinic with lattice parameters $a = 7.90\text{ \AA}$, $b = 6.03\text{ \AA}$, $c = 13.53\text{ \AA}$, $\alpha = 100.3^\circ$, $\beta = 113.2^\circ$, $\gamma = 80.3^\circ$ and the molecules are arranged in a herringbone structure with an edge-to-face pattern.⁹ The XRD data reveal that the sonicated wires are crystalline and the molecular stacking is different from that of the TCN precursor. All the diffraction peaks of the sonicated TCN can be indexed to the triclinic structure, with a different lattice of $a = 11.94\text{ \AA}$, $b = 8.36\text{ \AA}$, $c = 8.25\text{ \AA}$, $\alpha = 66.30^\circ$, $\beta = 110.05^\circ$ and $\gamma = 107.21^\circ$. The peak assignments are shown in Fig. 3a, in which there are several peaks corresponding to the d-spacings of $3.2\text{--}3.8\text{ \AA}$ which are within the range of effective $\pi\text{--}\pi$ stacking distance. Fig. 3b shows the TEM image of a crystalline nitric acid-sonicated nanowire, with the inset giving the corresponding electron diffraction pattern. The diffraction pattern of the transmission electron microscopy (TEM) and the measured spacings are in agreement with the XRD data. The d-spacings of (201) and (010) were determined to be 3.8 \AA and 8.4 \AA , respectively. Analysis of the d-spacing reveals that the single crystal nanowire grows along the [201] direction.

One interesting question is to ask why the stacking arrangement has changed from the herringbone stacking in the parent TCN crystal to a face-to-face $\pi\text{--}\pi$ stacking arrangement in the sonicated TCN. One reason is due to the extra stabilization of the aromaticity in the TCN rings by the electron-withdrawing nitro and carbonyl functional groups. It is instructive in this

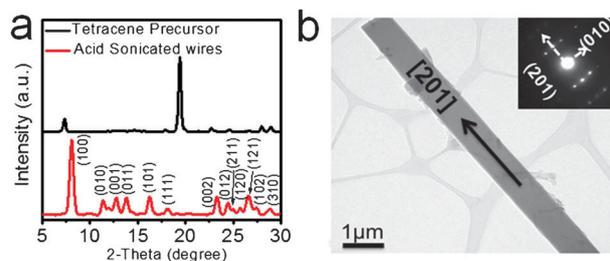


Fig. 3 (a) XRD patterns of the tetracene crystal and nitric acid-sonicated sample. (b) TEM image of a single nitric acid-sonicated wire. The upper-right inset shows its SAED pattern.

regard to compare the electrostatic potential (ESP) maps of the parent TCN and 8-nitrotetracene-5,12-dione (Fig. S2a and b, ESI[†]), which have been recently used to explain the stacked arrangements observed in several fluorinated thiophene and selenophene-based polymers.¹⁰ In the parent TCN molecule, due to the repulsive force of the π -electrons, the face-to-face stacking of TCN molecules is energetically unfavorable and it adopts a herringbone structure instead of a face-to-face stacking structure.¹¹ In contrast, for 8-nitrotetracene-5,12-dione, the electron density on the TCN backbone is significantly reduced by electron-withdrawing carbonyl and nitro groups. Therefore, the C–H/ π intermolecular bonds which can induce an edge-to-face arrangement are weakened and this redistribution of π -electrons favors a face-to-face stacking arrangement.¹² Furthermore, 8-nitrotetracene-5,12-dione possesses a planar structure, as proven by the geometry optimization simulation (Fig. S2c, ESI[†]). The electron-withdrawing, terminal nitro group forms a coplanar agreement with the ring system which facilitates the co-facial π – π stacking and minimizes the lateral offset of the molecular stacking potentially, leading to 1D self-assembly.²

The UV-vis absorption spectra are shown in Fig. 4a. The characteristic peaks of TCN at 374 nm, 396 nm, 417 nm, 443 nm and 473 nm due to $B_{3u} \leftarrow A_g$ transitions vanish after the sonication, which suggests a reordering of the aromatic framework.¹³ The sonicated product with an absorption maximum around 380 nm has a spectral feature which is quite similar to that of 5,12-tetracenequinone.¹⁴

Thermogravimetric analysis (TGA) was performed to examine the thermal stability of TCN and the product obtained by the nitric acid sonication method, as shown in Fig. 4b. The onset decomposition temperature of acid sonicated wires is 275 °C, which is higher than that of TCN around 260 °C. In addition, the peak temperature in the derivative curves of acid sonicated wires is almost 40 °C higher than that of TCN.

It is worth emphasizing that, unlike solutions of TCN that decolorize within 48 hours when left exposed to light and oxygen, acid-sonicated TCN nanowires are remarkably stable in most organic solvents and are resistant to photobleaching even after being exposed to ambient conditions for more than three months. The chemical stability of acid sonicated nanowires may be attributed to the relatively high ionization potential, which is induced by the carbonyl and nitro functional groups, making it more difficult to be oxidized as compared to TCN.^{6,11} The enhanced solubility and stability found in this material afford advantages for solution-processable organic semiconductors.

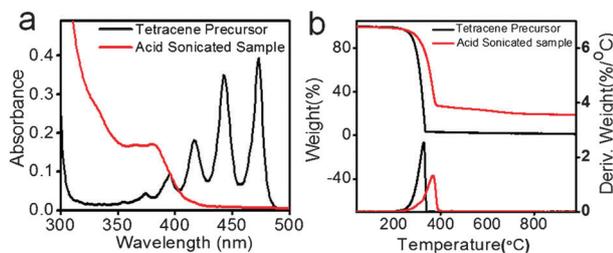


Fig. 4 (a) UV-vis absorption spectra of THF solutions of the tetracene and nitric acid sonicated sample. (b) TGA weight loss curves (upper) and derivative curves (below) of the tetracene and acid-sonicated sample.

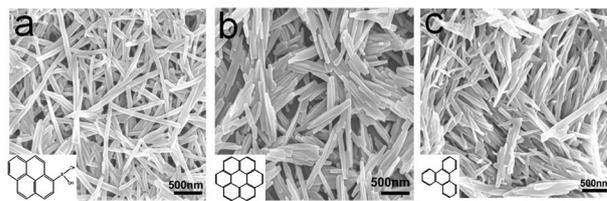


Fig. 5 SEM images of nitric acid-sonicated (a) 1-pyrenylboronic acid nanorods; (b) coronene nanorods and (c) triphenylene nanorods.

We have tested the applicability of this method to 1-pyrenylboronic acid, coronene and triphenylene, and in all cases organic nanorods can be obtained (Fig. 5). It can be generalized that 1D wires can be synthesized from a wide range of molecules which possess planar, non-collapsible aromatic skeletons with non-bulky side chains.

In summary, we report a general method to produce 1D organic nanowires with high yield in a simple, one-pot synthesis process using concentrated nitric acid as the solvent, and with water as the non-solvent. This method has broad validity and can generate derivatized organic wires from a large class of aromatic molecules. Through its strong oxidizing/nitrating ability, it can solubilize a wide range of organic molecules which have limited solubilities in most other solvents and which will pose a challenge for making saturated solutions in organic solvents. Second, the acid sonication functionalizes the organic molecules and modifies the molecular packing in the crystal. In fact, an entirely new class of derivatized organic wires can be generated very easily using this method and thus it has implications for crystal engineering.

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