



Cite this: *Chem. Commun.*, 2017, 53, 1132

Received 12th October 2016,
Accepted 14th December 2016

DOI: 10.1039/c6cc08237h

www.rsc.org/chemcomm

Discrimination of alkyl and aromatic amine vapors using TTF–TCNQ based chemiresistive sensors†

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We report a chemiresistive sensor approach based on a TTF–TCNQ charge transfer material, which can real-time detect and distinguish the vapors of alkyl amine and aromatic amine species under ambient conditions, based on the dramatic difference in the kinetics of the electric current recovery processes after the exposure of the two amine species.

Volatile amines are important biomarkers¹ and common pollutants.^{2–4} The discrimination between alkyl and aromatic amine vapors during detection impacts the quick diagnosis of diseases,^{5–7} food preservation,^{8–11} and environment protection.^{12,13} Compared to the traditional spectroscopic approaches, such as ion mobility spectroscopy, mass spectroscopy and Raman spectroscopy, chemical sensors usually feature good portability and low cost.¹⁴ But due to the similar electron donating nature of alkyl and aromatic amines, the design of chemical sensors to discriminate them meets challenges. For example, the sensors based on photo-induced charge transfer (PCT) may fail to discriminate between the two amines,¹⁵ while the chemical reaction sensors usually require large doses of amines in the reactions.^{16,17} The sensor array approach may be universal for gas detection, but to clearly discriminate such similar vapors, the number of array channels would be unavoidably increased, which increases the work and cost of sensor array preparation, prior analyte training, and complicated data interpreting.^{18,19} Therefore, to improve the detection efficiency, a specific sensor material that can distinguish between alkyl and aromatic amines in real-time is desired for practical applications.

Tetrathiafulvalene (TTF) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) (Fig. 1a) form a 1 : 1 charge transfer complex, TTF–TCNQ, which constitutes a metallic conductor with high charge mobility and density at room temperature.^{20,21} The TTF–TCNQ material has been studied as sensors for

oxidizing or electron-withdrawing gases,^{22,23} taking advantage of the high density of carriers. However, the sensing of reducing gases (*e.g.*, amines) with the same TTF–TCNQ material has been barely reported. In this work, we demonstrate a new approach of using TTF–TCNQ as a chemiresistive material to detect and discriminate alkyl and aromatic amines according to their kinetic difference in the response signals. In our further control experiment, by using the pure TCNQ material (in the morphology of microfibers), we confirmed that the observed sensing discrimination was unique in the TTF–TCNQ system, which probably originated from the different charge transfer interactions of alkyl and aromatic amines at the interface of TTF–TCNQ.

The TTF–TCNQ microfibers were fabricated *via* a surfactant-free solution-based method (Fig. 1b, detailed in ESI†), since the large surface-to-mass ratio of fibril structures is favorable for the chemiresistive sensing^{24,25} (Fig. 1c). The X-ray diffraction (XRD) measurements of these microfibers confirmed the clean cocrystalline structure by comparing with the powder simulated XRD spectra from the previously obtained single crystal structures of TTF, TCNQ and TTF–TCNQ (Fig. S1, ESI†). Then the TTF–TCNQ microfibers were transferred onto interdigitated electrodes (IDEs) patterned on glass to make the chemiresistive sensor chip with uniform surface dispersion of the microfiber materials (Fig. S2, ESI†). Interestingly, when the electric field along the TTF–TCNQ material exceeded $5 \times 10^4 \text{ V m}^{-1}$, the

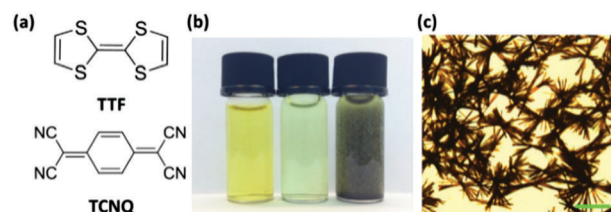


Fig. 1 (a) The molecular structures of TTF and TCNQ. (b) Photos of acetone solution of TTF (left), TCNQ (middle), and as-prepared TTF–TCNQ microfibers (right). (c) An optical microscopy image of TTF–TCNQ microfibers (scale bar = 50 μm).

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† Electronic supplementary information (ESI) available: Experimental details and supporting figures. See DOI: 10.1039/c6cc08237h

conductivity irreversibly decreased to a low state likely due to the thermally caused disorder of the crystal (Fig. S2a, ESI[†]). This phenomenon was observed for the sensor chips with finger gaps of 10 and 100 μm . To avoid this nonlinear I - V region, the TTF-TCNQ chemiresistors were tested under low voltage bias (0.1 V). For the sensing tests, vapors of seven alkyl amines (butylamine, hexylamine, dodecylamine, trimethylamine, benzylamine, cyclohexylamine, and dibutylamine) and five aromatic amines (aniline, *p*-toluidine, *o*-toluidine, *N,N*-dimethylaniline, and 4-fluoroaniline) were selected and diluted to the concentration range of 90–120 ppm for comparative investigations (with the exception of dodecylamine, for which the saturated vapor pressure at room temperature, 18 ppm, was used without further dilution).

Upon the exposure to the amine vapors, the electrical current measured over TTF-TCNQ showed similar and instant decreases, but with the removal of the amine vapors, the recovery of signals showed remarkable differences between the alkyl and aromatic amines (Fig. 2). To make a quantitative comparison between the signal recovery of different amines, we introduced a term named “recovery time” (RT), which was defined as the period of time from the end of amine exposure to the time when $1/e \times 100\%$ (36.8%) of the current change remains. It was found that after the removal of aromatic amines the decrease in current quickly and almost fully recovered, with RTs less than 3 s (Table 1). So the chemiresistive sensing response to aromatic amines can be considered as a reversible process, implying that the interaction between aromatic amines and the sensor material is relatively weak, likely in the order of van der Waals force, which usually dominates the intermolecular interaction in reversible chemical sensors.²⁶

In contrast, all the alkyl amines led to almost irreversible current decreases, as observed during the time frame of testing, 120 s, regardless of the molecular weights (butylamine or dodecylamine) or the steric conformations (primary, secondary or tertiary) of the amines (Table 1). To this regard, the RTs for alkyl amines are simply marked as > 120 s, as shown in Table 1.

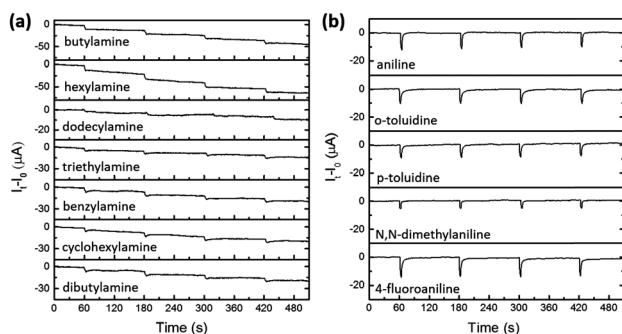


Fig. 2 Change of electrical current of TTF-TCNQ chemiresistors upon exposure to the vapor of (a) alkyl amines (from top to bottom): butylamine (110 ppm), hexylamine (120 ppm), dodecylamine (18 ppm), triethylamine (100 ppm), benzylamine (95 ppm), cyclohexylamine (90 ppm), and dibutylamine (100 ppm), and (b) aromatic amines (from top to bottom): aniline (100 ppm), *o*-toluidine (100 ppm), *p*-toluidine (100 ppm), *N,N*-dimethylaniline (100 ppm), and 4-fluoroaniline (100 ppm). Each amine was tested for four consequent cycles. The bias voltage was 0.1 V.

Table 1 Comparison of recovery times (RTs) of the TTF-TCNQ chemiresistor when exposed to different amine vapors (from data in Fig. 2)

Alkyl amines	RT (s)	Aromatic amines	RT (s)
Butylamine	> 120	Aniline	1.0 ± 0.1
Hexylamine	> 120	<i>p</i> -Toluidine	2.6 ± 0.2
Dodecylamine	> 120	<i>o</i> -Toluidine	1.6 ± 0.3
Triethylamine	> 120	<i>N,N</i> -Dimethylaniline	0.6 ± 0.1
Benzylamine	> 120	4-Fluoroaniline	2.1 ± 0.2
Cyclohexylamine	> 120		
Dibutylamine	> 120		

Clearly, the interaction between alkyl amines and the sensor material should be much stronger than that between aromatic amines and the same material. Considering the high electron deficiency of TCNQ (a strong electron acceptor) and the strong basicity (or nucleophilicity) of amines, a donor-acceptor type interaction would be expected between amines and TCNQ, either in the format of a neutral complex or further ionic charge separation pair amine⁺-TCNQ⁻ (with the latter being more strongly bound and much harder to dissociate). As to be further discussed below, the irreversible response of alkyl amines was likely due to their stronger basicity, which affords the formation of the charge pair through steady state charge separation. Nonetheless, bindings with both types of amines to TCNQ led to fierce competition to the TTF-TCNQ complex, and thus a decrease in conductivity (or current) as observed in Fig. 2.

Indeed, there is the possibility that the observed reversible response of aromatic amines was due to the steric hindrance caused by the aromatic rings, which often weakens the intermolecular interactions. To exclude this possibility, we selected an alkyl amine that is substituted with a benzene group, namely benzylamine. It was interesting to observe that this amine gave a similar irreversible response to other alkyl amines shown in Fig. 2a, implying that the strong donor-acceptor interaction (dominated by the amine moiety) sufficiently surpasses the steric effect. Nonetheless, the steric hindrance effect of side groups was indeed observed among the aromatic amines themselves as shown in Fig. 2b, wherein the sensing response magnitude of *N,N*-dimethylaniline was about 60% lower and the RT was 40% shorter than the unsubstituted aniline tested under the same concentration. Such a significant difference in response can be reasonably attributed to the bulkier dimethyl groups. Moreover, to exclude the possibility that the observed different responses may be caused by the variation between devices (*e.g.*, fabrication fluctuations), we used a single TTF-TCNQ chemiresistor sensor to test both aniline and hexylamine (representing aromatic and alkyl amine, respectively) by exposing to each amine three times consequently as shown in Fig. S4 (ESI[†]). The results demonstrated good consistency between the three times of exposure to the same amine, and more importantly the dramatic difference in signal recovery (reversible *vs.* irreversible) still remains between the aromatic and alkyl amines, the same as observed in Fig. 2. It is thus confirmed that aromatic and alkyl amines can be distinguished from the reversible *vs.* irreversible signal recovery as measured over the TTF-TCNQ chemiresistor.

To study the different sensing responses between alkyl and aromatic amines, we re-performed the experiments under the same setups, but using the pure TCNQ material as the chemiresistive sensor, which was fabricated by drop-casting a TCNQ solution onto the same IDEs. The self-assembly of TCNQ molecules led to the formation of microfibers, whose dimension sizes were similar to those of the microfibers of TTF-TCNQ (Fig. S5, ESI[†]). As a strong electron acceptor, TCNQ functions as a typical n-type semiconductor with electrons as the major charge carrier.²¹ Binding with electron donors like amines would increase the electrical conductivity of TCNQ through charge transfer interaction. Indeed, as shown in Fig. 3, both alkyl and aromatic amine vapors caused a significant increase in electrical current of TCNQ, in sharp contrast to the decrease in current observed for TTF-TCNQ (Fig. 2). Another difference from the case of TTF-TCNQ was that all the amines demonstrated quick reversible responses (Fig. 3), with the RTs comparable between alkyl and aromatic amines (Table 2). This observation indicates that the binding of the two types of amines with TCNQ was similar in strength, likely in the format of a donor-acceptor complex, which was reversible for dissociation. However, for TTF-TCNQ the surface binding of alkyl amines was much stronger, leading to an irreversible sensing response (Fig. 2), while the aromatic amines retain about the same reversible response with RTs about the same order as for pure TCNQ (Tables 1 and 2). Such a dramatic difference observed for alkyl amines between TTF-TCNQ and pure TCNQ can be attributed to the different polarities at the surface of the two materials.

As a typical charge transfer (metallic) material, the degree of charge transfer was reported over 0.5 and its interface was believed to be more polar than that of the pure, neutral organic materials such as TCNQ.^{27–29} In general, a polar medium (solvent) is conducive to stabilizing the geminate pair of charge separation species such as TCNQ[−]-amine⁺ in this study.^{30–32} It is likely that the observed irreversible response of alkyl amines at TTF-TCNQ was due to the local stabilization of the charge

Table 2 Comparison of recovery times (RT) of the TCNQ chemiresistor when exposed to different amine vapors (from data in Fig. 3)

Alkyl amines	RT (s)	Aromatic amines	RT (s)
Butylamine	0.6 ± 0.1	Aniline	1.8 ± 0.2
Hexylamine	2.7 ± 0.2	<i>p</i> -Toluidine	2.5 ± 0.1
Dodecylamine	17 ± 2	<i>o</i> -Toluidine	3.0 ± 0.2
Triethylamine	32 ± 7	<i>N,N</i> -Dimethylaniline	3.6 ± 0.2
Benzylamine	6.6 ± 0.3	4-Fluoroaniline	2.4 ± 0.2
Cyclohexylamine	2.2 ± 0.2		
Dibutylamine	8.2 ± 0.8		

separation pair of TCNQ[−]-amine⁺, for which the strong electrostatic attraction makes it hard to dissociate. On the other hand, the aromatic amines would be in favor of forming a neutral donor-acceptor complex with TCNQ at the same interface, thus making them reversible for desorption. To support such a polarity effect on interfacial binding, we carried out comparative UV-vis spectral measurements for aniline and hexylamine (representing aromatic and alkyl amine, respectively) in a mixture with TCNQ in three different organic solvents, acetonitrile, chloroform, and toluene, representing polar, medium polar and non-polar mediums, respectively. As shown in Fig. S6 (ESI[†]), in the polar solvent, like acetonitrile, both aniline and hexylamine formed the anionic radical of TCNQ[−], as confirmed by the characteristic absorption bands in the visible region of 650–900 nm.³³ The higher concentration of TCNQ[−] produced with hexylamine was mainly due to its stronger basicity (or electron donating power). With decreasing the polarity from acetonitrile to chloroform, a significant amount of TCNQ[−] could still be detected with hexylamine, whereas aniline generated only the neutral donor-acceptor complex (characteristic of the broad absorption in the visible range).³⁴ With further decreasing the solvent polarity to toluene, neither of the two amines efficiently produced the charged species, indicating the lack of stabilization of the charge separation. The results of Fig. S6 (ESI[†]) revealed clearly that the charge separation species of TCNQ with alkyl amines formed much more easily than that with aromatic amines, so in a certain polarity range (for example, in chloroform), the charge transfer complexes between TCNQ and alkyl amines could develop into ions, while that with aromatic amines still stayed in the neutral state. Such different dependences on polarity may suggest that alkyl amines are bound to TTF-TCNQ in the format of a TCNQ[−]-amine⁺ pair at the interface, while the aromatic amines took the format of a neutral donor-acceptor complex. The stronger electrostatic interaction of TCNQ[−]-amine⁺ explains the irreversible sensing response observed for the alkyl amines, and the relatively weak complexation between aromatic amine and TCNQ is consistent with the observed reversible response in both TCNQ and TTF-TCNQ chemiresistors. The strong charge transfer interaction between alkyl amine and TCNQ was also evidenced by infrared spectroscopy (IR) characterization of the TTF-TCNQ cocrystal³⁵ mixed with dodecylamine (Fig. S7, ESI[†]). Moreover, due to the competitive D-A interaction with TCNQ between TTF and adsorbed amine, the desorption of amines from the surface of pure TCNQ would be slower than that from the surface of TTF-TCNQ cocrystal.

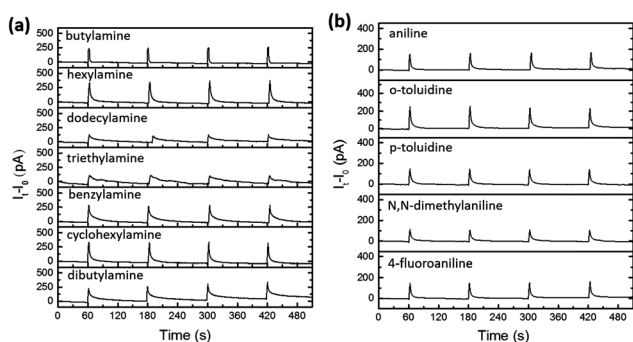


Fig. 3 Change of electrical current of TCNQ chemiresistors upon exposure to the vapor of (a) alkyl amines (from top to bottom): butylamine (110 ppm), hexylamine (120 ppm), dodecylamine (18 ppm), triethylamine (100 ppm), benzylamine (95 ppm), cyclohexylamine (90 ppm), and dibutylamine (100 ppm), and (b) aromatic amines (from top to bottom): aniline (100 ppm), *o*-toluidine (100 ppm), *p*-toluidine (100 ppm), *N,N*-dimethylaniline (100 ppm), and 4-fluoroaniline (100 ppm). Each amine was tested for four consequent cycles. The bias voltage was 10 V.

This is consistent with the signal recovery data shown in Tables 1 and 2, where the RTs of aromatic amines measured on the TTF-TCNQ material are overall faster than those measured on the pure TCNQ material under the same experimental conditions.

It was also interesting to note that the recovery time of alkyl amines on TCNQ is strongly dependent on the molecular weight, *i.e.*, the larger the molecule the longer the recovery takes. For example, among the three primary amine analogues tested, the RT was determined to be 0.6 s for butylamine, 2.7 s for hexylamine, and 17 s for dodecylamine (Table 2), showing a clear trend of increase with molecular weight. Similar molecular weight dependence of signal recovery kinetics was also observed for other chemiresistive sensors.²⁶ The slow recovery of large analytes is mostly due to the more difficult desorption process. For the similar reason, larger molecules are easier to condense on the surface, resulting in more efficient increase in the sensor signal. For example, under the similar vapor concentrations, the signal amplitude generated by butylamine was about 50% smaller than hexylamine. Such a molecular weight effect may be incorporated into the sensor systems to enhance the differential sensing by comparing the recovery kinetics.

In summary, we developed a chemiresistive sensor based on the TTF-TCNQ charge transfer material, which demonstrated dramatically different sensing responses towards vapors of alkyl and aromatic amines, with the former being irreversible (*i.e.*, no signal recovery) and the latter quickly reversible, in the time range of seconds. This remarkable difference in signal recovery can be potentially used to discriminate the two types of amines, helping in enhancing the differential sensing capability of sensor arrays. The unrecoverable response of alkyl amines was attributed to the strong interfacial binding through the charge separation pair, TCNQ⁻-amine⁺, which can be stabilized at the polar surface of the TTF-TCNQ material. In comparison, the nonpolar surface of the pure TCNQ material does not favor the existence of the charge separation state, and the surface binding is mostly through the neutral donor-acceptor complex, which is relatively easy to dissociate, resulting in a reversible sensing response. This work implies that the interfacial charge transfer interaction can be employed as a unique design rule to develop new sensor materials to expand the differential sensor arrays, in order to enhance the detection selectivity.

This work was supported by the funding from the NSF (CHE 0931466 and CBET 1502433), DHS Science and Technology Directorate (2009-ST-108-LR0005) and the USTAR Program.

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