

Single Electron Transfer-Driven Multi-Dimensional Signal Read-out Function of TCNQ as an “Off-the-Shelf” Detector for Cyanide

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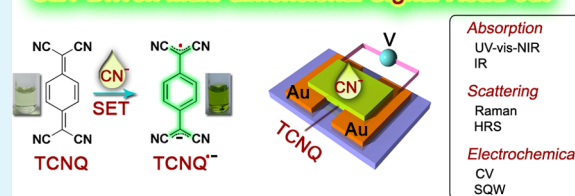
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S Supporting Information

ABSTRACT: Herein we report the first applications of TCNQ as a rapid and highly sensitive off-the-shelf cyanide detector. As a proof-of-concept, we have applied a kinetically selective single-electron transfer (SET) from cyanide to deep-lying LUMO orbitals of TCNQ to generate a persistently stable radical anion (TCNQ^{•-}), under ambient condition. In contrast to the known cyanide sensors that operate with limited signal outputs, TCNQ^{•-} offers a unique multiple signaling platform. The signal readability is facilitated through multichannel absorption in the UV–vis–NIR region and scattering-based spectroscopic methods like Raman spectroscopy and hyper Rayleigh scattering techniques. Particularly notable is the application of the intense 840 nm NIR absorption band to detect cyanide. This can be useful for avoiding background interference in the UV–vis region predominant in biological samples. We also demonstrate the fabrication of a practical electronic device with TCNQ as a detector. The device generates multiorder enhancement in current with cyanide because of the formation of the conductive TCNQ^{•-}.

KEYWORDS: single electron transfer, radical anion, signal read-out, TCNQ, cyanide, off-the-shelf detector

SET Driven Multi-dimensional Signal Read-out



1. INTRODUCTION

7,7,8,8-Tetracyanoquinodimethane (TCNQ) and its derivatives continue to attract enormous interest in the areas of low-dimensional organic conductors, magnetic, nonlinear optical and multiproperty based charge-transfer materials.^{1,2} Also it provides an alternative as a biodegradable component to the semiconductor industry. However, despite the detailed understanding of the opto-electronic properties of TCNQ and its radical anion (TCNQ^{•-}), it has rarely been applied as a platform for signal transduction applications. On the other hand, conductive and semiconductive molecular systems have recently been shown to be excellent platforms for successful incorporation into electronic devices for sensing explosives and other analytes.³ Recently, we have been interested in the design and synthesis of small organic molecules that can rapidly undergo electron transfer (ET) under controlled chemical/redox stimulation and form persistent to stable radical anions and cations.⁴ Molecular architecture, functional group disposition, and its steric protection along with appropriate HOMO–LUMO levels play an integral part in stabilization of these radical ions.^{4c,d} It has been our endeavor to develop these stable radical ion probes as next-generation of signal transducing agents as they provide multidimensional signal outputs, rarely found in conventional sensor probes.^{4a,b} In this context, it occurred to us that TCNQ with its low-lying LUMO levels

would offer an excellent platform for multidimensional signal read-out ability.

Herein, we report the first application of TCNQ as a highly sensitive and selective cyanide detector. An instantaneous reaction-based single-electron transfer (SET) from cyanide to TCNQ is utilized in developing a highly stable radical anion probe. This versatile probe generates highly differentiable signal outputs that are readable by both absorption and scattering based signal outputs e.g. optical outputs covering the whole UV–vis–NIR range and signal read-out by Raman and hyper-Rayleigh scattering (HRS) based techniques. The ET from cyanide was found to be kinetically highly selective in comparison to closely related anions like azide, acetate, dihydrogenphosphate, fluoride and thiocyanate. Finally, two different types of practically applicable TCNQ based electronic devices could be fabricated that produces several order of magnitude higher current in the presence of cyanide.

Anion recognition and sensing has received considerable interest because of the pivotal role anions play in the areas of biology, environmental hazards, medicine, catalysis, etc.⁵ Among the anions, cyanide is the most toxic as it inhibits oxygen utilization of cells. Cyanide sensors have been designed

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based on H-bonding,^{6a-c} complexation to Lewis acids,^{6d-f} time-gated fluorescence,^{6g} metal ion complexes,^{6h,i} quantum dots,^{6j} Au nanoparticle,^{6k} sensing on Al₂O₃-based thin-film matrix,^{6l} reaction,^{7a-kl} and displacement-based⁸ approaches.

In general, cyanide sensors require multiple synthetic steps increasing the effective cost of the sensor. In addition, time-lag in sensing, elevated temperatures, biphasic solvent mixtures, inability to differentiate closely related anions like acetate, fluoride, or hydroxide are major impediments in sensing cyanide. Also, limited number of readable signal output drastically hinder on-the-spot precise sensing of cyanide because of weak signal outputs, signal interference and background overlap, instrumental artifact, etc.

Off-the-shelf detectors that can circumvent these problems and offer attractive multimodal signal transduction pathways⁹ (STPs) are greatly desired for advanced sensing applications. Recent results on multimodal signaling agents suggests that a single STP does not possess all the required merits for rapid, comprehensive and precise sensing.^{4a,b} We and subsequently other groups have shown that anion selective single or multiple electron transfer can be achieved in rationally designed low-LUMO organic molecules.^{4,10} We have been interested in applying these persistent radical ions as new generation of probes and utilize them in an effective way to achieve multimodal STPs.⁴ For instance, a SET process in an organic molecule with functional groups, e.g., carbonyl, imide, etc. is generally characterized by multichannel signature absorption peaks in the vis-NIR region because of the low energy $D_0 \rightarrow D_n$ electronic transition.

2. EXPERIMENTAL SECTION

Chemicals were sourced from Fluka, Sigma-Aldrich, Spectrochem India or Thomas-Baker-India and were used as received. The tetrabutylammonium salts of CN⁻, F⁻, SCN⁻, OAc⁻, NO₃⁻, HSO₄⁻, BF₄⁻, and PF₆⁻ were sourced from Sigma-Aldrich. Tetrabutylammonium salts of Cl⁻, ClO₄⁻ were procured from Fluka. Tetrabutylammonium salts of Br⁻, I⁻, H₂PO₄⁻, and OH⁻ and the reducing anions were procured from Spectrochem, India.

Spectroscopy. UV-vis-NIR spectra were recorded on a JASCO V-670 model, with all the reported spectra taken either instantaneously or in a time-dependent manner. The spectroscopic experiments were carried out in UV grade MeCN and THF, which were sourced from Spectrochem, India. Raman and Infrared spectra were recorded using a Varian 7000 FT-RAMAN & FT-IR instrument. For the hyper Rayleigh scattering (HRS) technique, a Q-switched Nd:YAG laser that delivers a fundamental beam at 1064 nm was used as the incident light source.

Electrochemistry. Cyclic voltammetry (CV) and square wave voltammetry (SWV) were carried out using a computer controlled potentiostat (CHI 650C) and a standard three electrode arrangement that consisted of both platinum working and auxiliary electrodes and a saturated calomel reference electrode (SCE). All electrochemical measurements were carried out in Ar-purged dry MeCN or MeCN/H₂O (9:1 v/v) with 0.1 M TBAClO₄ as the supporting electrolyte. The scan rate for the measurements was typically 200–300 mV/s. The parameters for the SWV set as follows: freq. = 15 Hz, increment = 4 mV, amplitude = 25 mV.

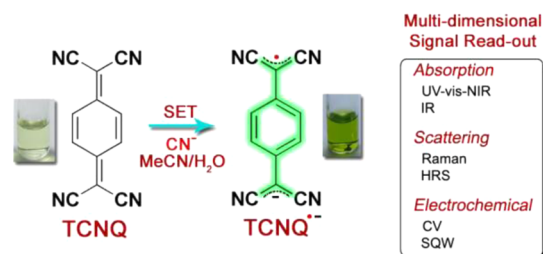
Device Fabrication. The two-terminal device was fabricated in planar geometry configuration on a glass substrate. Glass substrate was initially cleaned with methanol, acetone and then trichloroethylene at 100 °C. Two probe planar configurations were fabricated using the well-known shadow masking technique. The channel length was fixed at ~30 μm and dimensions of 3 × 3 mm², respectively. Thin film of Au (30 nm) was evaporated on cleaned glass substrates using vacuum evaporation technique under a base pressure of 2 × 10⁻⁶ Torr and at the rate of 0.4 Å/s in a thermal evaporation unit. *I*-*V* measurements

were carried out in rough vacuum (1 × 10⁻² mbar) at room temperature using Keithley pico-ammeter and Agilent voltage source.

3. RESULTS AND DISCUSSION

TCNQ offers plethora of advantages over other conventional sensors as an eco-friendly, abundantly available off-the-shelf detector for cyanide. Its highly sensitive and selective multidimensional signal addressability and its efficient performance in the form of an electronic device are some of the unique features (Scheme 1). TCNQ in a mixed aqueous solution of

Scheme 1



MeCN/H₂O (9:1 v/v) was tested for its ability to colorimetrically differentiate cyanide from a diverse variety of 15 anions, strongly reducing anions, and an organic donor. In the presence of cyanide, an instantaneous colorimetric change from a colorless to a bright green solution was observed, whereas other anions remained silent (Figure 1).

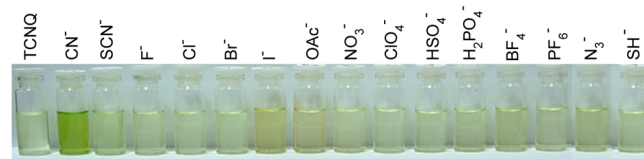


Figure 1. Instantaneous photographs of vials containing TCNQ and TCNQ with anions in MeCN/H₂O (9:1 v/v) depicting the colorimetric differentiation of cyanide (TCNQ, 2 × 10⁻⁴ M; and anions, 4 × 10⁻⁴ M).

With very few exceptions,^{6c,7k} sensing of cyanide has been limited to only tetrabutylammonium (TBA) as the counterion, while KCN/NaCN generally remains silent because of solvation in aqueous/mixed aqueous systems and solubility problems in pure organic media. In sharp contrast, TCNQ detects KCN with comparable efficiency as that of TBACN (Supporting Information, Figure S1). Further, TCNQ offers cyanide detection with increasing amounts of H₂O in MeCN as well as in nonpolar organic media like chloroform with high optical contrast (Supporting Information, Figure S2).

We then investigated the spectroscopic characteristics of TCNQ and the changes it undergo upon sensing of cyanide. In presence of incremental amounts of cyanide, the π - π^* transition for TCNQ, which appears at 395 nm decreases sharply with the appearance of new peaks at 480, 680, 740, and 840 nm (Figure 2). The peak positions and the intensity ratios match completely with the signature peaks of the radical anion (TCNQ•⁻). In case of TCNQ, the lowest energy $1^1A_g \rightarrow 1^1B_{1u}$ electronic transition (eT) is broad and vibrationally unresolved. In contrast, the lowest energy band for TCNQ•⁻ associated with the $1^2B_{2g} \rightarrow 1^2B_{3u}$ eT located at 840 nm shows moderately resolved vibronic structure. Similarly, the 740 and 680 nm eTs

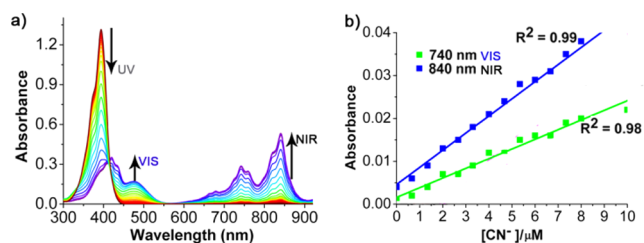


Figure 2. UV-vis-NIR spectra of TCNQ with incremental addition of cyanide (TCNQ, 2×10^{-4} M) in MeCN/H₂O (9:1 v/v).

for the TCNQ^{•-} have also been assigned by different theoretical groups.¹¹ The clear spectral plot along with the presence of isosbestic points signifies an uncluttered SET process from cyanide to TCNQ (Figure 2a). Therefore, spontaneous generation of such multichannel optical outputs encompassing UV, visible, and NIR region becomes attractive for precise detection of cyanide (Figure 2b).

Also, the highly intense NIR absorption at 840 nm should provide a platform to sense cyanide in biological systems avoiding background interference in the UV-visible region. The TCNQ^{•-} probe formed in the presence of cyanide was found to be stable in presence of OH⁻ as confirmed from the spectral fingerprints in the region of 300–900 nm (Supporting Information, Figure S3). In addition this probe was stable up to pH 4, providing a large pH window for investigation (Supporting Information, Figure S4).

It is important to note that the TCNQ^{•-} radical anion and the (TCNQ^{•-})₂ dimer can be easily distinguished by their signature absorption characteristics. The dimer is formed only at high concentrations in water and has a characteristic broad absorption band at 643 nm,¹² which makes it clearly differentiable from the multichannel UV-vis-NIR absorption characteristics of TCNQ^{•-}.

Cyanide detection was also readily possible using FT-IR spectroscopy which supported the SET driven formation of the TCNQ^{•-} (2180 cm^{-1} for $\nu(\text{C}\equiv\text{N})$) as compared to TCNQ (2220 cm^{-1}) (Supporting Information, Figure S5).

Signal read-out from the known cyanide sensors are overwhelmingly biased toward absorption or emission-based processes. Such signal transduction often leads to background interference and overlapping of fingerprint regions of the spectra. TCNQ on the other hand presents unique opportunity to investigate signal read-out by noninterfering and sensitive scattering based techniques (Raman and HRS). We found that Raman spectroscopy signals the cyanide driven formation of the TCNQ^{•-} radical anion from the neutral TCNQ. The three symmetric modes ν_3 , ν_4 , and ν_5 of TCNQ appearing at 1600 (C=C stretch), 1450 (exoring C=C stretch) and 1234 cm^{-1} (C-H bending) undergo large shifts and bands appear at 2189, 1612, 1388, and 1192 cm^{-1} , consistent with the formation of the TCNQ^{•-} probe (Figure 3a, b).¹³

In addition, TCNQ in the presence of cyanide shows 3-fold enhancement of the second harmonic intensity (SHI), which was measured by the highly sensitive HRS technique (Figure 3c). It should be noted that small interference in the SHI from the weak absorption of the TCNQ^{•-} at 532 nm cannot be ruled out. The large enhancement in the SHI is in line with the recent calculation that predicts high first and second hyperpolarizabilities of TCNQ^{•-}.^{14a} It is to be noted that HRS technique has rarely been applied for specific detection of anions and modulation of the nonlinear optical (NLO) property of NLO

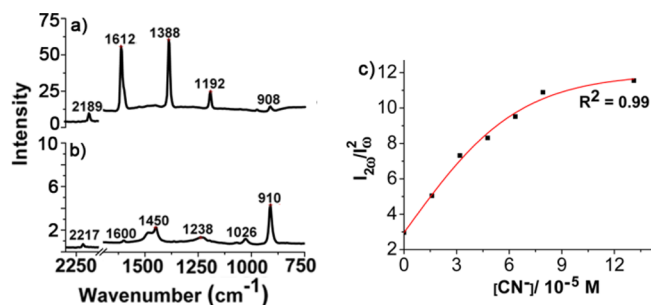


Figure 3. Raman spectra of (a) TCNQ^{•-}, (b) TCNQ in MeCN/H₂O (9:1 v/v) (TCNQ, 1×10^{-2} M; and CN⁻, 2×10^{-2} M), and (c) second harmonic intensity as a function of concentration of CN⁻ in THF (TCNQ, 1.2×10^{-4} M in THF).

active probes.^{14b,c} Thus formation of the stable TCNQ^{•-} allowed us to apply two sensitive scattering-based methods successfully to detect cyanide with highly modulated signal outputs.

Apart from the multichannel absorption and scattering based techniques, electrochemical outputs applying cyclic voltammetry (CV) and square wave voltammetry (SWV) could be applied to detect cyanide and differentiate from other closely related anions. Thus, the first and second reduction peaks of TCNQ show a shift of 10 mV and undergoes a decrease of 1.5-fold in current with cyanide, whereas for competitive anions like acetate, fluoride, etc., no shifts in the reduction potential and negligible decrease in current was observed (Supporting Information, Figure S6).

The multiple optical outputs, namely the three hyperchromic absorptions encompassing the visible region (435 and 740 nm), NIR region (840 nm) and one hypochromic absorption in the UV region (390 nm) was applied to determine the selectivity of cyanide (Figure 4a). Cyanide shows 30-times more selectivity

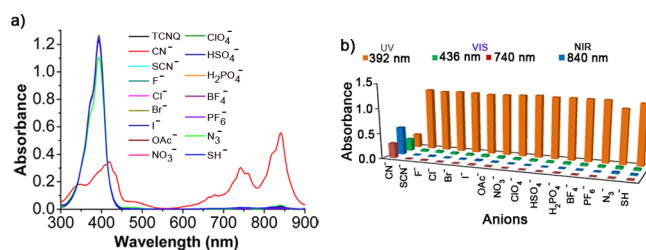


Figure 4. (a) UV-vis-NIR spectra of TCNQ in presence of various anions; (b) Selectivity profile of cyanide applying UV-vis-NIR optical channels (TCNQ, 2×10^{-4} M; and anions, 4×10^{-4} M in MeCN/H₂O (9:1, v/v)).

compared to other anions (Figure 4b).¹⁵ This selectivity was kinetic in nature and interference from acetate, azide, and fluoride could be observed only after monitoring for a long period of time (30 min to 4.5 h) because of the slow ET from these anions to TCNQ (Supporting Information, Figure S7a, b). We also examined the possibility of interference of the ET with the mixed anions (Supporting Information, Figure S7c). The selectivity for cyanide was further compared with other reducing anions like dithionite, sulfite, thiosulfate and nitrite. In all the cases, cyanide was found to be more selective (Supporting Information, Figure S8). Compared to cyanide, we observed weak ET from strong organic donor like tetrathiafulvene (TTF) even after 60 min under our solvent conditions (SI, Figure S9). Also, under our mixed aqueous

condition, metals (Na, K, etc.) with reducing character can be ruled out as a source of interference. Further, a highly attractive sensitivity of $0.5 \mu\text{M}$ (12.5 ppb) for cyanide could be easily established (Figure 2a). Therefore, this simple detector operates 4-fold lower than the WHO set cyanide standard in drinking water ($1.9 \mu\text{M}$).¹⁶ Further, addition of NOBF_4 could regenerate 60% of TCNQ from the $\text{TCNQ}^{\bullet-}$ radical anion. The high specificity toward cyanide can be explained by its strong ability to donate a single electron to the low-lying LUMO level of TCNQ and also because of the well-known α -effect.¹⁷ The stability of radicals α to a lone pair is available to cyanide in contrast to other anions studied here.

Detection of cyanide has also significant implication for homeland security as a chemical warfare. Therefore, there is a strong need for developing devices that are cost-effective, portable, easy to fabricate, and rapidly responsive. In this respect, TCNQ offers a promising platform with regards to a rapid and sensitive on-the-chip detection system. To achieve this goal, we fabricated two devices, Device-1 and Device-2. Device-1 was fabricated with two $3 \times 3 \text{ mm}$ Au electrodes, thickness of 30 nm and channel length $\sim 30 \mu\text{m}$, deposited over a glass surface using vacuum deposition technique (Figure 5a).

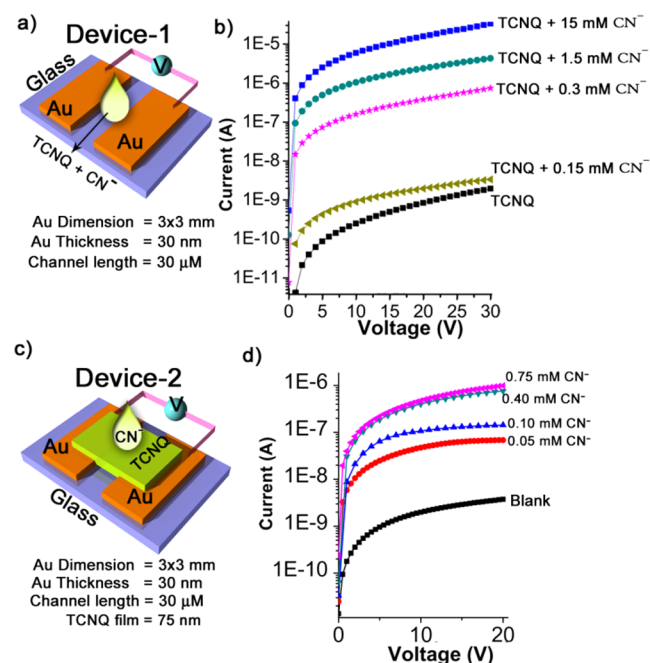


Figure 5. Schematic representation of (a) Device-1 and the respective (b) I - V profiles of TCNQ (15 mM) and different concentrations of CN^- (0.15–15 mM). Schematic representation of (c) Device-2 and the respective (b) I - V profiles at different concentrations of CN^- (0.05–0.75 mM); “blank” indicates the I - V response of Device-2 with $2 \mu\text{L}$ of $\text{MeCN}/\text{H}_2\text{O}$ (9:1 v/v).

Device-1 exhibits a change in I - V response upon exposure to cyanide (Figure 5b). First, we determined the I - V response of TCNQ in $\text{MeCN}/\text{H}_2\text{O}$ (9:1 v/v) solution. This device could even differentiate 0.01 equivalents of cyanide by observing a current in the range of 1×10^{-9} A which is significantly higher than that of the current obtained with TCNQ solution. With 0.1 equivalents of cyanide, the current output increases by more than three-orders of magnitude. Saturation in the current was seen with an increase in concentration of the cyanide probably due to the saturation of the number of carriers between the

electrodes (Supporting Information, Figure S10). The large increase in current response with gradual increase in the cyanide concentration is predominantly due to the formation of the conductive $\text{TCNQ}^{\bullet-}$.

Next, we modified the Device-1 by controlled vacuum deposition of a TCNQ film ($\sim 75 \text{ nm}$) over the Au electrodes at a deposition rate of 1.0 nm/sec (Figure 5c). Device-2 was exposed to respective solutions of anions and measured the I - V characteristics (Figure 5d).

The TCNQ film over the channel of Device-2 was treated with 0.05 mM cyanide solution and transferred to high vacuum chamber. I - V response was taken after 10 min and a current of 1×10^{-8} A was recorded, which is more than one order higher compared to that of the blank TCNQ. Upon increasing the cyanide concentration to 0.4–0.75 mM, current of Device-2 is dramatically increased to 1×10^{-7} A. The higher sensitivity of Device-2 compared to Device-1 could be attributed to the well-ordered molecular packing of the vacuum deposited film of TCNQ (Figure 5d). Furthermore, we could demonstrate the high degree of selectivity of Device-2 against other basic anions such as AcO^- , F^- , H_2PO_4^- , etc. (Supporting Information, Figure S11). The current achieved in the case of cyanide was several-fold higher than AcO^- , F^- , H_2PO_4^- . This loss in selectivity is due to the significant lag-time involved in recording the I - V response. These results are in line with that of the kinetic selectivity obtained by the colorimetric and spectroscopic studies done after 30 min.

The I - V characteristic in the Device-1 and Device-2 confirmed ohmic nature of the conductivity of the devices (Supporting Information, Figure S12). It is to be emphasized that such easy to fabricate on-the-chip electronic devices are not common even with the most sophisticated sensor molecules, functioning in the diamagnetic or neutral mode.

The mechanism of the detection is based on a SET process from the cyanide to the low-lying LUMO orbitals of cyanide (Scheme 1). This results in the formation of the radical anion, which gives signature spectroscopic characteristics and the conductivity. The ET in case of competing anions like AcO^- , F^- , H_2 , and PO_4^- being kinetically slower cyanide is detected by kinetic differentiation. Therefore, TCNQ offers a highly efficient way of transducing the SET-based chemical event from cyanide to multidimensional spectroscopic signal outputs as well as electrical signal output.

4. CONCLUSION

In summary, we have demonstrated that a rapid SET based reaction of cyanide anion with TCNQ can be utilized to generate multimodal signal outputs. The signal read-out ability of the $\text{TCNQ}^{\bullet-}$ radical anion was found to be outstanding and ranges from multichannel UV-vis-NIR absorption to scattering (Raman and HRS)-based processes. In particular, the intense 840 nm NIR absorption peak can be useful for detection of cyanide anion, minus the background interference found in biological samples. Importantly, the conductive property of $\text{TCNQ}^{\bullet-}$ has been utilized to fabricate a highly sensitive portable electronic device. The device efficiently converts the SET based chemical event into an electrical signal output with multiorder differentiation between closely related anions.

■ ASSOCIATED CONTENT

■ Supporting Information

UV-vis-NIR spectra and photographs of TCNQ with anions, FT-IR spectra of TCNQ with CN⁻, SWV titration of TCNQ with anions, I-V profiles of Device-2 in presence of various anions and other supplementary data. "This material is available free of charge via the Internet at <http://pubs.acs.org>."

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Notes

The authors declare no competing financial interest.

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