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Laboratory Experiment

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# Opposites Attract: Organic Charge Transfer Salts

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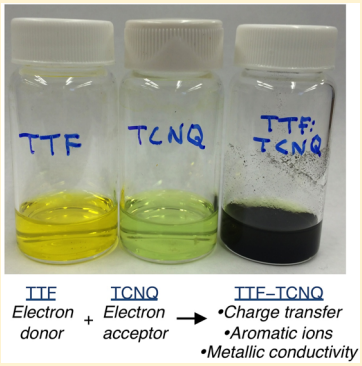
Supporting Information

**ABSTRACT:** A laboratory experiment is described that introduces second-year undergraduate organic chemistry students to organic electronic materials. The discovery of metallic conductivity in the charge transfer salt tetrathiafulvalene tetracyanoquinodimethane (TTF−TCNQ) is a landmark result in the history of organic electronics. The charge transfer interaction is not only relevant to real-world applications, it also has pedagogical value related to understanding redox chemistry, aromaticity, and conjugation. In this laboratory experiment, students carry out a solution phase synthesis of TTF−TCNQ from the molecular precursors TTF and TCNQ. The product is characterized by infrared spectroscopy. Characteristic changes in absorption frequency are correlated with increased aromatic character and observable lengthening of the nitrile bond. In an optional extension, students experimentally verify the great difference in conductivity between the charge transfer salt and the neutral parent components.




**KEYWORDS:** *Second-year undergraduate, upper-division undergraduate, organic chemistry, interdisciplinary/multidisciplinary, hands-on learning/manipulatives, aromatic compounds, conductivity, IR spectroscopy, materials science, synthesis*

The application of conductive organic materials to electronic devices is an important current focus of both academic and industrial research. In recognition of that prominence, a laboratory experiment has been developed for second-year undergraduate organic chemistry students in which students synthesize the charge transfer salt tetrathiafulvalene-tetracyanoquinodimethane (TTF−TCNQ). Though developed for an organic chemistry course, the experiment can easily be modified for introductory and physical chemistry courses by including photophysical characterization. In 1973, Ferraris and Cowan[1] and Heeger[2] showed that TTF[3] and TCNQ (Figure 1a) formed a 1:1 stoichiometry ionic organic salt with remarkable conductivity. This was the first observation of conductivity comparable to a metal in an organic material.[4] Notably, bulk TTF and TCNQ are by themselves insulators. A general design principle in organic electronics was established: charge-transfer interactions between electron donors and acceptors result in enhanced optical and electronic properties.[5] Heeger was later awarded the 2000 Nobel Prize in Chemistry with MacDiarmid and Shirakawa for the discovery of conductive polymers.

Despite the importance of organic electronics in current chemical research, this topic is underrepresented in undergraduate laboratory experiments and in this Journal. The experiment described herein addresses this gap and complements recent publications on intramolecular charge transfer[7] and conductive polymers.[8−11] A green mechanochemical synthesis of a tetrathiafulvalene-chloranil salt has also been reported.[12] In intermolecular charge transfer, only noncovalent interactions bind the donor and acceptor units, whereas in intramolecular charge transfer, at least one covalent bond links the units.

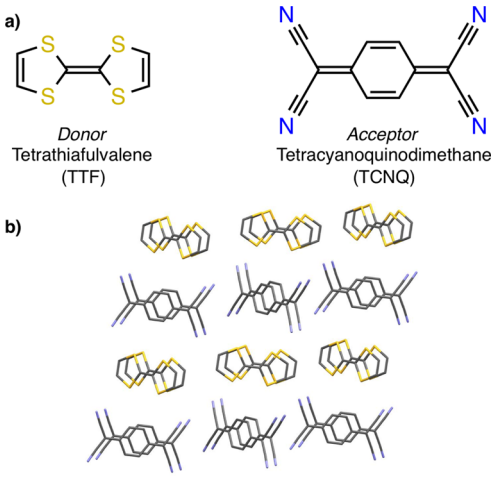



**Figure 1.** (a) Molecular structures of TTF and TCNQ. (b) Crystal structure of TTF−TCNQ showing alternating columns of TTF and TCNQ.[6] Hydrogens omitted for clarity; carbon = gray; nitrogen = blue; sulfur = yellow. The charge transfer salt is an example of ionic bonding in organic solids.

In the experiment, students carry out a solution phase synthesis of TTF−TCNQ and characterize the product by infrared (IR) spectroscopy.[13] The synthesis is ideal for an undergraduate laboratory as it is rapid and reproducible, requires no specialized equipment, and is easily performed on the microscale. An operationally simple procedure for measuring resistance is included. Students experimentally





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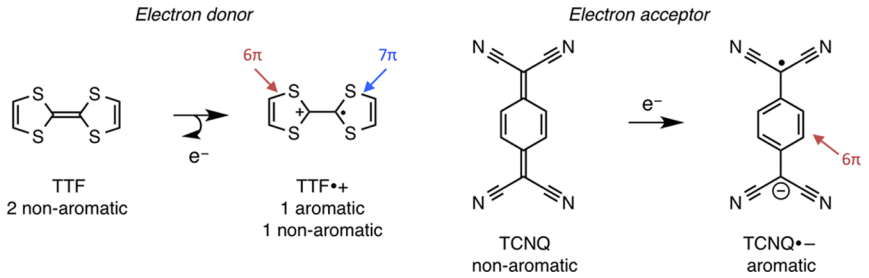
**Scheme 1. Connecting TTF and TCNQ Reactivity to Hückel's 4*n* + 2 Rule[a]**




[a]TTF oxidation yields a stable aromatic radical cation and TCNQ reduction yields a stable aromatic radical anion.

determine that the charge transfer salt TTF−TCNQ is more conductive than either TTF or TCNQ alone.

The pedagogical goals of this experiment are to introduce students to a current topic in organic chemistry and to understand some of the structural and electronic features of conductive organic materials. In the process, aromaticity concepts such as Hückel's rule are used to rationalize the redox chemistry of TTF and TCNQ. The experiment is coupled to a prelaboratory lecture and an in-class group exercise focused on the redox chemistry of the starting materials (Scheme 1) that challenges students to answer the question: why does TTF act as an electron donor and TCNQ as an acceptor? The experiment also provides training in infrared spectroscopy and the relationship of vibrational modes to organic structure.

Students learn that TTF−TCNQ is an example of a familiar concept, that oppositely charged entities attract one another. Electrostatic attraction between $TTF^{\bullet+}$ and $TCNQ^{\bullet-}$ contributes to the assembly of an organic ionic solid consisting of alternating columns of TTF and TCNQ (Figure 1b).[6] Students experimentally verify that the salt is much less soluble in organic solvents than either of the precursors, consistent with increased polarity and ionic bonding.

## PEDAGOGICAL GOALS

This experiment is designed to accomplish the following:

- To introduce undergraduates to a current topic in organic chemistry (organic electronic materials) and to understand some of the structural requirements for high conductivity in organic materials.
- To use aromaticity concepts like Hückel's rule to understand the redox chemistry of TTF and TCNQ.
- To provide training in infrared spectroscopy and the relationship of vibrational modes to organic structure.

## OVERVIEW OF LABORATORY EXPERIMENT

This experiment is designed for second-year undergraduate organic chemistry students. It was run in a second-semester organic chemistry laboratory course with 28 students working individually. The laboratory class was not associated with a separate lecture class and was required for Chemistry majors.

Students met for a prelaboratory discussion and small group active learning exercise that required 45 minutes to complete. The exercise and laboratory can be completed on the same or different days. Additional prelaboratory activities included a video and online quiz. The laboratory experiment (synthesis and characterization) was completed within 3 h. Students measured yields and analyzed their infrared spectra. At the following week's laboratory meeting, students handed in answers to short questions assessing their understanding of the characterization data. An optional extension (2−3 hours to complete) is described in which students compare the resistance of TTF−TCNQ to TTF and TCNQ. This experiment was tested by a two-person group of students as an independent project.

## EXPERIMENT

### Prelaboratory Active Learning Group Exercise

The goal of this exercise is for students to appreciate that TTF and TCNQ form aromatic radical ions and to connect the synthesis of TTF−TCNQ to redox half-reactions. As a lead-in to the active learning exercise, students are reminded of the relationship between the octet rule and the redox properties of Na and $Cl_2$ (eqs 1 and 2). Na is oxidized (electron donor) because the sodium cation has a stable noble gas electronic configuration. Likewise, chlorine is reduced (electron acceptor) to a chloride anion with noble gas configuration. Adding the half reactions gives sodium chloride (eq 3).

$$\mathrm{Na} \rightarrow \mathrm{Na}^{+} + \mathrm{e}^{-} \tag{1}$$

$$\frac{1}{2}\mathrm{Cl}_2 + \mathrm{e}^{-} \rightarrow \mathrm{Cl}^{-} \tag{2}$$

$$\mathrm{Na} + \frac{1}{2}\mathrm{Cl}_2 \rightarrow \mathrm{Na}^{+}\mathrm{Cl}^{-} \tag{3}$$

The formation of TTF−TCNQ can be expressed as the sum of two half reactions (eqs 4−6). The half-reactions refer to a molecular process. In the bulk, not all molecules are oxidized or reduced, for example, the degree of charge transfer $Z$ in the TTF−TCNQ bulk solid is partial ($Z$ = 0.59).[14]

$$\mathrm{TTF} \rightarrow \mathrm{TTF}^{+} + \mathrm{e}^{-} \tag{4}$$

$$\mathrm{TCNQ} + \mathrm{e}^{-} \rightarrow \mathrm{TCNQ}^{-} \tag{5}$$

$$\mathrm{TTF} + \mathrm{TCNQ} \rightarrow \mathrm{TTF}^{+}\mathrm{TCNQ}^{-} \tag{6}$$

After this introduction, students are organized into groups with up to three people and collaborate on a worksheet (see Supporting Information) to rationalize why TTF oxidation is facile. In this exercise, students draw Lewis line structures of TTF and its radical cation $TTF^{\bullet+}$, count $\pi$ electrons and draw curved arrows. Ultimately, students arrive at the conclusion that, when TTF is oxidized, it forms a stable aromatic radical cation (one ring has 6$\pi$ electrons and another has 7$\pi$ electrons, Scheme 1). Hückel's rule states that a planar ring with $4n + 2\pi$ electrons is aromatic. Similarly, TCNQ is reduced to a stable radical anion with a 6$\pi$ electron core. To assess comprehension, at the end of the group exercise, students are shown a cyclic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voltammogram of TTF, told that it shows TTF is oxidized twice, and challenged to explain with a Lewis structure the stability of $TTF^{2+}$.

### Synthesis of TTF−TCNQ

The synthesis is easily performed by individual students in 30 minutes. Acetonitrile solutions (10 mL) of both TTF and TCNQ (2 mg/mL) in two 20 mL scintillation vials are prepared by students. The TCNQ solution may need swirling to dissolve. In a third vial, 5 mL of each solution are combined. A greenish-black solid rapidly precipitates (Figure 2). The solid is isolated by gravity filtration through a tared piece of filter paper. Students obtain the mass of their product by weighing the tared filter paper with solid and then calculate yield.

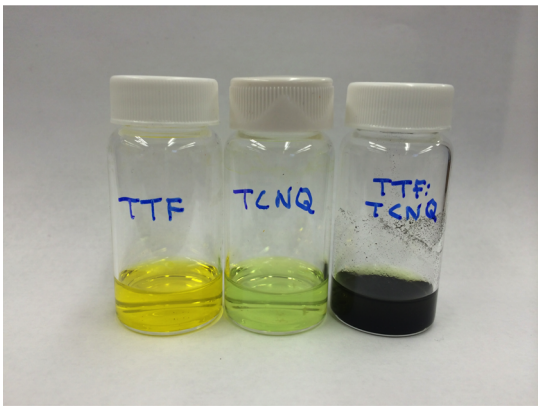


**Figure 2.** Acetonitrile solutions of TTF, TCNQ, and the TTF−TCNQ charge transfer salt.

### Characterization by Infrared Spectroscopy

Infrared spectroscopic characterization is performed on an FT-IR spectrometer with attenuated total reflectance (ATR). Two glass slides are required. One clean glass slide is used to record the background spectrum and on the second a thin film of TTF−TCNQ is solution deposited (drop cast). TTF−TCNQ (2 mg) is suspended in dichloromethane (1 mL). Dichloromethane is chosen for its volatility but can be replaced with acetonitrile if desired. A drop of solution is placed in the center of the slide and allowed to dry. Five to six additional drops, dried in between deposition, are layered over the original spot to make a thin film (Figure 3a). The slide is placed film-side down on the ATR crystal during data collection.

### Electrical Characterization

The acetonitrile solutions of starting materials may be reused if the electrical measurement is performed on the same day as the synthesis. Students prepare acetonitrile solutions of both TTF and TCNQ (2 mg/mL) in 20 mL scintillation vials. An acetonitrile suspension of TTF−TCNQ (2 mg/mL) is also prepared. Either commercially available TTF−TCNQ or synthetic TTF−TCNQ may be used. A drop of solution is placed in the center of the slide and allowed to dry (no heat is applied to the slide as it dries). Additional drops, dried in between deposition, are layered over the original spot until a crystalline film of material develops (see Supporting Information). At least ten drops are typically required. A digital multimeter (resistance range 200 Ω −2000 kΩ) is used to measure the resistance of the TTF−TCNQ thin film. The leads, without touching, are placed on a section of the film and the resistance recorded. TTF and TCNQ films (drop cast from acetonitrile onto glass slides as described above) are assayed as controls. The procedure is conducted in air and at room temperature. Replacing acetonitrile with more volatile dichloromethane reduces the drying time between drops. A green solvent-free film preparation method is also described in the Supporting Information.

## ■ HAZARDS

All procedures should be carried out in a fume hood. Appropriate personal protective equipment includes eye protection, nitrile gloves, and a lab coat. Both TTF and TCNQ are potential skin and eye irritants. The TTF−TCNQ salt is also a potential skin and eye irritant. Exposure by inhalation or ingestion should be avoided. Both solids are strongly colored and solutions of either solid could stain clothing. Acetonitrile is flammable. Acetonitrile and dichloromethane are skin and eye irritants. Dichloromethane is a suspected carcinogen. Exposure by inhalation or ingestion should be avoided.

Leftover solutions of starting materials are disposed of in liquid organic waste containers. Organic solids are washed off the glass slides with acetone into liquid organic waste containers. The glass slides are disposed of in sharps containers or broken glass waste containers. Used filter paper is disposed of in solid waste containers.

## ■ RESULTS AND DISCUSSION

Twenty-eight students in a second-semester undergraduate organic chemistry laboratory course ran the experimental

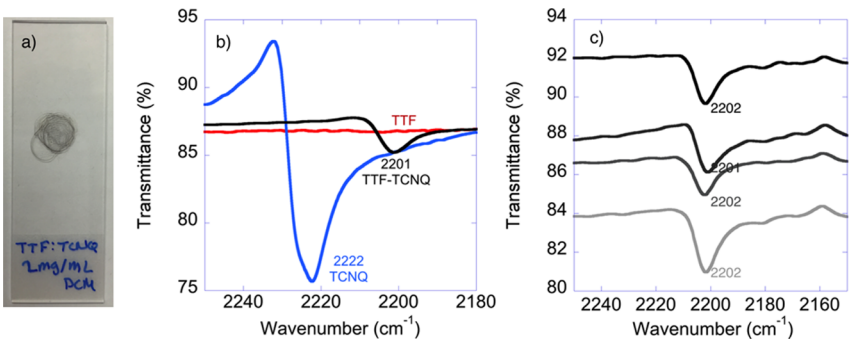


**Figure 3.** (a) Photograph of TTF−TCNQ film drop cast from dichloromethane for IR spectroscopy. (b) Instructor-generated IR spectra of authentic, commercial samples of TTF, TCNQ, and TTF−TCNQ. Only the nitrile stretch region is shown. Black = TTF−TCNQ; red = TTF; blue = TCNQ. (c) Student-generated spectra of synthetic TTF−TCNQ. Only the nitrile stretch region is shown.


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procedure. Every student in the class successfully synthesized and isolated the greenish-black solid. The reported yield for this reaction is 28%.[13] Students reported yields ranging from 5% to well over 100%. A challenge students faced in calculating yields is that they assumed a theoretical maximum yield based on massing out 20 mg of starting material, instead of basing their calculations on the number of millimoles of starting material in the volume of stock solution used. Other students did not dry their samples adequately before massing their filter paper and product. A sample yield calculation is suggested in the prelab worksheet (see Supporting Information).

Students characterized the product by ATR-FTIR spectroscopy. Although TTF−TCNQ films are patchy (Figure 3a), reasonable and reproducible IR spectra were obtained. There are striking spectral differences between the starting materials and the product in the nitrile region (typically 2260 to 2220 $cm^{-1}$) (Figure 3b). TTF, with no nitriles, has no features in this region. TCNQ has a strong absorbance at 2222 $cm^{-1}$, which is characteristic of the lower frequency absorbance of conjugated nitriles. The TTF−TCNQ charge transfer salt has a weak intensity absorption band at the even lower frequency of 2201 $cm^{-1}$. The student-generated ATR-FTIR spectra of synthetic TTF−TCNQ were distinct from starting material spectra (Table 1) and matched the spectrum obtained with an authentic, commercial sample of TTF−TCNQ (Figure 3c). Other characteristic absorptions are unsaturated C−H stretching absorptions above 3000 $cm^{-1}$; images of this region are found in the Supporting Information.

**Table 1. Diagnostic ATR-FTIR C−H and Nitrile Stretching Frequencies of TTF, TCNQ, and TTF−TCNQ[a]**

| Material | C−H Stretch ($cm^{-1}$) | C−H Stretch ($cm^{-1}$) | Nitrile Stretch ($cm^{-1}$) |
|---|---|---|---|
| TTF | 3063.1 | | |
| TCNQ | 3050.4 | 3138.8 | 2222.1 |
| TTF−TCNQ[b] | 3091.3 ± 0.6 | 3071.7 ± 0.3 | 2201.5 ± 0.6 |

[a]TTF and TCNQ data are instructor-generated and TTF−TCNQ data are student-generated. [b]Frequencies are the mean of 28 student spectra. Values for one standard deviation are also included.

This experiment challenged student assumptions about chemical reactions because no new covalent bonds were formed. Some students had trouble appreciating that a chemical reaction had occurred and, instead, thought of TTF−TCNQ as a mixture of the two starting materials. The laboratory experiment reinforced that a chemical reaction had occurred because students appreciated the very different physical properties (color, solubility) of the charge transfer salt compared to the starting materials. Furthermore, IR analysis allowed students to observe that the charge transfer salt had a unique infrared spectrum, which provided student-acquired data confirming that a new product was formed.

An explanation of the change of the nitrile frequency appropriate for students follows. Conjugation shifts the nitrile stretching absorption to lower frequency (acetonitrile, $\bar{\nu}$ = 2253 $cm^{-1}$; benzonitrile, $\bar{\nu}$ = 2240 $cm^{-1}$) because delocalization reduces triple bond character and lengthens the CN bond. Neutral TCNQ is cross-conjugated ($\bar{\nu}$ = 2222 $cm^{-1}$), whereas partially reduced TCNQ has aromatic character and is more "conjugated" than the neutral structure. Crystal structures show a slight lengthening of the relevant bond: the C−N bond length is 1.14 Å in neutral TCNQ[15] and 1.16 Å in TTF−TCNQ (Figure 4).[6,16] Analyzing the X-ray structures of neutral TCNQ ($TCNQ^0$) and TTF−TCNQ ($TCNQ^{-0.59}$) further reinforces the aromaticity concept as $TCNQ^0$ shows greater bond length alteration in the cyclic core than does the $TCNQ^{-0.59}$ subunit of TTF−TCNQ. See the Supporting Information for an expanded discussion of partial charge transfer.

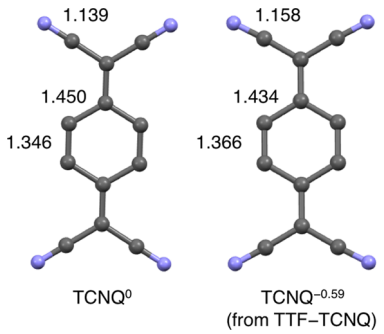


**Figure 4.** Single crystal X-ray structures of $TCNQ^0$ and $TCNQ^{-0.59}$ (refs 15 and16). All bond lengths are in angstroms. After partial reduction, the CN bond lengthens and the endocyclic CC bonds approach uniformity (CC bonds in benzene = 1.39 Å). Gray = carbon; blue = nitrogen. Hydrogens omitted for clarity.

The nitrile absorption is linearly correlated with the degree of charge transfer $Z$ in a TCNQ charge transfer salt.[14] The nitrile stretching absorption in completely reduced $K^+TCNQ^-$ ($Z$ = 1.0) is observed at 2183 $cm^{-1}$, whereas neutral TCNQ ($Z$ = 0) absorbs at 2222 $cm^{-1}$. The intermediate stretching absorption in TTF−TCNQ (2202 $cm^{-1}$) is indicative of partial charge transfer ($Z$ = 0.59). The partial charge transfer is essential to conductivity as both $TCNQ^0$ and $K^+TCNQ^-$ are insulators.

## Electrical Characterization

Electrical characterization was carried out as an independent project by a two-person group of students. It is included here as an optional variation. The procedure can be included on the same day as synthesis and IR characterization or carried out on a separate day.

Students measured resistance, the reciprocal of conductance, using a standard multimeter available in most physical chemistry laboratories. Drop-cast crystalline films of starting materials and TTF−TCNQ were prepared in triplicate and the results are summarized in Table 2. An alternative solvent-free film deposition procedure is also available in the Supporting Information. The difference is striking: TTF and TCNQ films are many orders of magnitude more resistive than TTF−TCNQ films. The results in Table 2 were collected with an authentic sample of TTF−TCNQ.

**Table 2. Resistance Measurements of TTF, TCNQ, and TTF−TCNQ Showing Lower Resistance in the Charge Transfer Salt**

| Material | Mean Resistance (Ω) |
|---|---|
| TTF | 168,000 ± 6000[a] |
| TCNQ | 135,000 ± 2000[a] |
| TTF−TCNQ[b] | 6.47 ± 0.60[a] |

[a]Mean resistance is an average of three unique devices and measurements. Values for one standard deviation are also included. [b]An authentic, commercial sample.


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As most undergraduate laboratories do not have equipment to measure film thickness, the simplification was taken to compare resistance instead of resistivity. Others have reported this simplification for undergraduate laboratory experiments in this Journal.[9] Multiplying the resistance ($R$) by the film thickness ($t$) gives the resistivity $\rho$ ($\rho = R \bullet t$), which would be the most appropriate value to compare across materials of different dimensions. This simplification contributes to the considerable batch variability in instructor-generated resistance measurements, which ranged between $10^0$−$10^3$ Ω.

The variability is not surprising given that the electrical characterization described herein is significantly less sophisticated than typical measurements. Literature procedures in which conductance measurements are undertaken generally report multiple recrystallizations of starting materials,[17] recrystallization of the TTF−TCNQ salt,[18] and/or synthesis by physical vapor transport.[19] Growing large crystals of TTF−TCNQ from solution suitable for electronic characterization also requires specialized glassware.[13,20] The conductivity of TTF−TCNQ is highly anisotropic (higher in the direction of one crystal axis than others) and is dependent on purity and crystal size, suggesting that a lack of control of crystallite size and orientation could contribute to variable resistance values. Nonetheless, the characterization is appropriate for an undergraduate teaching laboratory due to the minimal equipment needs and it successfully demonstrates that charge transfer enhances electrical properties.

### Relevance to Introductory and Physical Chemistry Courses

An alternative rationalization of TTF and TCNQ redox chemistry arises from analysis of the frontier molecular orbital energies; this approach generalizes the experiment for general chemistry and physical chemistry courses. An experimental photophysical characterization procedure that estimates the frontier molecular orbital energies of TTF and TCNQ is included in the Supporting Information.

## ■ CONCLUSION

The synthesis and characterization of TTF−TCNQ reinforced organic chemistry concepts (electrostatic interactions, aromaticity, and substituent effects), taught infrared spectroscopy characterization, and introduced undergraduates to organic electronics, a current and active area of chemical research.

All students successfully synthesized and characterized by IR spectroscopy TTF−TCNQ. In a postlaboratory assessment, a majority of students (26/28) correctly identified both the nitrile and C−H stretching frequencies in the TTF−TCNQ IR spectrum. Student retention of the pedagogical goals and concepts was excellent, as reflected in a high average score on a final exam question in which students were challenged to identify novel donor−acceptor materials and rationalize their choices.

Indirect assessments showed very high student enthusiasm for this laboratory experiment. A quarter of the class (7/28) designed mini research projects based on organic electronic materials as part of an independent final project in the course. In a voluntary exit survey students ranked this experiment one of the most exciting of the course.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00340.

Video showing a resistance measurement. (ZIP)

Detailed procedures, complete characterization data, instructor notes, an expanded discussion of partial charge transfer, optional photophysical characterization, and active learning exercise. (PDF)

Detailed procedures, complete characterization data, instructor notes, an expanded discussion of partial charge transfer, optional photophysical characterization, and active learning exercise. (DOCX)

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### Notes

The authors declare no competing financial interest.

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