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Organic Materials in the Undergraduate Laboratory: Microscale Synthesis and Investigation of a Donor−Acceptor Molecule

Ted M. Pappenfus,*,[†] Karl B. Schliep,[†] Anudaththa Dissanayake,[†] Trevor Ludden,[†] Belén Nieto-Ortega,[‡] Juan T. López Navarrete,[‡] M. Carmen Ruiz Delgado,[‡] and Juan Casado[‡]

[†]Division of Science and Mathematics, University of Minnesota, Morris, Minnesota 56267, United States
[‡]Department of Physical Chemistry, University of Málaga, Campus de Teatinos s/n, Málaga 29071, Spain

Ⓢ Supporting Information

ABSTRACT: A series of experiments for undergraduate courses (e.g., organic, physical) have been developed in the area of small molecule organic materials. These experiments focus on understanding the electronic and redox properties of a donor−acceptor molecule that is prepared in a convenient one-step microscale reaction. The resulting intensely colored material exhibits an electronic transition in the visible portion of the electromagnetic spectrum and is indicative of intramolecular charge transfer (ICT). The ICT and redox properties are investigated with conventional analytical techniques and are understood with the use of density functional theory. These experiments illustrate the importance of organic materials in areas such as solar energy conversion. As a result of these experiments, students are exposed to a number of important chemical concepts as well as useful physical and theoretical methods used by experts in the field.

KEYWORDS: Second-Year Undergraduate, Upper-Division Undergraduate, Laboratory Instruction, Organic Chemistry, Physical Chemistry, Computational Chemistry, Materials Science, Oxidation/Reduction, NMR Spectroscopy, UV-Vis Spectroscopy
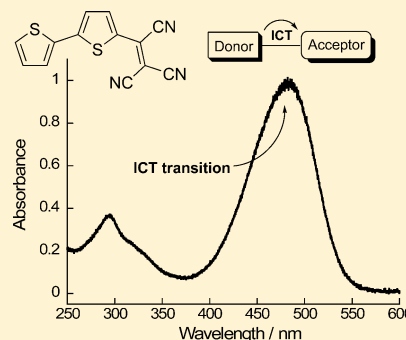
O rganic materials for electronic applications is a blossoming area of interdisciplinary research including fields such as chemistry, physics, and engineering. In the past 50 years, organic materials have gone from laboratory curiosities to important materials for a number of technological applications.[1] For example, the discovery of light emission by a polymer in 1990[2] has led to the development of organic light-emitting diodes (OLEDs) for displays in products from televisions to mobile phones.[3] Providing students with a fundamental understanding of the synthetic routes to these materials as well as their physical properties is important as the next generation of chemists and engineers is developed.

Conjugated organic materials fall within one of two categories: polymers or "small" molecules, where small molecules refer to materials with discrete (nonpolymeric) molecular structures. Although many excellent undergraduate laboratory experiments outlining the investigation of conducting polymers have been reported in this *Journal*[4] and others,[5] molecular organic materials have been largely overlooked. In device applications, small molecules can have several potential advantages over polymers including ease of preparation and purification, higher charge mobility, and monodispersity.[6] This current report describes a series of experiments related to the preparation and investigation of a small-molecule organic material relevant to the field of organic materials. These experiments have high pedagogical value as students will better understand how the physical properties of organic materials can be used to solve problems related to energy, electronics, and the environment.

The current focus is on a donor−acceptor (D-A) molecule because D-A organic molecules and polymers are one of the most important classes of conjugated materials for use in a number of technological applications.[7] Of particular interest is the use of these materials in organic photovoltaics.[8] Because most organic molecules absorb high-energy light (i.e., have large optical band gaps), only small amounts of sunlight can be absorbed because most sunlight is at wavelengths >500 nm. D-A molecules, on the other hand, do a much better job of absorbing the red and infrared portions of the solar spectrum. In these materials, electron-donating and electron-accepting groups are connected through a variety of architectures (e.g., D-A, A-D-A, D-A-D). The exact nature of the acceptor and donor can be tuned precisely to create a variety of materials with unique physical and chemical properties. Specifically, when covalently linked, these conjugated D-A molecules possess an inherent intramolecular charge transfer (ICT) transition that reduces the optical band gap and allow the absorption of the molecule to match well with the solar spectrum (Figure 1). ICT can be defined as electron transfer in a conjugated π-system between the donor and acceptor substituents present in a D-A molecule.

A small sample of the more common donor and acceptor groups used in D-A materials is shown in Figure 2. Among the donors available, functional thiophene-based materials have attracted considerable interest in this field.[9] Oligothiophenes

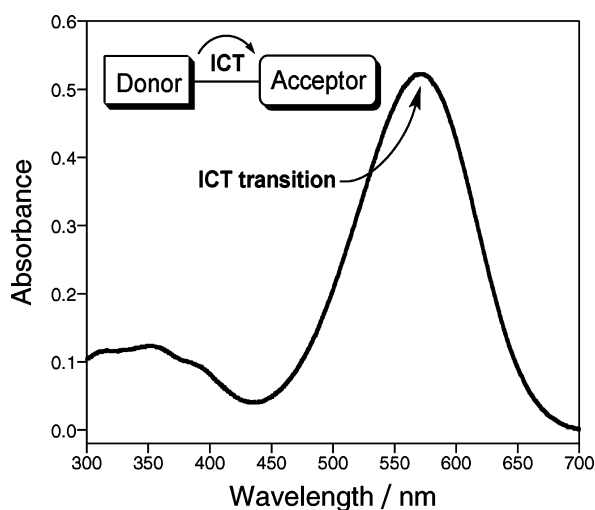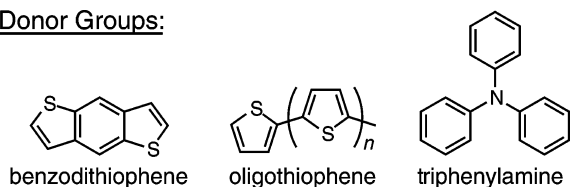**Figure 1.** ICT transition diagram and resulting absorption spectrum of a typical D-A molecule.
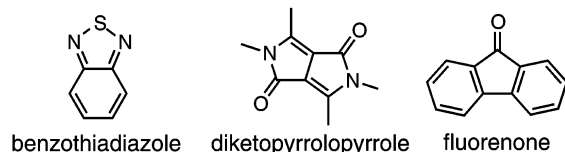

Figure 2. Common donor and acceptor groups used in D-A molecules.

(abbreviated as nT, where n is the number of repeating thiophene units, T) have been functionalized with many electron-withdrawing groups such as carbonyl,[10] nitro,[11] and perfluoroalkyl.[12] A particular class of electron acceptors that has received considerable attention are cyano-based electron acceptors.[13] For example, previous studies[14] have used the tricyanovinyl (TCV) moiety in oligothiophenes such as TCV-3T to create materials displaying nonlinear optical behavior[15] and TCV-3T-TCV that exhibits n-type behavior in an organic thin-film transistor (Figure 3).[16] N-type (electrons as major charge carriers) and p-type (holes as major charge carriers) are two types of organic semiconductors based on the type of majority charge carriers. The first report of ambipolar transport (i.e., both p- and n-type conduction) in a thin-film transistor based on a single conjugated organic semiconductor was the dicyanomethylene material DCMT.[17] Additionally, Baeuerle and co-workers have utilized the dicyanovinyl (DCV) moiety in materials such as DCV-3T-DCV for use in solar cells.[18] Given the wide applicability of these and related materials, there is value in designing experiments for the preparation of small molecules containing both thiophene-based electron donors and cyano-based electron acceptors for use in undergraduate laboratory experiments.
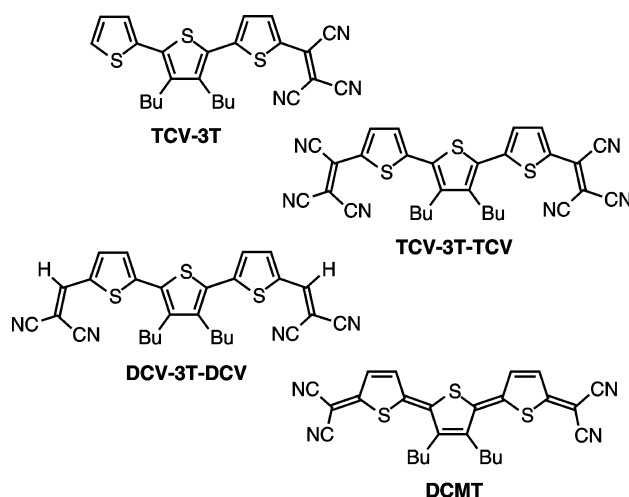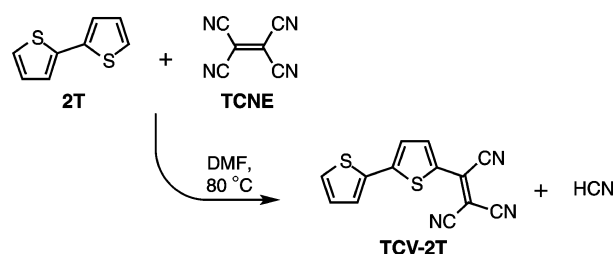

Figure 3. Representative cyano-based organic materials.

■ EXPERIMENTAL OVERVIEW

Students prepare the D-A molecule TCV-2T using the procedure outlined in Scheme 1. This specific molecule was

Scheme 1. Synthesis of TCV-2T

chosen because it can be prepared in a convenient one-step reaction from the commercially available reagents 2,2′-bithiophene (2T) and tetracyanoethylene (TCNE). Two approaches toward the preparation of this molecule have been reported in the literature: (i) the formation of organolithium species of bithiophene followed by quenching with TCNE[14d] and (ii) the addition of TCNE directly to the molecule in a polar solvent.[19] The later approach was chosen as it does not involve using air- and moisture-sensitive chemistry and avoids using pyrophoric organolithium reagents. The intent in designing this experiment was to have a straightforward synthetic procedure so the bulk of the student's time could be focused on the physical chemistry rather than the synthesis of the material.

The microscale synthesis of TCV-2T is performed by the addition of 0.116 g of TCNE to a solution of 0.100 g of bithiophene (2T) in DMF (1 mL). After 2 h of stirring at 80 °C, the reaction is cooled and quenched with HCl. The resulting red microcrystalline product is filtered and washed with water and hexanes for purification. Typical student yields for the preparation of TCV-2T are 80 mg (50%). A detailed mechanism for this reaction is found in the Supporting Information.

This material can be utilized by students in a number of different laboratory courses. For example, when performing this experiment with second-semester organic chemistry students, they are required to obtain the melting point and mass spectrum of the material along with an analysis using ^{1}H NMR
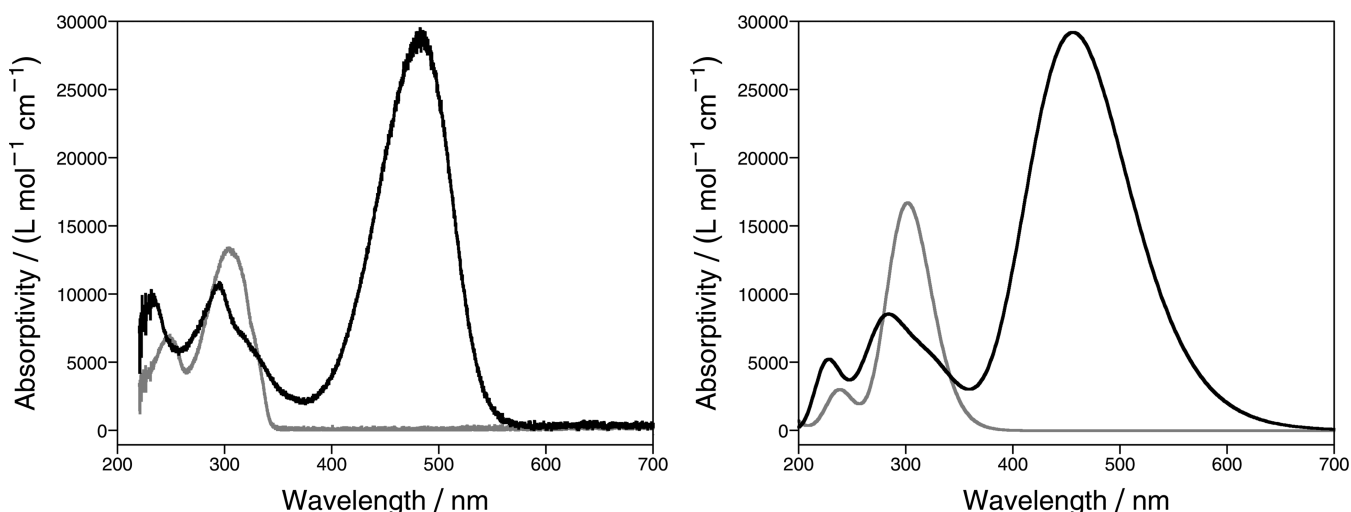
Figure 4. Experimental UV−vis solution spectra in THF (left) and simulated electronic spectra from the TDDFT calculations (right) for 2T (gray) and TCV-2T (black).

and IR spectroscopy. When working with more advanced students (e.g., in physical organic or physical chemistry laboratories), students are required to perform an in-depth analysis of the electronic and redox properties of the material using experimental techniques such as UV−vis spectroscopy and cyclic voltammetry and computational techniques such as density functional theory (DFT). Details of these methods are found in the Supporting Information. In practice, the best implementation of this experiment occurs when students have the opportunity to both synthesize the material and investigate its properties through experiment and theory as an exercise in physical organic chemistry. In this scenario, two lab periods (3 h each) are necessary: (i) synthesis and isolation of the material in the first lab period and (ii) characterization of the material in the second lab period. DFT calculations are spread across the two lab periods.

■ **HAZARDS**

N,N-Dimethylformamide (DMF) is a teratogen and irritant. Tetracyanoethylene is a cancer suspect agent and mutagen. Hexanes are flammable and both hexanes and bithiophene (2T) are considered irritants. The reaction for the preparation of TCV-2T should be conducted only in a well-ventilated fume hood to account for the formation of hydrogen cyanide.

■ **RESULTS AND DISCUSSION**

Reactions of TCNE with activated aromatic molecules such as bithiophene results in intensely colored materials. For example, tetrahydrofuran solutions of TCV-2T (λ_{max} = 485 nm, 2.56 eV) are significantly red-shifted relative to the parent bithiophene molecule (λ_{max} = 304 nm, 4.08 eV). UV−vis spectra in tetrahydrofuran of these two molecules are shown in Figure 4. Students are also asked to compare their values to those found in the literature for bithiophene[12b] and TCV-2T[19] respectively. The dramatic changes observed upon TCV addition to bithiophene can be attributed to intramolecular charge transfer (ICT)[11a,15] and, in this particular case, occurs within the visible portion of the electromagnetic spectrum.

ICT present in these materials can be rationalized using quantum mechanical methods. In this experiment, students use density functional theory (DFT) calculations to understand the experimental data of the molecules. Owing to their computa-

tional efficiency and accuracy, DFT calculations have become one of the most popular and versatile quantum mechanical methods utilized by chemists.[20] Not surprisingly, chemical applications of DFT have been extended to undergraduate chemistry laboratories.[21] In this investigation, students calculate HOMO and LUMO energy levels (determined at the B3LYP/6-31G(d,p) level) for bithiophene, TCV-2T, and tricyanoethylene (TCV-H) for comparison purposes. The results of the calculations are shown in Figure 5.
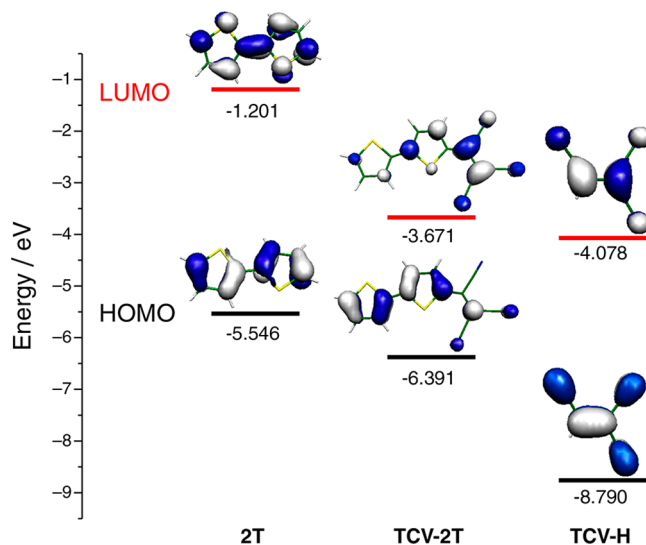

Figure 5. B3LYP/6-31G(d,p) molecular orbital diagram of the coupling between 2T and TCV-H fragments with HOMO (black) and LUMO (red) frontier-orbital mixing.

The frontier orbitals of TCV-2T indicate that its HOMO is most closely associated with the HOMO of 2T, whereas its LUMO is very similar in energy to the LUMO of TCV-H. As a result, the HOMO → LUMO excitation of TCV-2T has significant charge-transfer character in which the bithiophene and tricyanovinyl moieties act as the donor and acceptor groups respectively. Time-dependent density functional theory (TDDFT) calculations predict one-electron HOMO → LUMO transitions for TCV-2T at 2.72 eV (oscillator strength,

$f = 0.72$) and at 4.11 eV ($f = 0.41$) for 2T. As shown in Figure 4, the theory predicts nicely both the intensity increase and dramatic red shift of the electronic transition upon TCV substitution.

In advanced courses, students can gain insight into the redox properties of the materials by analysis with cyclic voltammetry (Figure 6). Whereas bithiophene, 2T, exhibits an irreversible
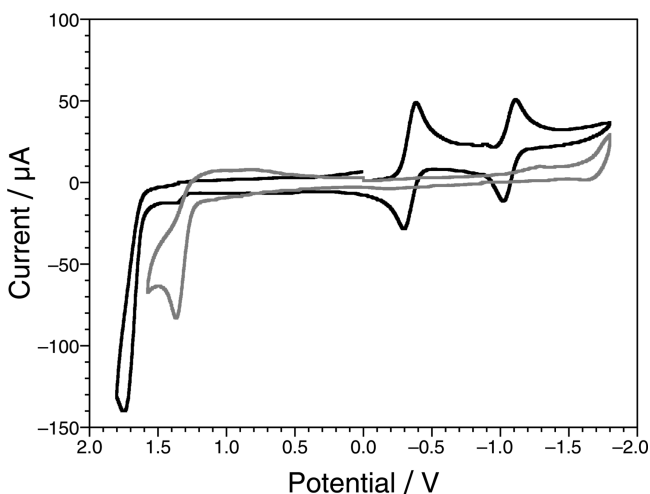

Figure 6. Cyclic voltammogram of 2T (gray) and student prepared TCV-2T (black) in 0.1 M TBAPF$_6$/CH$_3$CN solution at a carbon electrode, $\nu = 100$ mV/s.

oxidation process ($E_{pa} = 1.36$ V)[22] and no reductions, TCV-2T exhibits reversible reductions ($E^\circ = -0.34, -1.07$ V) and an irreversible oxidation ($E_{pa} = 1.75$ V) under the experimental conditions. This is further evidence that 2T has been transformed from a reasonable electron donor to a good electron acceptor in the case of TCV-2T. These data can be rationalized again using the MO diagram in Figure 5. The DFT calculations accurately reflect the redox trends of 2T and TCV-2T as predicted by Koopmans' theorem[23] that suggests that the HOMO and LUMO energies relate, respectively, to the first oxidation and redution potentials. For example, here the DFT calculations accurately predict that TCV-2T should be the easiest to reduce (i.e., lowest energy LUMO) and 2T should be the easiest to oxidize (i.e., highest energy HOMO). Knowing the energy levels of these frontier orbitals is crucial because in an organic semiconductor, holes and electrons are transported in the solid state via the HOMO and the LUMO, respectively.

Although the performance of organic materials depends largely on the energy of the molecular orbitals, another crucial factor is how the molecules pack in the solid state including thin film morphologies.[24] Whether an amorphous or crystalline state exists, the morphology will ultimately help dictate the structure−property relationship of the material. When analyzing crystalline materials, the Cambridge Structural Database (CSD) has been shown to be an effective teaching tool by several examples reported in this *Journal*.[25] As the structure of TCV-2T has been reported,[14d] students are asked to download the crystallographic information file (CIF) for this molecule from the CSD for analysis. Interestingly, in the solid state, TCV-2T adopts a cis orientation of adjacent thiophene rings, which is different than the trans orientation (Scheme 1) the students are initially asked to calculate. Consequently, students are asked to calculate the energy of this conformer from the experimental atomic coordinates. This leads to the finding of

the trans orientation actually being about 1.0 kcal/mol lower in energy than the cis conformation observed in the solid state. This example illustrates to students that crystal-packing forces dictate the conformation of the material in the solid state over what is predicted in the gas-phase calculation.[26]

■ SUMMARY

These experiments have been tested and can be performed with confidence by undergraduate chemistry students. The synthesis is straightforward and can be accomplished with commercially available reagents and standard glassware and equipment. This feature allows students to not focus on the synthesis, but rather on understanding the physical properties of the material. Overall, the experiment has a high pedagogical value owing to the strong coupling of a variety of experimental and theoretical methods used by those in the field of organic materials. Moreover, these experiments are suitable for introductory organic or upper-level physical chemistry laboratory courses. Regardless of the specific implementation, however, the experiments outlined here illustrate the rich and interesting chemistry of organic materials that have been received favorably by undergraduate students.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Student handouts, instructor notes. This material is available via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pappe001@morris.umn.edu.

Notes

The authors declare no competing financial interest.

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(26) Note: The relative stabilities of cis and trans conformers of TCV-2T have also been investigated using DMSO as a solvent within the SCRF (self-consistent reaction field) theory using the PCM approach to model the interaction with the solvent. Although the energy difference between the cis and trans conformers is smaller in the presence of the solvent (0.57 kcal/mol in DMSO solution versus 1.01 kcal/mol in gas phase), the trans conformer is the most stable conformation of TCV-2T in both cases.

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