Doping of an organic molecular semiconductor by substitutional cocrystallization with a molecular n-dopant[†]

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Dopants for organic molecular semiconductors that yield immobile dopant ions are necessary for the creation of stable molecular semiconductor p–n junctions, the basis for almost all traditional inorganic semiconductor devices. We present evidence for the substitutional cocrystallization of tris(4-nitrophenyl)methyl radical (1) with small amounts of tris[4-(dimethylamino)phenyl]methyl radical (2), resulting in n-doped 1 with immobile 2^+ counterions. Cyclic voltammetry indicates that electron transfer from 2 to 1 is favored by 0.51 eV. The powder X-ray diffraction patterns of pure 1 and 1 doped with 2 are very similar, indicating substitutional cocrystallization. The electrical conductivity of doped 1 increases with increasing concentration of 2, and the conductivity is constant over time. Variable-temperature conductivity measurements of 1 doped with 2% and 5% 2 indicate that the activation energy of conduction is 0.32 eV at both dopant concentrations.

Introduction

Organic molecular and polymeric semiconductors¹ are being widely investigated as the active components of electronic devices.^{2,3} The performance of organic thin-film transistors^{4–6} and organic solar cells^{7,8} continues to improve, and displays that utilize organic light-emitting diodes⁹ are now commercially available. As impressive as these gains have been, significant advances in the performance of organic semiconductor devices remain desirable. For example, the light-to-electrical energy conversion efficiency of organic photovoltaics,⁸ while recently greatly improved,¹⁰ is still substantially lower than that of photovoltaics made with crystalline inorganic semiconductors such as silicon and gallium arsenide.

A fundamentally different approach to organic semiconductor devices, and one that may offer significant performance advances and even completely new devices, is through doped organic semiconductors. Almost all of the research on the devices cited above has involved undoped organic semiconductors. That is in stark contrast to traditional inorganic semiconductor devices, which, in the vast majority of cases, rely upon junctions between n- and p-doped semiconductor regions for their operation.¹¹ The different path in the development of organic semiconductor devices can be traced to the origins of modern organic semiconductor research. The classic discovery by Heeger, MacDiarmid, Shirakawa, and coworkers involved a doped organic semiconductor: p-doped^{12–14} and n-doped¹⁴ polyacetylene. Soon after the discovery of doped polyacetylene, the same group reported the construction of a

polyacetylene p-n junction.¹⁵ However, the current-voltage curve of that junction exhibited hysteresis, and the junction was presumably unstable over time because the dopant counterions, Na^+ and AsF_6^- , are mobile and can migrate to form NaAsF₆ and undoped polyacetylene. The same instability is expected in any organic molecular or polymeric semiconductor doped with an element or molecule that results in a small, mobile counterion. Most of the subsequent development of organic semiconductor devices, therefore, has focused on device architectures that utilize undoped organic semiconductors. Organic solar cells, for example, are based on heterojunctions between two different, and undoped, organic semiconductors. In contrast, inorganic solar cells are simply silicon p-n homojunctions or, in thin-film solar cells, p-n heterojunctions (of *doped* semiconductors). Doped inorganic semiconductors are able to maintain the space-charge region characteristic of a p-n junction because the dopant atoms are covalently bound within the crystalline lattice and are therefore immobile.

A method for doping organic semiconductors that yields immobile dopant counterions would allow stable organic p-n junctions to be made, and, in principle, allow any traditional inorganic semiconductor device architecture to be realized with organic semiconductors. Several research groups are exploring a variety of methods for creating immobile dopants for organic semiconductors. Gregg and coworkers have thoroughly studied a singly reduced perylene diimide with a covalently attached cation that acts as an n-dopant when cocrystallized with a perylene diimide host.^{16–21} Utilizing a similar strategy, Lonergan and coworkers have covalently attached ions to polyacetylene^{22,23} and formed polyacetylene p-n junctions.^{24,25} Leo and coworkers have co-sublimed a very strong reducing agent, bis(terpyridine)rutheniuum⁰, with the semiconductor zinc phthalocyanine (ZnPc) to create n-doped ZnPc, while co-sublimation of ZnPc and the strong oxidizing agent tetrafluorotetracyanoquinodimethane (F₄-TCNQ) resulted in

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p-doped ZnPc. A ZnPc p-i-n (i = intrinsic, or undoped) homojunction was created by sequential sublimation of the appropriate materials.²⁶ The p-i-n junction acted as an electrical diode and was stable for weeks under vacuum. That stability is somewhat surprising in light of other experiments that showed that F₄-TCNQ quickly diffused through ZnPc at room temperature.²⁷

Our own efforts have focused on a strategy that we have dubbed "isostructural doping".²⁸⁻³³ It is closely analogous to the standard method for doping inorganic semiconductors. Silicon, for example, is n-doped by the formal replacement of a small fraction of the silicon atoms with an atom with one more valence electron, such as phosphorus. An isostructural dopant for an organic semiconductor is created by replacing, for example, a carbon atom in the molecular semiconductor with a nitrogen atom, while maintaining charge neutrality of the molecule. A small amount of the isostructural n-dopant is then cocrystallized with the parent molecular semiconductor to create an n-doped material. Because the dopant is isostructural with the semiconductor, it should cocrystallize substitutionally with the semiconductor and will therefore be immobile. The dopant has an excess electron (compared to the parent semiconductor), and therefore should be easily ionized to dope the semiconductor and form an immobile cation. We have found that cocrystals of molecular semiconductors and relatively high proportions (at least 10%) of isostructural dopants can be formed.^{28,30–32} However, in no case has an isostructural dopant been a strong enough electron donor or acceptor to electrically dope its parent semiconductor.

In the current study we have relaxed the requirement that a dopant be exactly isostructural with its parent molecular semiconductor, and instead sought a pair of molecules that are sufficiently structurally similar to be substitutionally cocrystallized, and which we also expect to undergo a spontaneous electron transfer. Previous solution phase electrochemical studies of tris(4-nitrophenyl)methyl radical (1, Fig. 1) and tris[4-(dimethylamino)phenyl]methyl radical (2, Fig. 1) indicated that 2 would spontaneously transfer an electron to $1.^{34}$ An additional indication that electron transfer from 2 to 1 would occur was provided by another study: a one-to-one mixture of 1^{-} and the bis(4-dimethylamino)trityl cation (a molecule very similar to 2) has been shown to exist in solution as an equilibrium mixture of a cation-anion pair and a pair of neutral radicals, with the position of the equilibrium dependent upon the polarity of the solvent.³⁵ The similarity of the structures of 1 and 2 led us to believe that they could be substitutionally cocrystallized. Herein we describe the



Fig. 1 Structures of tris(4-nitrophenyl)methyl radical (1) and tris[4-(dimethylamino)phenyl]methyl radical (2).

synthesis, isolation, and characterization of 1 and 2. The electrical properties of 1 doped with 2 will be discussed.

Experimental

General procedures and materials

All manipulations were carried out using Schlenk line or glovebox techniques unless otherwise noted. All manipulations involving radicals were carried out with light excluded. Reagents were purchased from commercial suppliers and used as received unless their purification is noted as follows. Tetrabutylammonium hexafluorophosphate, [NBu₄][PF₆], was recrystallized twice from ethanol. Acetonitrile was distilled from P₂O₅ onto 3 Å molecular sieves and vacuum transferred immediately prior to use. Pyridine was distilled from KOH onto 3 Å molecular sieves and vacuum transferred immediately prior to use. Dimethylformamide (DMF) was vacuum-distilled from P₂O₅ and stored over activated 3 Å molecular sieves in a nitrogen-filled glove box. Ethereal solvents were distilled from a purple sodium benzophenone solution and hydrocarbon solvents were distilled from purple sodium benzophenone solutions with added tetraglyme. Pyridine- d_5 was vacuum transferred onto 3 Å molecular sieves from KOH and stored in a nitrogen-filled glove box. Acetonitrile- d_3 was vacuum transferred onto 3Å molecular sieves from P₂O₅ and stored in a nitrogen-filled glove box. Tris(4-dimethylaminophenyl) methane was prepared by the reaction of 2^{+} Cl⁻ with NaBH₄.³⁶ Addition of an aqueous solution of KI to commercial 2⁺Cl⁻ yielded a precipitate of $2^{+}I^{-}$,³⁷ which was purified by recrystallization from CH₂Cl₂-hexanes. Published procedures were employed for the syntheses of ferrocenium hexafluorophosphate (Fc⁺PF₆⁻)³⁸ and tris(4-nitrophenyl)methane,³⁹ and a modified literature procedure was used for its deprotonation to $Na^{+}1^{-}.40$

¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer with the solvent signal as the standard. Infrared spectra were obtained on a Perkin-Elmer Spectrum BX FT-IR system as Nujol mulls on NaCl plates. UV-vis spectra were obtained using a Varian Cary 100 Bio UV-vis spectrometer. ESR spectra were obtained on a Bruker X-band spectrometer with 0.1 G modulation. ESR spectral simulations were created with WINEPR SimFonia.⁴¹ X-Ray powder diffraction was performed on a Rigaku Geigerflex D/max diffractometer interfaced to a PC. Microanalysis was performed by the University of Illinois Microanalysis Laboratory, Urbana, IL.

Solution phase magnetic susceptibility of **2** was measured as a solution in pyridine- d_5 by the Evans method as described previously.^{28,42} Solid state susceptibilities were measured at room temperature on a Johnson Matthey Mark I magnetic susceptibility balance.

Cyclic voltammetry and room temperature solid state conductivity measurements were performed with an EG&G/ PAR 263A potentiostat with electrical connection to the inside of a nitrogen-filled drybox, where all materials and solutions were maintained during the measurements. Cyclic voltammetry was performed in anhydrous THF with 0.10 M $[Bu_4N][PF_6]$ supporting electrolyte and a ferrocene internal standard. The working electrode and pseudoreference electrode were 0.50 mm diameter platinum disks and the counter electrode was a 2.5 mm diameter platinum disk. Scans were run at 50 mV s⁻¹. Solid state conductivity of pressed powders was measured in a two-electrode configuration on a lab-built apparatus that consists of a Delrin block with a 6.35 mm cylindrical hole and two 6.35 mm copper cylindrical contacts. The material to be studied was inserted between the two contacts within the Delrin block and a mass of 3.85 kg was placed on the top contact, thus applying 12 bar of pressure. A 5.3 Hz low-pass filter was utilized in making cyclic voltammetry and conductivity measurements.

For variable-temperature conductivity measurements, samples were prepared as pressed pellets of 6.4 mm diameter in a nitrogen-filled glovebox. The thickness of the pellets was computed using their mass and an estimated density of 1.50 g cm^{-3} , calculated from the crystal structure of 1.43 The two surfaces of the pressed pellet were coated in silver paint and an electrical connection to each was made with 25 µm diameter platinum wire. The entire sample was then coated in poly(vinyltoluene) by evaporation of a solution of the polymer in toluene. The sample was protected from exposure to air by sealing in two Ziploc[®] bags and then quickly transferring the sample from the bags to the cryostat of a Quantum Design Physical Properties Measurement System (PPMS). The system was interfaced to an EG&G/PAR 263A potentiostat for current-voltage measurements. A cooling and heating rate of 1 K min⁻¹ was used, and at 5 K intervals a current-voltage curve was recorded over a potential range of +4 to -4 V at a sweep rate of 100 mV s⁻¹. For the sample with 2% doping, conductivity was calculated from the data from +4.0 to +3.5 V and -4.0 to -3.5 V because there was a small amount of non-linearity in the current-voltage curves.

Tris(4-nitrophenyl)methane³⁹. ¹H NMR (CDCl₃): δ 8.24 (d, 6H, J = 8.8 Hz), 7.29 (d, 6H, J = 9.0 Hz), 5.86 (s, 1H). ¹³C NMR (CDCl₃): δ 148.2, 147.5, 130.3, 124.5, 56.1.

Sodium tris(4-nitrophenyl)methyl (Na⁺1⁻)⁴⁰. Tris(4-nitrophenvl)methane (761 mg, 2.01 mmol), sodium methoxide (119 mg, 2.21 mmol), and 60 mL of pyridine were heated to reflux for 12 h to give a deep blue solution. The solution was concentrated to 15 mL to yield a purple precipitate, which was collected by filtration. Recrystallization by concentrating a CH₃CN-toluene solution gave a purple, microcrystalline product that was held under vacuum at 80 °C for 4 h. Yield: 664 mg, 83%. ¹H NMR (CD₃CN): δ 7.91 (d, 6H, J = 9.3 Hz), 7.33 (d, 6H, J = 9.3). ¹³C NMR (CD₃CN, partial spectrum): δ 150.8, 140.5, 128.3, 125.6. UV-vis in CH₃CN, 7.5 \times 10⁻⁵ M: $\lambda_{\text{max}} = 792 \text{ nm}, \varepsilon = 2.9 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$. IR (Nujol, cm⁻¹): 1590 (m), 1573 (s), 1505 (s), 1397 (s), 1331 (m), 1231 (w), 1215 (w), 1174 (m), 1106 (s), 966 (w), 861 (m), 848 (s), 828 (m), 780 (s), 758 (m), 701 (s), 682 (w), 636 (w), 614 (w). Anal. calcd for C₁₉H₁₂N₃NaO₆: C, 56.87; H, 3.01; N, 10.47. Found: C, 56.39; H, 3.14; N, 10.35%.

Tris(4-nitrophenyl)methyl radical (1). A solution of $Fc^+PF_6^-$ (250 mg, 0.756 mmol) in 15 mL of CH₃CN was added dropwise over 1 h to a stirred solution of Na⁺1⁻ (252 mg, 0.628 mmol) in 20 mL of CH₃CN. A green precipitate began to

form immediately when the addition began. The suspension was stirred for 12 h. The precipitate was collected by filtration and washed with CH₃CN. The product was recrystallized by the slow concentration of a solution in 70 mL of pyridine to 15 mL. The deep green microcrystals were collected by filtration and held under vacuum at 80 °C for 4 h. Yield: 145 mg, 61%. UV-vis in CH₃CN, saturated: $\lambda_{max} = 619$ nm. IR (Nujol, cm⁻¹): 3093 (m), 2428 (vw), 1579 (m), 1567 (s), 1501 (vs), 1333 (vs, br), 1314 (s), 1270 (m), 1180 (m), 1125 (w), 1103 (s), 866 (s), 857 (s), 847 (s), 833 (m), 762 (m), 749 (m), 701 (s), 674 (w). Anal. calcd for C₁₉H₁₂N₃O₆: C, 60.32; H, 3.20; N, 11.11. Found: C, 59.85; H, 3.44; N, 10.72%.

Tris[(4-dimethylamino)phenyl]methyl iodide $(2^+I^-)^{37}$. ¹H NMR (DMSO-*d*₆): δ 7.28 (d, 6H, J = 9.0 Hz), 7.00 (d, 6H, J = 9.0), 3.22 (s, 18H). ¹³C NMR (DMSO-*d*₆, partial spectrum): δ 176.3, 155.3, 139.2, 125.8, 112.6. UV-vis in CH₃CN, 7.8 × 10⁻⁷ M: $\lambda_{max} = 593$ nm, $\varepsilon = 9.9 \times 10^4$; $\lambda_{max} =$ 551 nm, $\varepsilon = 9.5 \times 10^4$ L mol⁻¹ cm⁻¹ (overlapping peaks fit with two Gaussians peaks). IR (Nujol, cm⁻¹): 1679 (w), 1656 (w), 1582 (s), 1524 (w), 1360 (s, br), 1298 (m), 1229 (m), 1173 (s, br), 1135 (s), 1066 (m), 959 (w), 940 (s), 912 (m), 838 (m), 825 (m), 798 (w), 758 (w), 743(w), 666 (w).

Tris[(4-dimethylamino)phenyl]methyl radical (2). A mixture of $2^{+}I^{-}$ (845 mg, 1.69 mmol), sodium amalgam (38.9 mg Na, 1.69 mmol; 4.01 g Hg), and 10 mL of DMF was stirred at 22 °C for 12 h. The red solution was filtered to remove the mercury. The DMF was removed under reduced pressure and 60 mL toluene was added to the residue. The solution was filtered to remove NaI. The toluene was removed under reduced pressure, and the product was recrystallized by dissolving in 40 mL THF, adding 10 mL heptane, and concentrating the solution to 20 mL. The product was collected by filtration and dried under vacuum for 4 h. Yield: 390 mg, 62% [the product typically contains 10% tris(4-dimethylaminophenyl)methane]. UV-vis in THF, 3.3×10^{-4} M: $\lambda_{max} = 405$ nm. IR (Nujol, cm⁻¹): 2795 (m), 1884 (w), 1678 (w), 1658 (w), 1610 (s, br), 1563 (w), 1517 (s), 1444 (m), 1349 (s, br), 1225 (m), 1201 (m), 1185 (m), 1164 (m), 1129 (m), 1060 (m), 947 (s), 836 (w), 812 (s), 795 (w), 752 (w). Anal. calcd for C₂₅H₃₀N₃: C, 80.60; H, 8.12; N, 11.28. Found: C, 80.05; H, 8.39; N, 10.98%.

Cocrystallization of 2 and 1. In a typical cocrystallization, **1** (93.2 mg, 0.246 mmol) and **2** (4.8 mg, 0.013 mmol) were dissolved in 70 mL of pyridine. The solution was slowly concentrated to 2-3 mL to precipitate a green solid. The product was collected by filtration and held under vacuum for 4 h. Isolated yield: 75.6 mg, 77%.

Results and discussion

Synthesis

Both 1^{44-48} and 2^{49} have been studied spectroscopically, generally as solutions that were generated *in situ*. Single crystals of 1 large enough for X-ray structure determination have been grown by the reduction of tris(4-nitrophenyl)bromomethane (1-Br) with a zinc rod.⁴³ However, we found that none of the reported procedures for the generation of either

radical 1 or 2 was suitable for their synthesis and isolation in bulk.

Because of the low solubility of 1, its synthesis by the reduction of 1-Br with zinc or other metals was complicated by a difficult separation from the salt byproduct. We instead took advantage of the low solubility of 1 for its isolation after the oxidation of 1^- . Tris(4-nitrophenyl)methane (1-H) was prepared by nitration of triphenylmethane with a mixture of sulfuric acid and nitric acid.³⁹ Deprotonation of 1-H by sodium methoxide gave Na⁺1⁻.⁴⁰ Oxidation of a solution of Na⁺1⁻ in CH₃CN with a solution of 1, which was purified by recrystallization from pyridine.

Commercially available 2^+ Cl⁻ (crystal violet) was converted to $2^{+}I^{-}$ by precipitation from aqueous solution by the addition of aqueous KI. Reduction of $2^{+}I^{-}$ with sodium amalgam in DMF yielded 2, which was inevitably contaminated with 10-20% of tris(4-dimethylaminophenyl)methane (2-H, leuco crystal violet). The 2-H could not be separated from 2, and reductions of $2^{+}I^{-}$ with different metals (magnesium or zinc) and in different solvents (THF or pyridine) also led to some 2-H as a side product. The amount of 2-H relative to 2 could be quantified by ¹H NMR before and after oxidation of a sample with I_2 , which converts both 2-H and 2 to 2^+I^- (see ESI \dagger). The electrochemical reduction of 2^+ has also been shown to produce 2 and a small amount of 2-H.⁵⁰ The contamination of 2 with 2-H was not a major concern for our doping studies, as the small amount of 2-H would either be electrically inactive in the doped crystals of 1, or would itself act as an n-dopant for 1, as 2-H has previously been shown to n-dope C_{60} .⁵¹

Spectroscopy

The ¹H NMR spectra of Na⁺1⁻ and 2⁺1⁻ are normal, while the radicals 1 and 2 have no detectable ¹H NMR signal (except for that of the 2-H impurity in 2). The UV-vis spectra of Na⁺1⁻,⁴⁷ 1,⁴⁴ 2⁺1⁻,⁵² and 2⁴⁹ all match previously reported spectra.

The ESR spectrum of **1** as a dilute solution in pyridine, shown in Fig. 2, agrees with a spectrum simulated using published hyperfine couplings.⁴⁸ The *g*-value of **1** was calculated to be 2.0085 (measured relative to external TCNE⁻ at $g = 2.00278^{53}$), larger than the reported value of 2.0037 for **1** in the solid state.⁴⁵

An ESR spectrum of a dilute solution of 2 in benzene (Fig. 3, top) consists of a series of lines spaced by 0.151 G (as determined by a Fourier transform of the spectrum). Using



Fig. 2 ESR spectrum of a dilute solution of 1 in pyridine.

reported hyperfine couplings for other 4-substituted triphenylmethyl radicals as a starting point, a simulated spectrum (which also has lines spaced by 0.151 G) was created with $a_{\text{H,ortho}} = 2.550 \text{ G}$, $a_{\text{H,meta}} = 1.115 \text{ G}$, $a_{\text{N}} = 0.500 \text{ G}$, $a_{\text{H,methyl}} = 0.337 \text{ G}$. The g-value of **2** is 2.0040.

Magnetic susceptibility

(i) Solution phase. The solubility of 1 was too low for a solution phase determination of its magnetic susceptibility. The Evans method⁴² was used to determine the magnetic susceptibility of 2 as a solution in pyridine- d_5 . Concentrations of 0.0451, 0.0349, and 0.0171 M (the presence of 2-H was accounted for) gave magnetic moments of 0.488, 0.509, and 0.514 $\mu_{\rm B}$, respectively. Those values are all significantly lower than the free-electron value of 1.73 $\mu_{\rm B}$, indicating that some reversible π - or σ -dimerization of 2 is occurring in solution. The increasing magnetic moment with decreasing concentration is consistent with a reversible dimerization.

(ii) Solid state. The magnetic susceptibilities of two samples of microcrystalline 1 were measured at room temperature and, after a correction for diamagnetism, indicated magnetic moments of $1.74 \ \mu_B$ and $1.62 \ \mu_B$ for the two samples measured. Those susceptibilities are close to the free-electron value and indicate that there is little intermolecular spin–spin interaction for 1 in the solid state. Measurements of the magnetic susceptibility of solid 2, after a correction for its diamagnetism, indicated a magnetic moment of $0 \ \mu_B$. The total lack of paramagnetism in solid state 2 indicates complete spin pairing, most likely through the formation of π -dimers, and is consistent with the reversible dimerization observed in solution.

Electrochemistry

The electrochemistry of 1 ³⁴ and 2 ^{34,54,55} have been investigated previously, but we examined both again by cyclic voltammetry. The cyclic voltammogram of a saturated solution of Na⁺1⁻ in THF showed its fully reversible 1^{0/-} couple at -0.65 V versus ferrocene^{+/0} (see ESI[†]). The cyclic voltammogram of 2⁺1⁻ in THF indicates that its reversible 2^{+/0} couple occurs at -1.16 V versus ferrocene^{+/0}, followed by an irreversible reduction at approximately -2.35 V (see ESI[†]). The



Fig. 3 ESR spectrum of a dilute solution of **2** in benzene (top) and a simulated spectrum (bottom).

relative potentials of $1^{0/-}$ and $2^{+/0}$ mean that the electron transfer reaction of eqn 1 is favored by 0.51 eV (12 kcal mol⁻¹),

$$1 + 2 \rightleftharpoons 1^- + 2^+ \tag{1}$$

so the equilibrium constant of the reaction is 5×10^8 (at 22 °C in THF with 0.10 M [NBu₄][PF₆]). The previously reported electrochemistry of 1 and 2 in benzonitrile³⁴ revealed a similar potential difference of 0.52 V between $1^{0/-}$ and $2^{+/0}$, indicating an equilibrium in benzonitrile that favors electron transfer to a similar extent. While the energetics of electron transfer are somewhat different in the solid state, the solution phase electrochemical results are a strong indication that 2 as a solid state dopant for 1 will be almost completely ionized to 2^+ .

The cyclic voltammogram of a one-to-one mixture of 1 and 2 (and a ferrocene standard) in THF shows the $1^{0/-}$ and $2^{+/0}$ waves at their normal potential and an additional, larger, reversible wave at -1.75 V (see Fig. 4). It has not been possible to definitively identify the species responsible for the new redox wave, but it may be the tightly associated ion pair 2^+1^- .

Cocrystallization of 1 and 2

The single-crystal X-ray structure of 1 has been published.⁴³ The powder X-ray diffraction pattern of microcrystalline 1, obtained by crystallization from pyridine, matches well with a pattern simulated using the single-crystal diffraction data (see Fig. 5). The small variations in peak intensities between the two patterns are probably due to the preferred orientation of the crystallites in the powder diffraction sample. Cocrystals of a 9 : 1 mixture of 1 and 2 were obtained from pyridine, and their powder diffraction pattern matches reasonably well with that of pure 1. No other crystalline phases are evident. Our aim in the cocrystallization of 1 and 2 was to obtain substitutional cocrystals that are isomorphous with crystals of pure 1, and the powder diffraction patterns are consistent with that result.

We were unable to obtain highly crystalline samples of a 1:1 mixture of 1 and 2, which we would expect to be the salt 1^-2^+ . The difficulty in obtaining crystalline 1^-2^+ may be due to the large solubility difference between 1 and 2 (2 is much more soluble than 1 in every solvent), combined with the reversibility of the charge transfer between 1 and 2. However, the low conductivity of the 1 : 1 precipitate of 1 and 2 (see below) is



Fig. 4 Cyclic voltammogram of a 1 : 1 : 1 molar mixture of 1 and 2 and ferrocene in THF.



Fig. 5 Simulated powder X-ray diffraction pattern of 1 (top), experimental powder X-ray diffraction of 1 (middle), and powder X-ray diffraction of 1 cocrystallized with 10% 2 (bottom).

most consistent with it being mainly 1^{-2^+} , since phases containing 1 and a small amount of 2 and phases containing 2 and a small amount of 1 would both be more conductive, as in the doped materials described below.

Solid state electrical conductivity of 1 doped with 2

(i) Room-temperature conductivity. Cocrystals of 1 and 2 were obtained by cocrystallization from pyridine. Solid state

Table 1 Room-temperature electrical conductivity of 1, 2, and cocrystals of 1 and 2.

% 1	% 2	Conductivity/ Ω^{-1} cm ⁻¹
100	0	1.5×10^{-9}
99	1	9.5×10^{-8}
98	2	6.2×10^{-7}
97	3	7.7×10^{-7}
95	5	1.2×10^{-6}
90	10	9.1×10^{-7}
50	50	4×10^{-11}
0	100	5×10^{-12}

conductivity measurements of pressed pellets of microcrystalline samples were performed in a nitrogen-filled glovebox. The conductivity data for 1, 2, and cocrystals with a range of compositions are given in Table 1. For the cocrystals of 1 doped with 1%, 2%, 3%, 5%, and 10% 2, each entry in Table 1 represents the average of four measurements: two samples from each of two separate cocrystallizations at a given dopant concentration. Those results are shown graphically in Fig. 6.

Although there is a fairly large uncertainty in the measured conductivities, there is clearly a monotonic increase in conductivity from pure 1 through 1 doped with 1%, 2%, 3%, and 5% 2, as expected if 2 is an n-dopant in 1. The measured conductivity for the 1% doping level appears to be anomalously low, possibly because some of the 2 was oxidized to 2^+ by an impurity present in 1 at less than 1% concentration. At the 10% doping level, the conductivity is lower than at 5%doping. It is likely that at the high doping level of 10% the dopants are interacting with each other. At an even higher concentration of 2, 50%, where the material is presumably mainly 2^+1^- , the conductivity is significantly lower than in pure, undoped 1. Pure 2 has the lowest conductivity of all the materials. The increasing conductivity with increasing concentration of 2 in 1, in addition to showing that 2 is a dopant for 1, is a strong indication that cocrystallization of 1 and 2 has occurred, since neither 2 nor $2^{+}1^{-}$ as a physical mixture with 1 would increase the conductivity of 1.

For comparison, two samples of sodium-doped 1 were prepared by cocrystallization of 1 and Na^+1^- from pyridine.

At molar concentrations of 2% and 5% Na⁺, the conductivity of doped **1** is only 5×10^{-8} and $6 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$, respectively (see Fig. 6). The Na⁺1⁻ apparently forms tightly bound ions pairs in the solid state that do not easily transfer an electron to **1**.

The mobility (or lack of mobility) of 2^+ in 1 was examined by measuring the conductivity of doped samples as a function of time. If the 2^+ was mobile there would be an ionic component to the conductivity that would decay over time, and the movement of 2^+ might also affect the electrical conductivity of doped 1. The conductivity of pressed pellets of 1 doped with 2%, 5%, and 10% 2 was measured in a two point configuration, with the applied potential switched from +4 V to -4 V at intervals as short as 1 s, and no change in the current was evident at any time scale. Additionally, a constant bias of 4 V was applied for several hours, and no decay in the current occurred (see ESI†).

(ii) Variable-temperature conductivity. The conductivity of pressed pellets of 1 doped with 2% 2 and 1 doped with 5% 2 were measured as a function of temperature from 300 K to the lowest temperature at which the resistance was still measurable with our instrument, which was 200 K for the 2% doped sample and 170 K for the 5% doped sample. For the 5% doped sample, the measurements were repeated as the temperature was raised from 170 K to 300 K, and no hysteresis was observed between the cooling and warming cycles. The data are shown in Fig. 7. For both samples, electrical conduction is an activated process with an activation energy of 0.32 eV, which is comparable to that observed in other neutral radical conductors.⁵⁶ The fact that the activation energy is the same in both samples indicates that the activated process is the same in both materials. The activation energy probably represents the energy required to overcome the Coulombic attraction to move an electron from a 1^{-} anion neighboring a 2^+ cation to a 1 radical without a cationic neighbor. Alternatively, the activated process could be the simple hopping of an electron from 1^{-} to a neighboring 1, or the measured activation energy may be due to a combination of these two processes.²¹



Fig. 6 Room-temperature electrical conductivity of 1 doped with varying concentrations of 2. At each concentration, identical symbols indicate samples from the same cocrystallization.



Fig. 7 Pressed pellet conductivity of 1 doped with 2% (\bigcirc) and 5% (\Box) 2 as a function of temperature.

Our goal in this study was to create a dopant for a molecular semiconductor that fulfilled two criteria: (1) the dopant would substitutionally cocrystallize with the semiconductor to yield immobile dopant ions in the doped semiconductor, and (2) the dopant would spontaneously transfer an electron to the molecular semiconductor in the solid state. The electrochemical redox potentials of 1 and 2, along with their similar overall molecular size and shape, led us to believe that they would fulfil the roles as an appropriate molecular semiconductor and dopant, respectively. Evidence for substitutional cocrystallization was found in the similar powder X-ray diffraction patterns of pure 1 and 1 cocrystallized with 2. Additional evidence for substitutional cocrystallization comes from the increased electrical conductivity of 1 doped with 2 compared to pure 1, as both 2 and 2^+1^- have significantly lower conductivity than pure 1. And, of course, the increased conductivity in doped 1 compared to pure 1 is evidence that criterion (2) has been fulfilled. There was no indication of ionic conductivity in doped 1, confirming that the 2^+ dopants are immobile. Systems such as the one presented herein will lead to new organic semiconductor devices that utilize true p-n junctions.

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