



Is there such a thing as a molecular organic alloy?

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In inorganic materials, an alloy is a mixture of two or more substances that generally exhibits electronic and/or physical properties that differ from those of its constituents. In organic systems, the formation of a “molecular alloy” comprising mixtures of molecular organic materials has also been proposed. We test the validity of this concept via the study of the optoelectronic properties of a ternary system that has previously been identified to form a molecular acceptor alloy, namely a blend of a poly(3-hexylthiophene) (P3HT) donor, with two acceptors indene-C₆₀ bisadduct (ICBA) and phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) [R. A. Street, *et al.*, *J. Am. Chem. Soc.*, 2013, 135, 986–989]. Using photoelectron spectroscopy, we find that the ICBA:PC₆₁BM blend shows the same highest occupied molecular orbital and exciton energies as that of ICBA, indicating the absence of a new exciton state in the blend. Furthermore, charge transfer state spectra of ternary blends are found to comprise a simple linear superposition of the corresponding binaries. From these results, no evidence of new, emergent electronic states is found to support the existence of a molecular alloy in this system. To our knowledge there is as yet no clear evidence of the existence of an alloy in any organic semiconductor system. We discuss the criteria that should be met by a molecular organic alloy and procedures needed for their unambiguous identification.

Introduction

An alloy is commonly understood to be a physical mixture of two or more constituents with variable proportions that exhibits electronic and/or physical properties different from its components.¹

New concepts

For 30+ years, the concept of molecular alloy has been used to explain a variety of phenomena in organic materials from doping in OLEDs, to charge transfer salts. Recently, the term has been used in the context of charge transfer in ternary mixtures of donor and acceptor molecules in organic solar cells. However, there is no coherent or consistent definition of what, exactly, is a molecular alloy. In this paper we describe the conventional definition of an alloy, and then proceed to set forth criteria that, if met, would clearly define the presence of such behavior in molecular organic solids. We then apply these criteria, as an example, to the analysis of a recently published ternary mixture found in organic solar cells. We find no evidence for alloy formation for this particular example ternary mixture. To broaden our discussion from this archetype substance, we apply our criteria to a variety of molecular systems including charge transfer salts, polymer eutectics, heavily conductivity-doped organic films, and so on. None appear to show clear alloy behavior. Yet we do not rule out the possibility that such will be found in the future, but rather suggest means for identifying these potentially interesting materials.

Common examples of metal alloys are steel (C + Fe) or brass (Zn + Cu). Binary semiconductors such as Si_xGe_{1-x}, ternary semiconductors such as In_xGa_{1-x}As, and other quaternary and quinary inorganic semiconductors are also commonly referred to as alloys.¹ All of these materials have optical and electrical properties that are distinct from the substances of which they are comprised. The physical properties (*i.e.* Young's moduli, melting points, *etc.*) are also different in most alloy mixtures than in their constituents.² Their characteristics derive almost entirely from the strong chemical bonds formed between atoms in the mixtures.

In contrast to inorganic alloys comprising atomic constituents, organic materials are bonded by far weaker, electrostatic van der Waals forces. It has been proposed that in some cases these weakly bonded organic mixtures form a new substance which is called a “molecular alloy”. One potential class of molecular alloys are charge transfer (CT) salts and their solid solutions,³⁻⁷ another are organic eutectics.⁸⁻¹² The formation of molecular alloys has also been claimed to be observed in disordered

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organic solid solutions.¹³ Recently, ternary blends in the active regions of organic photovoltaic (OPV) cells and so-called organic co-crystals have been identified to form organic alloys.^{14–23} Although there has been frequent mention of molecular organic alloys over many decades, to our knowledge no uniform framework has been developed to clearly define what is meant by this term, and how an organic alloy differs from chemically bonded mixtures whose electronic, optical and physical properties are not a mere extrapolation of those of the individual constituents.

A chemical bond between organic molecules commonly results in an entirely new compound, not an alloy mixture. Given the absence of chemical bonds between molecules, the correspondence between a molecular organic alloy and alloys found in metals and inorganic semiconductors admittedly cannot be precise. The weak and electrostatic nature of van der Waals forces in molecular alloys as compared with chemical bonds in atomic alloys implies that the term alloy, itself, will have a different meaning for mixtures in these different systems. To clarify these substantially different definitions, we propose that a molecular alloy should meet the following criteria:

1. It should be a physical mixture of two or more species of organic molecules with no chemical reaction occurring during mixture formation. The proportion of constituents can vary over a wide range.
2. It should have electron orbital interactions between different molecular species that result in modifications of electronic states that cannot be ascribed to a simple linear superposition of those inherent to the constituents.
3. The orbital interactions should lead to electronic or physical properties clearly distinguishable from those of its constituents.

Note that electron transfer between molecules needs special attention relative to Criterion 2. For example, the electron transfer in a donor:acceptor blend is driven by the energy offset between the corresponding states in the participating molecules. This does not meet the requirements of Criterion 2 if the inherent properties of the electronic states involved are left unchanged by the transfer process.

The changes in electronic or physical properties mentioned in Criterion 3 are often observed. Specifically, changes in electronic properties have been used to claim the formation of a molecular organic alloy.^{3,5,6,14–18,22} Also, changes in physical properties (e.g. eutectic formation) may indicate the presence of an alloy.^{9–11} These changes, too, are often the result of electronic interactions, although prior studies have not provided evidence that the other two criteria are also fulfilled.

In this work, we investigate a ternary mixture that forms the active region of an organic photovoltaic (OPV) cell that has previously been claimed to be an organic alloy.¹⁴ The ternary system comprises a donor (D) poly(3-hexylthiophene) (P3HT), blended with two acceptors indene-C₆₀ bisadduct (ICBA, A₁), and phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM, A₂).^{14,24} Evidence for the existence of an alloy between the two acceptors was based on the observed dependence of the CT state absorption energy and the open circuit voltage (V_{OC}) of the OPV on the blend ratio. Although these composition-dependent electronic

properties may suggest the formation of an organic alloy, investigation of the origins of the observed changes are needed to identify whether or not they fully meet the three criteria discussed above. Here we provide a detailed investigation of the highest occupied molecular orbital (HOMO), the Frenkel exciton, and CT states of this system. The various electronic states of the blends are found to be linear superpositions of those of the constituents, without evidence for the emergence of new electronic properties that are expected for an organic alloy. Based on these findings and those in other such reports, we provide a set of criteria that should be met when characterizing a molecular material mixture as an alloy. To our knowledge, there is as yet no definitive identification of such a substance that unambiguously meet these criteria.

Results

Fig. 1 shows the ultraviolet photoelectron spectra (UPS) of the two acceptors and their blends in the ratios of 1:4, 1:1 and 4:1. The short vertical lines in Fig. 1(a) indicate the emission cutoff extracted from the spectra due to the 21.2 eV He-I transition. Fig. 1(b) shows the low-binding-energy region of the spectra. The short vertical lines show that the HOMO energy for ICBA and the blends is at -5.8 ± 0.1 eV (referenced to vacuum), and for PC₆₁BM the HOMO energy is at -6.0 ± 0.1 eV.

Photoluminescence (PL) was used to study the exciton states of individual acceptors and blends, with the results shown in Fig. 2. The normalized steady-state PL spectra are provided in Fig. 2(a). The dominant 0–0 transition peaks have energies of 1.66 ± 0.01 eV for ICBA, 1.70 ± 0.01 eV for PC₆₁BM, and 1.66 ± 0.01 eV for all of the blends. Also, ICBA and the blends show 0–1 transition emission at 1.60 ± 0.01 eV, and 0–2 transition peaks at 1.51 ± 0.01 eV. PC₆₁BM has its 0–1 transition at 1.55 ± 0.01 eV. Fig. 2(b) presents the first derivatives of the normalized PL spectra to more accurately determine the peak positions. The data indicate that all acceptor blends have the same peak positions as that of ICBA. To further explore whether there exists a new excitonic state, the dynamics of the exciton state recombination were studied using time-resolved PL, with results shown in Fig. 2(c). The transients are fit by a single exponential decay shown by solid lines, yielding exciton lifetimes of $\tau = 0.98 \pm 0.04$ ns for ICBA, $\tau = 0.94 \pm 0.04$ ns for PC₆₁BM, and $\tau = 0.95 \pm 0.04$ ns for the blend. All of these decay rates are equal to within experimental accuracy.

The electroluminescence (EL) spectra of ternary OPVs with different blend ratios are shown Fig. 3(a). The CT state emission peak monotonically blue shifts from 1080 nm to 990 nm as the proportion of ICBA in the two acceptors increases from 0 to 100%. To understand this hypsochromic shift, we used a series of Gaussians to fit the EL spectra. As shown in Fig. 3(b), the EL spectrum of the DA₁ binary is fit using a P3HT exciton peak at 646 nm, ICBA exciton peaks at 725 nm and 823 nm, and the DA₁ binary CT state at 990 nm with a full width at half maximum of FWHM = 205 nm. Fig. 3(c) is the EL spectrum of the DA₂ binary fit assuming a P3HT exciton peak at 645 nm, and of PC₆₁BM at

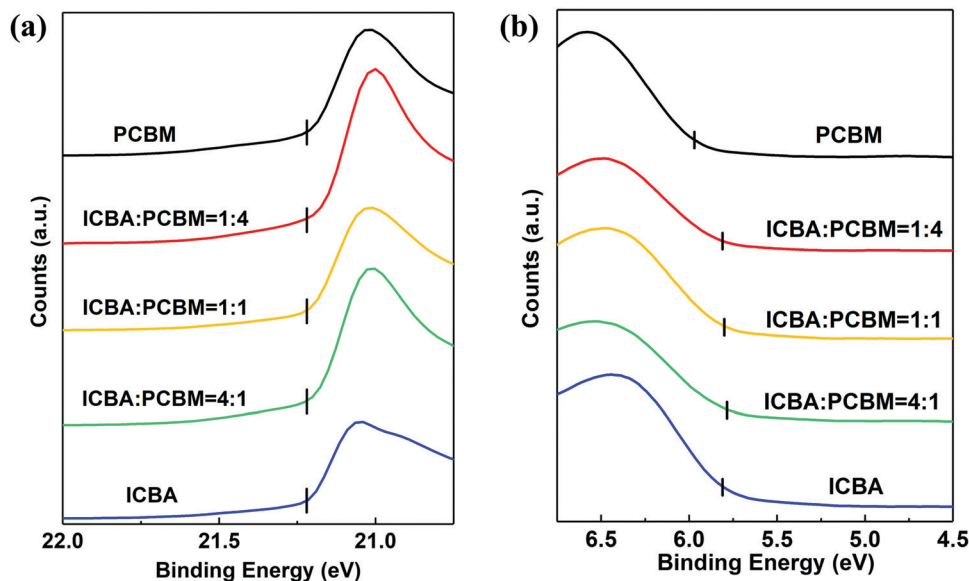


Fig. 1 (a) High-binding-energy region of ultraviolet photoelectron spectra (UPS) of ICBA, PC₆₁BM and their blends at ratios indicated. The short vertical lines represent the emission cutoff energies. (b) Low-binding-energy region where the short vertical lines indicate the highest occupied molecular orbital energies.

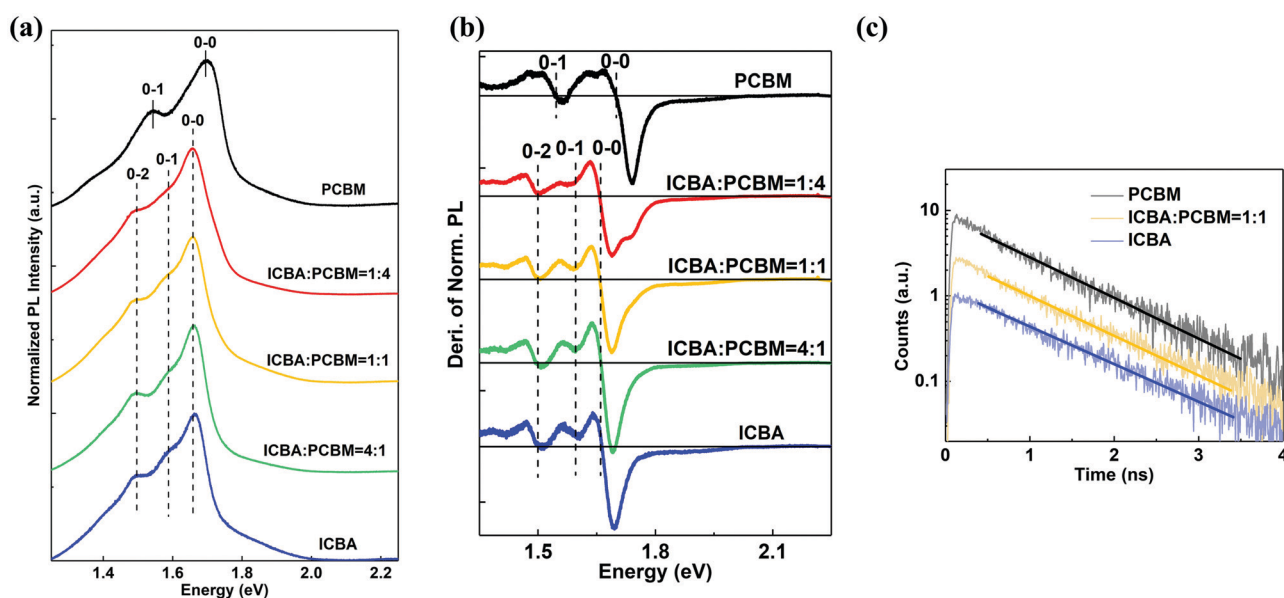


Fig. 2 (a) Normalized steady-state photoluminescence (PL) spectra of ICBA, PC₆₁BM and their blends at indicated ratios. The short vertical lines indicate the exciton energies of PC₆₁BM, the long dashed lines indicate the exciton energies of the various vibronics of ICBA and the blends. (b) Derivative of the normalized steady-state PL spectra to more clearly indicate the alignment of the transition energies. (c) Time-resolved PL of ICBA, PC₆₁BM and their 1 : 1 blend. The solid lines are monoexponential fits used to extract the exciton lifetimes.

708 nm. Then the DA₂ binary CT state is at 1080 nm with FWHM = 215 nm. Fig. 3(d) is an example of the Gaussian fit to the EL spectrum of the ternary DA₁A₂ with ratio 1 : (0.5 : 0.5). It has the same exciton peak positions of P3HT and PC₆₁BM. The CT emission peak comprising the two binaries is fit by their linear superposition with peaks at 990 nm and 1080 nm, and with FWHM = 205 nm and 215 nm, respectively.

A similar fitting procedure is applied to DA₁A₂ junctions of the same composition but with different acceptor blend ratios.

The intensities of the DA₁ and DA₂ CT emission are found from the areas under the corresponding Gaussian distributions. In Fig. 4(a), the ordinate is the fraction of DA₂ CT state emission intensity, CT(DA₂), in the total ternary CT emission, CT(DA₁) + CT(DA₂). The abscissa is the fraction of PC₆₁BM (A₂) in the acceptor mixture (A₁ + A₂). We find a linear relationship between CT(DA₂) and A₂ blend fraction with unity slope and an intercept at the origin. Fig. 4(b) shows CT state energy (E_{CT}) vs. blend ratio. The blue solid line represents the simulated

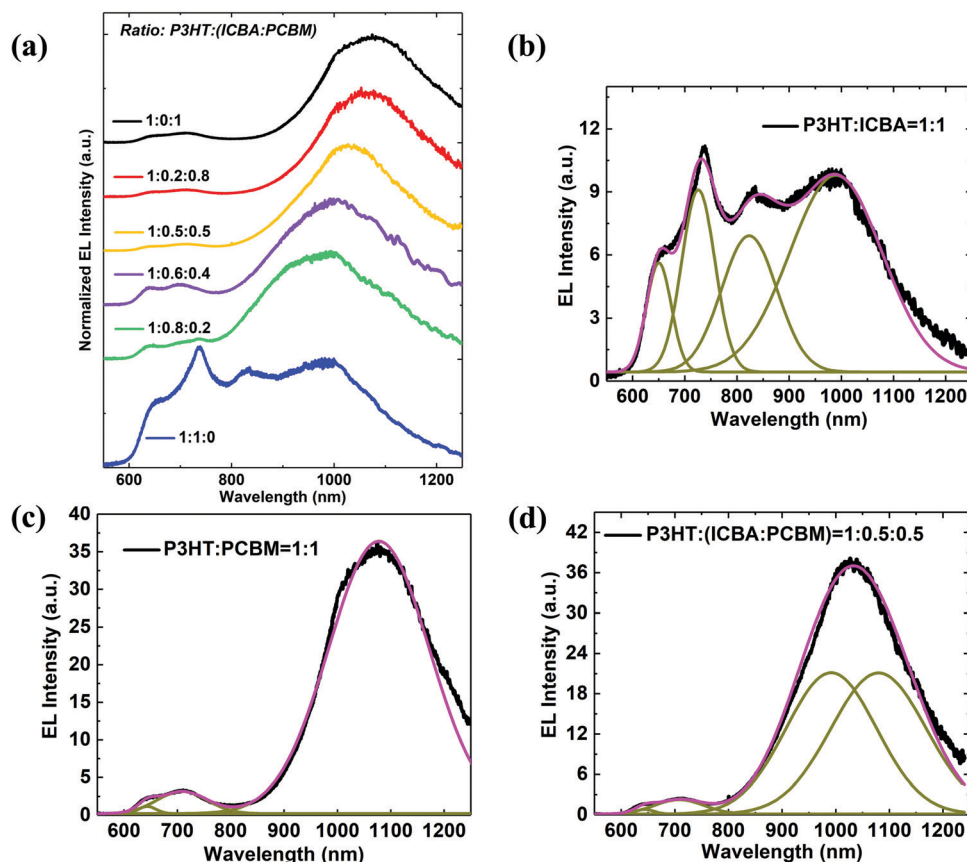


Fig. 3 (a) Electroluminescence (EL) spectra of binary and ternary OPVs with different P3HT : (ICBA : PC₆₁BM) blend ratios indicated. (b) The EL spectrum of 1 : 1 P3HT : ICBA. The Gaussian distributions used to fit the spectrum and the sum of these Gaussians are shown by the green and pink lines, respectively. (c) The EL spectrum of 1 : 1 P3HT : PC₆₁BM with the series of Gaussians (green lines) and their sum (pink). (d) The EL spectrum of 1 : 0.5 : 0.5 P3HT : (ICBA : PC₆₁BM) with fits as in (c).

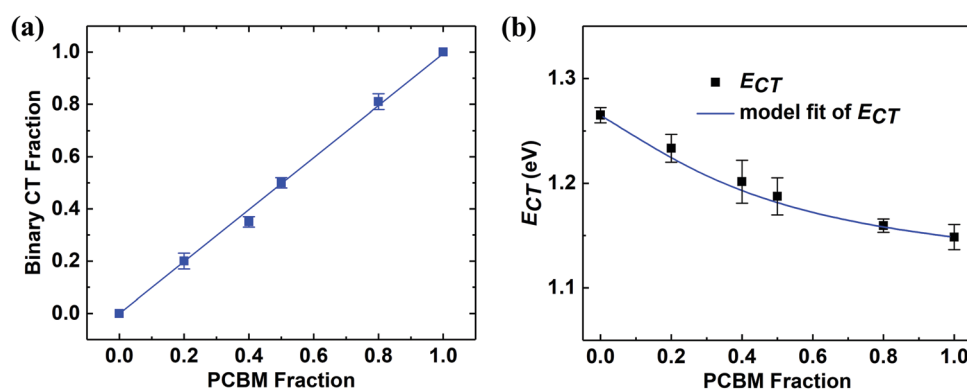


Fig. 4 (a) Relationship between the intensity fraction of the P3HT:PC₆₁BM charge transfer state vs. the fraction of PC₆₁BM in the acceptors in the ternary blend. The line is a least squares fit with unity slope and intercept at the origin. (b) Charge transfer state energy vs. PC₆₁BM fraction in the acceptors. The line shows the calculated relationship between the peak position of the sum of two binary Gaussians vs. blend ratio. The fit to the data show the measured peak positions are equal to the linear superposition of the Gaussian line shapes.

peak position found from the sum of two Gaussians centered at $E_{CT1} = 1.15$ eV and $E_{CT2} = 1.25$ eV, corresponding to the two binary CT state energies. The peak position is plotted as a function of the intensity fraction, which is the same as PC₆₁BM fraction as illustrated in Fig. 4(a).

Discussion

Analysis of the UPS data in Fig. 1 indicates that the HOMO levels of the acceptor blends are the same as that of ICBA, independent of the acceptor blend ratio, with no evidence found for the emergence of new ground state. The steady-state

PL data in Fig. 2(a) and (b) show that the exciton energies of the acceptor blends are also the same as for ICBA, nor does the exciton lifetime extracted from time-resolved PL in Fig. 2(c) depend on the blend ratio. Thus, the excited states in the acceptor blends also do not appear to be influenced by the mixture composition.

The CT state EL spectrum in Fig. 3 for a 1:(0.5:0.5) DA₁A₂ blend does not exhibit spectral features independent of those of the individual binaries. In addition, the CT emission of the ternary blends is a linear superposition of the binary spectra whose intensities are proportional to their concentration in the blends, see Fig. 4(a).

In the less clearly resolved absorption spectral analysis of Street, *et al.*,¹⁴ it was found that the CT peak position of the blend follows Vegard's law *via*:

$$E_{CT} = (1 - x)E_{CT1} + xE_{CT2} - bx(1 - x)$$

where x is the fraction of PC₆₁BM to the total acceptor concentration, and $b = 0.15$ is the bowing parameter. Vegard's law is a simple, extrapolative expression with no analytical physical origin. Nevertheless, the existence of a bowing parameter suggests that the CT peak position may indeed be influenced by electronic orbital interactions in the mixture, although no comment was made to explain this in the previous work.¹⁴ To explore this apparent nonlinearity, in Fig. 4(b) we simulate the sum of Gaussian distributions representing the two binary CT states. The simulation indicates that the linear superposition of these two Gaussian distributions results in an identical extrapolative dependence found by Vegard's Law, where the bowing arises from the simple addition of the two, Gaussian-shaped CT emission spectra.

Since the totality of our measurements show no evidence for the emergence of new electronic states, we conclude that the properties of the P3HT:ICBA:PC₆₁BM active region are explained by the linear superposition of the characteristics of the two constituent heterojunctions. Hence, we can eliminate, at least in this case, the existence of a molecular alloy.

One exogenous cause for the lack of evidence for alloying in P3HT:ICBA:PC₆₁BM blends based on our three criteria may be phase separation between the two acceptor components. That is, if separate domains of P3HT:ICBA and P3HT:PC₆₁BM are formed in the blend, the opportunity for electronic interactions between the two acceptors would not exist, thus explaining why no alloys are detected. However, similar chemical structures and thin film surface energies of ICBA (24.9 mN m⁻¹) and PC₆₁BM (27.6 mN m⁻¹) suggest the two molecules are highly miscible.²⁵ Furthermore, detailed nuclear magnetic resonance studies of the acceptor and ternary blends show shifts of the ¹H and ¹³C resonance frequencies of the two acceptors compared to their individual spectra. This is attributed to homogeneous, random contacts between acceptors in the blends, indicating a lack of phase separation.²⁶ Hence, at least in this particular system, the lack of evidence for an alloy cannot be attributed to spatial separation of the two donor:acceptor constituents in the blend.

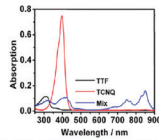
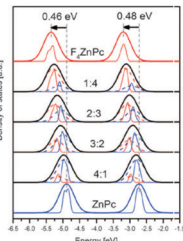
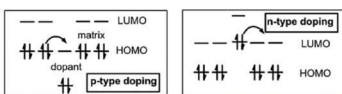
The forgoing characterization illustrates a general procedure by which to identify the existence of an alloy. Based on the criteria stated in the introduction, the first step is to measure and compare the electronic states of the organic constituents and mixtures. If the electronic states of the mixtures are unchanged from those in the constituents, no alloy has been formed. If a difference is found, other reasons should be considered and if possible excluded, such as a linear superposition of electronic states of the constituents, aggregation of one molecular species when introducing another or other morphology changes,²⁷ and trap-state filling,²⁸ *etc.* The final identification of a molecular alloy can be made after this procedure is complete.

With these criteria in mind, we can attempt to evaluate other possible molecular alloy systems. Table 1 is a summary of some of the organic mixtures that have previously been described as alloys. Organic CT salt complexes and their solid solutions are frequently mentioned as representing a class of organic alloys.³⁻⁷ The absorption and Raman spectra of organic CT salts are composed of the superposition of the spectra of the individual anionic and cationic states.^{4,5,7,29} This suggests that even though there is substantial charge transfer between constituents of the salts, the result is again a simple mixture of anions and cations that do not form alloys whose properties differ from those of the partially reduced or oxidized constituents.

Another materials class with potential to form alloys are organic co-crystals, defined as a single phase material comprising two or more molecular organic species.^{22,23,30} Although some co-crystals appear to have tunable energy levels such as halogenated benzodifurandione-based oligo(*p*-phenylene vinylene) (BDOPV)-based small molecules,²² the origin of this energy level change is due only to electrostatic interactions between molecular dipoles or higher order multipoles.^{31,32} Note that in this situation it is important to distinguish electrostatic interactions from intermolecular orbital interactions. For example, simulations based on electrostatic interactions and its consistency with experimental results³¹ can provide evidence as to whether electrostatic effects or alloying is responsible for the modification in electronic states. Furthermore, organic eutectics are materials that have phase transition temperatures dependent on the relative proportion of their constituents.⁸⁻¹² This distinct physical property is similar to inorganic alloys and may, indeed, indicate formation of an organic alloy. But the evidence thus far presented has not shown intermolecular electronic coupling. Hence, it is inconclusive that these mixtures are true alloys.

Doped organic semiconductors whose conductivities and Seebeck coefficients depend on doping concentration have also been studied as possible examples of alloys.³³⁻³⁷ Doping with donors or acceptors results in the charge transfer between electronic states from the dopant to the host.^{36,37} Even at the high molar densities typically used in highly doped organics (~0.1 molar ratio of dopant to host), new electronic states have not been reported. Other organic mixtures that do not belong to these categories have also been studied,^{13,38,39} including disordered organic solid solutions and binary helices, yet once again no evidence has been presented to support the claim of a

Table 1 Summary of potential systems of organic alloy

Material system	Example	Properties	Electronic states	Alloy or not?
Ternary OPV	P3HT:ICBA A:PC ₆₁ BM	V_{OC} depends on the blend ratio	In the P3HT:ICBA:PC ₆₁ BM ternary system, the excitonic and CT states are just the simple superposition of those of the two binaries.	No for P3HT:ICBA:PC ₆₁ BM case. Insufficient evidence to identify in other cases.
Organic CT complexes	TSeF _x TTF _{1-x} TCNQ ^a	Metal-insulator transition temperature and conductivity depending on mixture ratio	TTF-TCNQ ^b UV-vis absorption spectra ²⁹  Absorption of the mix: TTF radical cations (330, 430, and 650-700 nm); TCNQ radical anions (700-800 and 800-900 nm)	No. Spectra are a linear superposition of individual, partially charged anions and cations.
Organic co-crystals	BDOPV/F ₆ -BDOPV co-crystal	Tunable bandgap	DOS simulation of ZnPc:F ₄ ZnPc ^{d 31}  Simulation based on electrostatic interactions of molecular quadrupole fits to experimental results	No. The change in energy levels is due to electrostatics.
Organic eutectics	Camphor-SCN ^e	Solidification temperature depending on mixture ratio	No evidence presented to show modification of electronic states	Insufficient evidence to identify presence of alloys.
Doped organic semiconductors	NTCDA ^f doped BEDT-TTF ^g	Conductivity and Seebeck coefficients depend on doping concentration	Scheme of organic molecular doping process ³⁷ 	No. Increased conductivity arises from electron transfer between unchanged electronic states.

^a Tetraselenafulvalene (TSeF)-tetrathiafulvalene (TTF)-tetracyano-*p*-quinodimethane (TCNQ). ^b Tetrathiafulvalene (TTF)-tetracyano-*p*-quinodimethane (TCNQ). ^c Zinc phthalocyanine. ^d Tetrafluoro-zinc phthalocyanine. ^e Succinonitrile. ^f Naphthalenetetracarboxylic dianhydride. ^g Bis-ethylenedithio-tetrathiafulvalene.

modification of the parent electronic states. To our understanding, therefore, there is yet no complete evidence to identify electronic coupling that would justify unambiguous identification of a molecular alloy in any of these previously reported systems.

Conclusion

In this work we propose criteria that must be met to unambiguously identify a molecular organic alloy: that is, a mixture of two or more molecular organic substances that have intermolecular electron coupling that results in modification of the electronic states of the constituent molecules. Specifically, we investigated the P3HT:(ICBA:PC₆₁BM) ternary system which has previously been proposed to form an alloy between the two acceptors in the blend. The HOMO levels and the exciton energies of the acceptor blends are the same as for the individual components. Furthermore, the CT states in the ternary blends of varying acceptor ratios are a linear superposition of the two distinct binary CT states. According to our criteria, this ternary system is simply a combination of two binary heterojunctions that do not form an organic molecular alloy. Using our procedure to identify a molecular organic alloy,

no clear example has yet been found for the existence of such a material.

Methods

The ICBA/PC₆₁BM acceptor blends with ICBA weight fractions of 0, 0.2, 0.5, 0.8, 1 were dissolved in chlorobenzene (CB) at total concentration of 20 mg mL⁻¹ and stirred overnight at 60 °C at 300 rpm. The solutions were then spin-coated at 1000 rpm for 60 s on 150 nm thick indium tin oxide (ITO) on glass substrates to form 90–100 nm thick acceptors films for UPS measurements. The films were thermally annealed at 150 °C for 60 min, 20 min, 50 min, 20 min, and 10 min, respectively. The measurements were done in an ultrahigh vacuum chamber (base pressure < 1 × 10⁻⁹ Torr) using the 21.22 eV He-I gas-discharge lamp emission. The spectra were collected by a hemispherical electron energy analyzer (Thermal VG) with a pass function FWHM = 0.16 eV.

The acceptor films were similarly prepared for PL measurements on quartz substrates. The samples were excited in low vacuum at wavelength λ = 422 nm using a continuous wave He-Cd laser to obtain steady-state PL. The spectra were collected using a fiber-coupled monochromator (Princeton Instruments SP-2300i) equipped with a Si charge-coupled device (CCD)

(PIXIS:400). For time-resolved PL measurements, the samples were excited at $\lambda = 480$ nm using 150 fs pulses at a 1 kHz repetition rate from a Ti:sapphire laser (Clark-MXR CPA series) pumped optical parametric amplifier (TOPAS-C). The photon counts were measured using a time-correlated single photon counter (PicoHarp 300) coupled to a Si single photon avalanche detector (PDM series).

The OPV devices were grown on a solvent cleaned, 145 nm thick film of ITO, patterned into 1 mm wide stripes on a glass substrate. The ternary blends comprising P3HT:(ICBA:PC₆₁BM) of different acceptor weight ratios were separately prepared in CB at total concentration 20 mg mL⁻¹ and stirred overnight at 60 °C at 300 rpm. A 45 nm thick layer of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (CLEVIOSTTM P VP AI 4083, filtered with a WhatmanTM 0.45 μ m nylon filter w/glass micro fiber) was first spin-coated on the ITO and baked at 150 °C for 30 min. Subsequently, the P3HT:(ICBA:PC₆₁BM) active layer was spin-coated in an ultrapure nitrogen environment ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm) on top of the PEDOT:PSS at 1000 rpm for 60 s to form a 90–100 nm thick film. Then the samples were transferred into a high vacuum chamber (base pressure $\sim 10^{-7}$ Torr) for Al thermal evaporation at 1 Å s⁻¹ to form a 100 nm thick film. The samples were transferred back to the nitrogen environment for thermal annealing at 150 °C. The thermal annealing time was 10 min for 1:1:0, 20 min for 1:0.2:0.8 and 1:0.8:0.2, 40 min for 1:0.6:0.4, 50 min for 1:0.5:0.5 and 60 min for 1:0:1.²⁴ The charge transfer state EL spectra were measured under 4 V forward-bias, collected using a fiber-coupled monochromator equipped with a Si CCD and an InGaAs photoreceiver with sensitivity from $\lambda = 800$ to 1700 nm (Newport Model 2153). The EL spectra were fit with Gaussian distributions using OriginPro 2017. The V_{OC} were measured in a glovebox filled with nitrogen ($O_2 < 0.1$ ppm, $H_2O < 0.1$ ppm), using a solar simulator with a 300 W Xe lamp with an AM1.5G filter, whose 1 sun intensity was calibrated with a National Renewable Energy Laboratory-traceable Si reference cell.

Conflicts of interest

There are no conflicts of interest to declare.

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