Virtual screening of electron acceptor materials for organic photovoltaic applications

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Abstract. Virtual screening involves the generation of structure libraries, automated analysis to predict properties related to application performance and subsequent screening to identify lead systems and estimate critical structure–property limits across a targeted chemical design space. This approach holds great promise for informing experimental discovery and development efforts for next-generation materials, such as organic semiconductors. In this work, the virtual screening approach is illustrated for nitrogen-substituted pentacene molecules to identify systems for development as electron acceptor materials for use in organic photovoltaic (OPV) devices. A structure library of tetra-azapentacenes (TAPs) was generated by substituting four nitrogens for CH at 12 sites on the pentacene molecular framework. Molecular properties (e.g. \(E_{\text{LUMO}}\), \(E_g\) and \(\mu\)) were computed for each candidate structure using hybrid DFT at the B3LYP/6-311G** level of theory. The resulting TAPs library was then analyzed with respect to intrinsic properties associated with OPV acceptor performance. Marcus reorganization energies for charge transport for the most favorable TAP candidates were then calculated to further determine suitability as OPV electron acceptors. The synthesis, characterization and OPV device testing of TAP materials is underway, guided by these results.

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Organic semiconductors are a class of materials that have a wide-range of electronic device applications, including organic light-emitting diodes, organic solar cells and detectors, and organic thin-film transistors. One attractive characteristic of organic optoelectronic materials is their very large and complex design space, providing great opportunity for chemical design to achieve diverse physical and chemical properties. The discovery and optimization of new materials underpins the development of next-generation technologies. Traditionally, the development of a new material is the result of chemical insight combined with tremendous effort toward the synthesis, purification, characterization and testing of a limited number of candidate systems, with varied success. For some classes of materials, combinatorial experimentation is being used to help accelerate the process [1], however there is a pressing need for the development of efficient and low-cost methods to systematically explore chemical design space and advise experimental efforts.

Virtual screening is an approach first developed and applied in the pharmaceutical industry to identify leads in the drug discovery process [2]. The process involves the automated computational analysis and subsequent filtering of chemical structure libraries based on predicted properties to identify promising systems for further investigation. The application of the virtual screening paradigm to problems in materials science and specialty chemicals is a promising new development. Advances in the efficiency of electronic structure codes and the significantly improved performance of commodity computing resources has significantly reduced the time required for the first principles analysis of chemical systems; ranging from small molecules to extensive surface models and bulk systems. Moreover, electronic structure packages are extremely robust for routine analysis and property prediction, usually requiring no user intervention once the chemical models and parameters have been decided. This makes it possible for automated quantum chemical property predictions for a library of candidate systems with varying structure and composition. The structure library can then be sorted and screened based on the computed properties to identify lead systems and estimate critical structure–property limits across a target chemical design space.

Organic photovoltaic (OPV) cells hold great promise to become a viable alternative to the existing solar cell technologies, which are dominated by silicon-based devices [3–8]. The basic mechanism of photocurrent generation in OPV cells, using the frontier orbital energy levels for a simple OPV device containing two organic materials, is illustrated in figure 1(A). The process shown there involves light absorption leading to formation of a bound electron–hole pair (exciton) (1). Excitons are formed in both the donor (D) and acceptor (A) layers. The excitons can either diffuse to the donor–acceptor (D/A) interface or alternatively decay to the...
Anode
Cathode
Donor Acceptor
h
e
e
HOMO
LUMO
e
A B
1
2
4 N

Figure 1. (A) General mechanism for photocurrent generation in OPVs; (B) elemental substitution pattern used for generating the TAP structure library (4N for CH, over 12 sites on the pentacene scaffold).

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ground state. At the D/A interface the exciton can undergo a charge transfer reaction, forming a hole and electron in the D and A layers, respectively (2). The driving force for charge transfer is the offset in available energy between the excited state of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor. A large driving force makes charge separation an efficient process. After the hole and electron are generated, they are conducted through the organic layers and extracted by the electrodes.

One of the key challenges limiting the development of OPV devices is the availability of suitable electron acceptor materials [9]. While a wide range of donor materials have been used in OPVs, fullerenes are by far the most common acceptors and are found in all of the high efficiency cells. The choice of fullerenes limits the number of donor materials that can be used in OPVs to only those that are energetically well matched to fullerenes. Neat C$_{60}$ absorbs strongly between 400 and 500 nm and has high electron mobility [10–12]. The high mobility stems from the extensive π overlap in the condensed phase. C$_{70}$ gives a red shifted absorption spectrum (500–600 nm) and good electron mobility as well [13]. Limited tuning of the electron affinities in fullerenes can be accomplished by switching between C$_{60}$ and C$_{70}$ or chemical functionalization, however the accessible range of electron affinities is small. Moreover, fullerenes are costly and have been highlighted as a key source of instability in lifetime tests of high performance OPVs [14, 15].

The development of alternative acceptor materials with varying LUMO energies would be beneficial for designing OPVs with a given donor, since this will allow better control over the maximum LUMO energy offset for the cell. A key initial step is the identification of suitable molecular scaffolds as starting points for new chemical families of OPV acceptors. Acenes, such as pentacene, are a widely studied class of organic semiconductors and have been used as active materials in OPVs [16–20]. Adding electron withdrawing substituents such as halides, cyano or nitro groups has been used to increase the electron affinities of acenes for use as n-type material in organic electronics. Incorporating these functional groups shifts the LUMO to lower energy, but often alters the solid state packing in such a manner that decreased intermolecular interactions lead to lowered device performance. In addition, these groups often increase reorganization energies for electron transfer, decreasing carrier mobilities [21, 22]. An alternative approach for tuning the LUMO energies of acenes without substantially altering the molecular shape is to substitute nitrogen for CH into the molecular framework. This effect has
been evaluated theoretically [23, 24] and demonstrated experimentally [25–27]. Substitution of nitrogen for CH or CR in an organic molecule like tetracene or pentacene leads to a marked increase in the electron affinity and N-substituted acenes have reorganization energies consistent with efficient electron mobility [23, 24]. This suggests that these materials can be used as good n-type materials, i.e. acceptors, in OPVs.

In the present work, the application of virtual screening is illustrated for the investigation of nitrogen substituted pentacenes as a scaffold for development of electron acceptor materials for OPVs. Specifically, this work focuses on tetra-azapentacenes (TAPs) generated by substituting CH with single nitrogen on each of the four outer arenes in the base pentacene framework, as illustrated in figure 1(B). This particular substitution pattern was chosen in order to generate azapentacene derivatives with LUMO energies comparable to that of C$_{60}$ (−3.65 eV). For example, Winkler and Houk [23] have determined that penta-azapentacenes with single nitrogen in each arene ring have LUMO energies near −3.75 eV. In addition, the 6- and 13-positions on the acene core were left unsubstituted since it has been shown that aryl or alkylnyl groups at these positions in pentacene lead to materials that are more soluble and tractable in the solid state [28]. The resulting TAPs are analyzed in an automated fashion using density functional theory to compute key intrinsic properties related to OPV acceptor suitability. The resulting virtual TAPs library is then screened to estimate the effects of nitrogen incorporation and inform experimental efforts to synthesize, characterize and test alternative OPV acceptors in devices.

2. Methods

The results presented in this work were obtained using the Schrödinger Materials Science Suite (Version 1.0) [29]. An electron acceptor candidate library was generated using the MSCombi structure enumeration module, substituting four nitrogen over 12 CH sites on the pentacene molecular framework producing 135 unique TAP structures, from a total of 495 symmetry-related structures. The molecular geometry, highest occupied molecular orbital (HOMO) energy, LUMO energy, HOMO–LUMO gap and dipole moment ($\mu$) for each TAP structure was calculated in an automated fashion with the Jaguar density functional theory (DFT) package (Version 8.R42) [30] using the B3LYP hybrid density functional, which corresponds to Becke’s three-parameter exchange functional (B3) [31] along with the Lee–Yang–Parr gradient-corrected correlation functional (LYP) [32]. The Pople triple-$\zeta$ polarized basis set, 6-311G** [33] was used in these calculations. Electron reorganization energies were computed for leading TAP structures using the Optoelectronic module, also at the B3LYP/6-311G** level of theory. Data analysis and interactive property visualization was carried out using the built-in functionality of the Materials Science Suite.

3. Results and discussion

The development of new classes of electron acceptor materials for OPV application would expand the selection of possible electron donor materials and enable new devices and architectures that could lead to greatly enhanced OPV efficiencies. Leading requirements for an electron acceptor to replace fullerenes in OPV include a low LUMO energy in the range $-3.0$ to $-4.1$ eV, for efficient charge separation, and a band gap $\leq 2.0$ eV, for increased solar absorption. Pentacene is one of the most widely used organic semiconductors [16–20] and as
such, represents a known molecular framework to chemically tailor for application as an OPV acceptor.

Substitution of nitrogen into the carbon framework (N for CH) of pentacene scaffold is a strategy that has been examined in previous reports [23–27]. Winkler and Houk [23] carried out a survey of N-rich pentacenes using hybrid DFT. It was found that replacement of CH by N strongly enhances the electron affinity and may facilitate electron transfer. Chemical modification involving added electron withdrawing substituents has also been examined. Chen and Cao [24] analyzed the properties related to charge transfer for fluorine-derivatized pentacenes and azapentacenes, also using hybrid DFT. They found that N-incorporation was preferable over fluorination for increasing the electron affinity while maintaining useful reorganization energies.

The performance of DFT in predicting HOMO and LUMO energies at a level useful for energy level engineering for organic optoelectronics has been studied previously [34, 35]. Although Koopman’s Theorem [36] is not strictly valid for DFT, Kohn–Sham orbital energies from hybrid DFT have been shown to correlate with experimental frontier orbital measurements. Dixon and co-workers [34], surveyed numerous atomic and molecular systems and found that for HOMO, LUMO and other related molecular properties, comparisons between results from hybrid DFT and experimental data gives generally applicable linear correlations. The prediction of LUMO energies was found to be more sensitive to basis set effects than HOMO energies. It was found that if a basis set produces negative LUMO energies then it is applicable for studying trends across a chemical library. Djurovich et al [35], compared hybrid DFT LUMO energies to experimental values measured for a series of organic semiconductor compounds using inverse photoelectron spectroscopy, optical or electrochemical measurements. A predictive linear correlation was found for experimental and calculated LUMO levels, with hybrid DFT LUMO providing an accurate estimate of the transport level for organic semiconductors.

A library of 495 TAPs structures was generated using a combinatorial substitution scheme producing 135 stereochemically unique TAPs to investigate the effect of nitrogen substitution on the properties of pentacene related to performance as an OPV acceptor material. The chemical space is defined by exhaustively substituting four N for CH over 12 sites on the pentacene scaffold as shown in figure 1(B). Quantum chemical analysis of these structures allows the determination of property limits and variability of this focused chemical library for alternative OPV electron acceptor materials.

Molecular properties for each TAP candidate, along with those for pentacene and C$_{60}$, was computed using the B3LYP/6-311G** level of theory. The properties under examination are the LUMO energies ($E_{LUMO}$), HOMO–LUMO energy gap ($E_g$) and electric dipole moment ($\mu$). The property ranges, averages and standard deviations for the calculated TAPS library are presented in table 1. To visualize the variation and distribution of the properties, ordered library plots and histograms for $E_{LUMO}$ and $E_g$ over the entire TAP library, and for the pyridyl-TAP subset of the library (containing one N substitution per six-member ring), are given in figures 2–5 respectively. In each of the figures, the plot shows the variability in the property across the library by means of a scatter plot (XY) with the TAP structures ordered so that the relative property of interest is increasing. For comparison, the ordered property plots for the complete TAP library are annotated to show the calculated values for pentacene and C$_{60}$. The insets on figures 2 and 3 show the property distribution across the library as a histogram of the calculated property. Figures 4 and 5 are annotated to label pyridyl-TAP structures of interest.
Table 1. TAP electron acceptor library characterized in terms of B3LYP/6-311G** calculated property minimum, maximum, mean, standard deviation and range.

| Molecular property | Min   | Max   | Mean  | Std Dev. | Range |
|-------------------|-------|-------|-------|----------|-------|
|                  |       |       |       |          |       |
| Full TAP library  |       |       |       |          |       |
| \(E_{\text{HOMO}}\) (eV) | −6.05 | −5.48 | −5.77 | 0.10   | 0.56  |
| \(E_{\text{LUMO}}\) (eV) | −3.75 | −3.31 | −3.52 | 0.09   | 0.44  |
| \(E_g\) (eV)   | 1.94  | 2.41  | 2.25  | 0.10   | 0.47  |
| \(\mu\) (Debye) | 0.00  | 9.32  | 4.05  | 2.33   | 9.32  |
| Pyridyl-TAP library subset  |       |       |       |          |       |
| \(E_{\text{HOMO}}\) (eV) | −5.95 | −5.75 | −5.84 | 0.06   | 0.20  |
| \(E_{\text{LUMO}}\) (eV) | −3.59 | −3.37 | −3.48 | 0.08   | 0.23  |
| \(E_g\) (eV)   | 2.31  | 2.40  | 2.37  | 0.03   | 0.09  |
| \(\mu\) (Debye) | 0.00  | 7.98  | 3.20  | 2.37   | 7.98  |

Figure 2. Ordered plot and histogram (inset) of the B3LYP/6-311G** calculated LUMO energies \(E_{\text{LUMO}}\) for the TAP OPV acceptor library. Reference structures, pentacene and \(C_{60}\) are shown with their respective \(E_{\text{LUMO}}\) values indicated.

An immediate observation in figures 2 and 3 is that across the chemical space defined by substituting 4N into the pentacene core scaffold, both \(E_{\text{LUMO}}\) and \(E_g\) vary nearly uniformly over their range, with no large discontinuous regions of property values. Figure 2 shows the
variability and distribution of the LUMO orbital energies across the structure library. The desired effect of nitrogen incorporation on $E_{\text{LUMO}}$ is obvious with all of the N$_4$-pentacene candidates having a $E_{\text{LUMO}}$ lower than that of pentacene by 1.09–0.65 eV. The entire TAPS library has $E_{\text{LUMO}}$ in a range that is comparable to that of C$_{60}$, to within 0.1–0.34 eV, indicating their suitability as potential candidates for electron acceptors for OPV. As shown in figure 2 and in table 1, the $E_{\text{LUMO}}$ values have a range of 440 meV, from $-3.75$ to $-3.31$ eV. The library LUMO average energy and standard deviation is $-3.52$ and 0.09 eV, respectively. Interestingly, some of the TAP structures are predicted to have an $E_{\text{LUMO}}$ lower than that of C$_{60}$.

One property that can affect the charge transport efficiency for organic semiconductor materials is the electric dipole moment. A sizeable dipole moment can promote strong electron–dipole interactions in the amorphous condensed phase that lead to charge trapping which in turn impede electron transport. The computed dipole moments ($\mu$) across the library vary from 0 to 9.32$D$. The mean and standard deviation for the TAPS library dipole moment are 4.05$D$ and 2.33$D$, respectively. The data points in figure 2 are colored by dipole moment, with the range represented by the colors blue to red, for $\mu = 0$ to 9.32$D$ respectively.

Another desirable characteristic for OPV acceptor materials is a small HOMO–LUMO gap, satisfying a partial requirement for enhanced optical adsorption. From figure 3 and table 1, the $E_g$ energies span from 1.94 to 2.41 eV, with a mean and standard deviation of 2.25 and 0.10 eV, respectively. All of the TAP library structures are predicted to have a more favorable $E_g$ than C$_{60}$ by 0.80–0.33 eV. The library minimum and maximum $E_g$ values almost evenly bracket the $E_g$ values.
Figure 4. Ordered plot of the B3LYP/6-311G** calculated LUMO energies ($E_{\text{LUMO}}$) for the pyridyl-TAP subset of the OPV acceptor library. Zero dipole pyridyl-TAP structures are shown and their respective $E_{\text{LUMO}}$ values are indicated, along with the $E_{\text{LUMO}}$ of C$_{60}$ for comparison.

of pentacene (+0.25, −0.22 eV). The data points in figure 3 are colored by $E_{\text{LUMO}}$, with values from low to high energies represented by blue to red, respectively.

To identify promising TAP acceptor candidates, the 135 structure library was first sorted by $E_{\text{LUMO}}$, selecting the top 25 low LUMO energy structures, which were then sorted by dipole moment to select 15 exemplary TAP structures. According to Marcus theory, electron transfer within a molecular homodimer can be described by an Arrhenius-like rate equation with an exponential dependence on the negative reorganization energy. For charge transport in organic solids, the intramolecular reorganization energy is the dominant contribution, over medium polarization effects (inner- and outer-sphere reorganization energy, respectively). The electron intramolecular reorganization energy is calculated as the sum of the difference between the vertical and adiabatic electron affinity for a neutral TAP molecule and the difference between the vertical and adiabatic ionization energy of the reduced TAP species. In this work, intramolecular electron reorganization energies were calculated for these systems using the B3LYP/6-311G** level of theory. The structure, frontier orbital energies and electron reorganization energies ($\lambda^-$) for the 15 exemplary TAP acceptor candidates are presented in table 2, along with data for pentacene for comparison. The pentacene properties under consideration are calculated to be $-2.66$, $2.20$ and $0.13$ eV, for $E_{\text{LUMO}}$, $E_g$ and $\lambda^-$, respectively. These values can be compared to results of previous theoretical studies, which give pentacene properties in agreement (< 0.1 eV) with those reported here. For example, pentacene $\lambda^-$ was computed to be 0.131 and 0.133 eV, with the 6-311+G** [23] and 6-31G** basis sets [24], respectively. Many of the TAP structures shown in table 2 incorporate pyrazinyl- or pyridazinyl-subunits that contain two nitrogens
Figure 5. Ordered plot of the B3LYP/6-311G** calculated HOMO-LUMO gap energies ($E_g$) for the pyridyl-TAP subset of the OPV acceptor library. Zero dipole pyridyl-TAP structures are shown and their respective $E_g$ values are indicated, along with the $E_g$ of pentacene for comparison.

substituted into one ring either on adjacent or opposing sites. For these structures the $E_{\text{LUMO}}$ range from $-3.57$ to $-3.69$ eV, whereas the $E_g$ vary from $2.41$ to $1.99$ eV. All of the computed $\lambda^-$ values for the TAP structures in table 2 are less than 0.25 eV and comparable to that of pentacene (+0.03 to +0.09 eV), suggesting that these structures should show efficient electron mobility as long as good electronic coupling in the condensed phase is achieved.

In addition to having desirable properties associated with performance as electron acceptors for OPV, a paramount requirement for lead TAP structures is that they are relatively inexpensive and synthetically accessible. In identifying suitable TAPs targets for synthesis we focus on a subset of the full TAPs library. TAP candidates that have a single N substitution per ring, composed of only pyridyl-subunits, should be more synthetically tractable. The subset of pyridyl-TAPs consists of 20 structures. From table 1, the subset $E_{\text{LUMO}}$ range is from $-3.59$ to $-3.37$ eV, which is 0.93–0.71 eV lower and 0.06–0.28 eV higher than the $E_{\text{LUMO}}$ of pentacene and C$_{60}$, respectively. For the pyridyl-subset the range of $E_g$ is 0.09 eV, with a minimal value of 2.31 eV, a mean value of 2.37 eV and a standard deviation of only 0.03 eV. The $E_{\text{LUMO}}$ and $E_g$ ordered subset plots are presented in figures 4 and 5. Selecting for pyridyl-TAP structures that have a zero dipole moment to minimize solid state trapping, defines another set of exemplary TAP structures. These structures are presented in table 3, with figures 4 and 5 annotated to indicate the associated $E_{\text{LUMO}}$ and $E_g$ data points. The pyridyl-TAP structure with the lowest $E_{\text{LUMO}}$ ($-3.59$ eV) and smallest $E_g$ (2.31 eV) is structure 17 (also structure 9 in table 2), corresponding to 2,6,8,12-TAP and has an electron reorganization energy, $\lambda^-$, of 0.16 eV. The pyridyl-TAP candidates in table 3, have LUMO energies from $-3.59$ to $-3.37$ eV, which are
Table 2. B3LYP/6-311G** calculated properties (HOMO energy ($E_{\text{HOMO}}$), LUMO energy ($E_{\text{LUMO}}$), HOMO–LUMO gap ($E_g$), electron reorganization energy ($\lambda^-$) and dipole moment ($\mu$) for TAP electron acceptor candidates having lowest $E_{\text{LUMO}}$ and small $\mu$.

| Molecular structure | TAP isomer  | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | $E_g$ (eV) | $\lambda^-$ (eV) | Dipole ($D$) |
|--------------------|-------------|-------------------------|-------------------------|------------|-----------------|--------------|
| 1                  | Pentacene   | −4.86                   | −2.66                   | 2.20       | 0.13            | 0.00         |
| 15 TAP structures with lowest $E_{\text{LUMO}}$ and small $\mu$ |
| 2                  | 2,6,9,12    | −5.82                   | −3.69                   | 2.13       | 0.18            | 0.62         |
| 3                  | 2,5,9,12    | −5.82                   | −3.68                   | 2.14       | 0.18            | 1.51         |
| 4                  | 5,6,11,12   | −6.04                   | −3.63                   | 2.41       | 0.16            | 0.00         |
| 5                  | 2,5,10,11   | −5.77                   | −3.63                   | 2.14       | 0.18            | 1.30         |
| 6                  | 2,6,10,11   | −5.77                   | −3.62                   | 2.15       | 0.18            | 2.03         |
| 7                  | 1,6,10,12   | −5.69                   | −3.61                   | 2.07       | 0.21            | 1.92         |
| 8                  | 1,5,10,12   | −5.69                   | −3.61                   | 2.08       | 0.22            | 2.52         |
| 9                  | 2,6,8,12    | −5.91                   | −3.59                   | 2.31       | 0.16            | 0.00         |
| 10                 | 2,6,7,12    | −5.79                   | −3.59                   | 2.20       | 0.17            | 0.64         |
| 11                 | 2,5,8,12    | −5.92                   | −3.58                   | 2.34       | 0.17            | 1.42         |
| 12                 | 1,6,7,12    | −5.69                   | −3.58                   | 2.11       | 0.17            | 0.00         |
| 13                 | 2,5,8,11    | −5.93                   | −3.58                   | 2.35       | 0.17            | 0.00         |
Table 2. (Continued.)

| Molecular structure isomer | TAP E\textsubscript{HOMO} (eV) | E\textsubscript{LUMO} (eV) | E\textsubscript{g} (eV) | \(\lambda^–\) | Dipole (\(D\)) |
|--------------------------|----------------|----------------|----------------|--------|---------|
| 14                       | 2,6,7,11       | -5.81          | -3.58          | 2.23   | 0.18    | 1.63    |
| 15                       | 1,2,9,10       | -5.56          | -3.57          | 1.99   | 0.19    | 2.14    |
| 16                       | 2,3,8,9        | -5.91          | -3.57          | 2.34   | 0.17    | 0.00    |

Table 3. B3LYP/6-311G\textsuperscript{**} calculated properties (HOMO energy (\(E\textsubscript{HOMO}\)), LUMO energy (\(E\textsubscript{LUMO}\)), HOMO–LUMO gap (\(E\textsubscript{g}\)), electron reorganization energy (\(\lambda^–\)) and dipole moment (\(\mu\)) for pyridyl-TAP electron acceptor candidates having lowest \(E\textsubscript{LUMO}\) and small \(\mu\).

| Molecular structure isomer | TAP E\textsubscript{HOMO} (eV) | E\textsubscript{LUMO} (eV) | E\textsubscript{g} (eV) | \(\lambda^–\) | Dipole (\(D\)) |
|--------------------------|----------------|----------------|----------------|--------|---------|
| Pyridyl-TAP structures with lowest \(E\textsubscript{LUMO}\) and \(\mu = 0\) |                      |                      |                      |        |         |
| 17                       | 2,6,8,12       | -5.91          | -3.59          | 2.31   | 0.16    | 0.00    |
| 18                       | 2,5,8,11       | -5.93          | -3.58          | 2.35   | 0.17    | 0.00    |
| 19                       | 1,2,7,8        | -5.76          | -3.37          | 2.40   | 0.15    | 0.00    |
| 20                       | 2,4,8,10       | -5.75          | -3.37          | 2.38   | 0.15    | 0.00    |

significantly lowered from the LUMO of pentacene (\(-2.66\text{ eV}\)) and are comparable to that of C\textsubscript{60} (\(-3.65\text{ eV}\)). Their HOMO-LUMO gaps are from 2.31–2.40\text{ eV}, which is 0.43–0.34\text{ eV} smaller than the \(E\textsubscript{g}\) for C\textsubscript{60}. The zero dipole pyridyl-TAPS have favorable \(\lambda^–\) values of about 150–170\text{ meV}.

The use of virtual screening to evaluate the TAP design space for application as OPV acceptors can provide valuable guidance to experimental efforts. With this data in hand, we have recently developed a synthetic route to synthesize TAPs in significant quantities for
characterization and device testing. In figure 6, the measured optical adsorption and emission spectra for 1,2,7,8-TAP in pyridine is shown (structure 19, table 3). While the observed optical gap (2.13 eV) is lower than the HOMO–LUMO gap predicted from calculation (2.39 eV), the transition energy and vibrationally structured lineshape is consistent with that displayed by dissolved pentacene [37]. The sharp, well-resolved vibronic progressions displayed in figure 6 are independent of concentration, indicating that the spectra originate from molecular, as opposed to aggregated, species. Synthesis, characterization and device testing of the electrical properties for this compound and other isomers is underway to establish TAPs as viable core scaffold for the development of OPV acceptors and will be reported elsewhere. However, preliminary data from simple bilayer heterostructure devices show behavior consistent for a material with a LUMO energy comparable to that of C_{60} (figure 7). A device made with pentacene/C_{60} displays the asymmetric $I–V$ curve expected for a diode due to the 1 eV offset between the frontier orbital energies of the two materials, whereas a similar device made with 1,2,7,8-TAP/C_{60} displays a near symmetric $I–V$ trace. The electrical response from the latter device is indicative of a near barrierless flow of electrons between the two materials thus indicating a close match in HOMO/LUMO energies for the two compounds.

The molecular design space for a target chemical application can be enormous, depending on the structural motifs and rules used to define the candidate structures. Exhaustive screening, illustrated here, provides a complete survey of the property landscape across the library, establishing limits and identifying lead candidates. Other virtual screening strategies can be used to attempt to reduce the computational effort required to identify lead structures. For example, inverse design approaches start with selected target properties and then use methods such as simulated annealing or genetic algorithms to identify candidates that fulfill the requirements with a minimal number of simulations [38, 39].

Figure 6. Experimental optical adsorption and emission spectra (in pyridine, right) and molecular structure and laboratory image for a representative pyridyl-TAP (1,7,8,14 N$_4$-pentacene).
Figure 7. Current–voltage (I–V) curves for a bilayer devices with structure ITO/pentacene (or 1,2,7,8-TAP) (250 Å)/C_{60} (400 Å)/BCP (100 Å)/Al (left) and calculated schematic energy level diagram for the active materials (right) (BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline).

4. Outlook and conclusions

The results presented here demonstrate a powerful approach for exploring the property limits of chemical design space for organic optoelectronic materials. This work provides details of the effect of incorporating four nitrogens into the pentacene scaffold (TAPs) on calculated LUMO energies and HOMO–LUMO gaps, primary properties associated with performance as electron acceptor materials in OPV devices. Additionally, exemplary TAP acceptor candidates were identified and further evaluated with respect to their electron reorganization energies. A subset of pyridyl-TAPs was discussed as tractable synthetic targets for experimental synthesis and development into a new class of OPV acceptor materials.

The prospect of automating complex material modeling workflows to explore formulation and chemical design space has the potential to rapidly accelerate materials discovery, analysis and optimization. In addition to identifying specific lead candidates to pursue experimentally, the resulting aggregate of data from high-throughput modeling studies will reveal structure–property trends and underlying physical patterns.

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