

1 The role of chemical design on the performance of organic semiconductors

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12 Abstract | Organic semiconductors are solution-processable, lightweight and flexible, such that they
13 are increasingly being used as the active layer in a wide range of new technologies. The versatility of
14 synthetic organic chemistry enables the materials to be tuned such that they can be incorporated into
15 biological sensors, wearable electronics, semi-transparent photovoltaics and flexible displays. These
16 devices can be improved not only by developing their synthetic chemistry but also by improving the
17 analytical and computational techniques that enable us to understand the factors that govern material
18 properties. Judicious molecular design provides control of the semiconductor frontier molecular
19 orbital energy distribution and guides the hierarchical assembly of organic semiconductors into
20 functional films where we can control the properties and motion of charges and excited states. This
21 Review describes how molecular design plays an integral role in developing organic semiconductors
22 for electronic devices in present and emerging technologies.

23 [H1] Molecular orbital design considerations

24 The energies of frontier molecular orbitals and the distribution of the orbitals in a π -conjugated
25 molecule play critical roles in intra- and intermolecular charge transport, light absorption/emission,
26 charge injection/extraction/trapping and electrochemistry. This is true for organic small molecules and
27 conjugated polymers alike. In each case, the energy of the highest occupied molecular orbital (HOMO)
28 largely depends on the electron density and delocalization of the π electrons throughout a π -
29 conjugated backbone. Substituents that donate electron density mesomerically (for example, lone pair
30 donation from N, O or S heteroatoms) or inductively (for example, alkyl chains) can contribute to
31 raising the HOMO energy E_{HOMO} , decreasing the solid-state ionization potential (IP, Box 1).
32 Conversely electron-withdrawing groups, such as $-\text{F}$, $-\text{C}(\text{O})\text{R}$ or $-\text{C}\equiv\text{N}$ groups, can act to lower both
33 the HOMO and lowest unoccupied molecular orbital (LUMO) energy, leading to an increase in the
34 solid-state electron affinity (EA).
35

36
37 The spatial distribution of a molecular orbital is important when considering intermolecular electronic
38 coupling, which relies on efficient π -orbital overlap between two or more conjugated systems. The
39 rational introduction of substituents into a conjugated organic molecule is a practical means to
40 manipulate molecular orbital energies levels. (Fig. 1).

41
42 As a starting point to illustrate ‘molecular engineering’, (5Z,5'Z)-5,5'-(((6,6,12,12-tetramethyl-6,12-
43 dihydroindeno[1,2-*b*]fluorene-2,8-diyl)bis(benzo[*c*][1,2,5]thiadiazole-7,4-
44 diyl))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one) (**IDFBR**, Fig. 1) was chosen. The
45 HOMO wavefunction is delocalized over its entire π -conjugated backbone whereas in contrast, the
46 LUMO wavefunction is predominantly localized on the electron-deficient 2,1,3-benzothiadiazole (BT)
47 and rhodanine moieties.¹ In order to efficiently accept electrons from a light absorbing donor polymer,
48 we are interested in tuning the LUMO energy of **IDFBR**, which is optimally achieved by the
49 introduction of substituents at its periphery. To tune the HOMO energy however, we can add
50 substituents at any conjugated part of the molecule. Replacing the central indenofluorene core with a
51 smaller fluorene unit affords **FBR**, which has fewer delocalised electrons, resulting in an increase in
52 HOMO energy (by almost 0.2 eV), with a smaller increase in the LUMO energy (less than 0.1 eV),
53 due to the larger fraction of the conjugated unit having electron withdrawing functionality. A
54 modification of **FBR** by replacing the BT units with a phenylene, results in **PH**, the LUMO energy of

55 which is substantially higher lying (~ 0.5 eV) because the phenylenes are less electron-deficient (the
56 HOMO is only marginally affected). Difluorinating the BT units in FBR gives **diFBR**, in which both
57 the HOMO and LUMO energies are 0.1–0.2 eV lower lying on account of electron-withdrawing
58 inductive effects of the electronegative F atoms. Another approach in the manipulation of the
59 molecular orbitals of FBR is to replace the C=S (thiocarbonyl) groups on the rhodanine periphery,
60 with dicyanovinyl moieties, which are more strongly electron-withdrawing than the thiocarbonyl.
61 Indeed, **diCN** has HOMO and LUMO energy levels that are ~ 0.3 eV lower than those of **FBR**. Both
62 the electron density distribution along the molecule, as well as the delocalization of the π orbitals play
63 a substantial role in determining the orbital energy levels. **FBR** has a non-planar backbone because
64 the BT and fluorene units have neighbouring H atoms that participate in repulsive interactions. These
65 steric effects can be alleviated by replacing the fluorene core with cyclopentadithiophene to give
66 **CPDT**, a molecule with more π orbital overlap between rings, which contributes to both raising the
67 HOMO energy and lowering the LUMO energy. The introduction of the electron-rich thiophene rings,
68 further raises the HOMO energy. **CPDT** also exhibits electrostatic S \cdots F interactions, with these
69 electropositive and electronegative atoms, respectively, interacting to stabilise the planar backbone,
70 affording additional raising of the HOMO energy and lowering of the LUMO energy. The greater π
71 orbital delocalization means that the LUMO is now distributed further over the core of the molecule,
72 and functionalization at any location within this region will affect the LUMO as well as the HOMO
73 energy. Substituting the sp^3 -hybridized C atom of the fluorene unit with either Si or Ge does not
74 appear to influence either the HOMO or LUMO energies. This is surprising because incorporating
75 larger heteroatoms between rings typically leads to a lengthening of the C–C bond linking the two
76 aromatic rings, thereby attenuating the antibonding interactions that arise from the node of the HOMO
77 between the rings and lowering the HOMO energy. Similarly, replacing the S atoms on the CPDT unit
78 with other chalcogen atoms does not affect the electronic structure of CPDT. In general, having a
79 larger chalcogen atom (E) in a ring lowers its aromatic character because the E–C bonds are longer,
80 such that the chalcogen non-bonding valence electrons are less delocalized. The ring thus has more
81 diene character, such that the overall molecule has a lower lying HOMO and a smaller bandgap².

82
83 Charge transport is sensitive to traps within the bulk,³ and transport within p-type materials benefits
84 from their low ionization potential, which makes the filling of deep traps thermodynamically
85 unfavourable. Similarly, n-type materials benefit from a large EA, when again there are less
86 accessible charge traps. Injecting holes from an electrode into the HOMO of a semiconductor is more
87 energetically facile when the electrode workfunction is close to, or preferably larger than, the IP of the
88 semiconductor. This allows for ohmic contact, with low contact resistance at the electrode–
89 semiconductor interface. Correspondingly, for electron injection, the EA should be as large as
90 possible. For an organic semiconductor device to be stable in operando, we must ensure that its
91 neutral and charged forms do not participate in chemical reactions.⁴ In order to prevent the most
92 thermodynamically favourable reactions (those involving a combination of O₂ and H₂O), a neutral p-
93 type semiconductor is predicted to require an ionization potential greater than 4.9 eV.⁴ When this is
94 not the case, the shallow HOMO semiconductor can, for example, reduce ambient O₂ in the presence
95 of H₂O to form OH \cdot . Under operation, deep HOMO semiconductors can accept holes that can oxidise
96 atmospheric H₂O. The activation barriers of these deleterious reactions fortunately lead to
97 overpotentials that allow many organic semiconductors to perform redox slowly so they can exhibit
98 reasonable shelf and operational stabilities. Electron transport is particularly affected by reactions
99 with air, and it is essential to prevent the electron polaron from reducing ambient species. To
100 accomplish this, the LUMO energy must be low enough to prevent excited electrons to reduce
101 hydrated O₂ complexes to O₂ $^{\cdot -}$ (one of the most favourable electrochemical reactions)⁵ or H₂O to OH \cdot .
102 These unwanted electrochemical processes can lower charge transport and also lead to further
103 irreversible reactions within a semiconductor. Defining a precise EA value that needs to be exceeded
104 to prevent these redox reactions requires consideration of the overpotential of the reaction and device
105 morphology. It has been proposed that organic molecules should have an EA greater than 4 eV to
106 suppress oxidation reactions⁶.

107
108 [H1] Organic field effect transistors

109 Charge transport in organic semiconducting polymers relies on a combination of intrachain polaron
110 conjugation, facilitated by π -electron delocalization across the polymer backbone, and intermolecular
111 charge-hopping between adjacent chains, facilitated by thin film microstructure. Charge carrier
112 mobility is very sensitive to the nature of the close-packed hierarchical assembly of polymer
113 backbones, which can be optimized by tuning inter- and intramolecular interactions. Intermolecular
114 contacts have been facilitated by many design motifs, including the μm -scale 3D ordering of
115 poly{2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-*b*]thiophene} (**pBTTT**, Fig. 2a) in thin films⁷. This
116 material adopts a morphology in which ordered lamellar sheets of π -stacked conjugated **pBTTT**
117 backbones exhibit out-of-plane order or “registration” directed by the interdigitation of vertically
118 adjacent polymer chains. Interdigitation was made possible by the conformationally-tolerant, regular
119 spacing of the side chains along the backbone, with optimal spatial separation to ensure an ordered
120 and close-packed side chain density on interdigitation.

121
122 The approach of utilising non-covalent intermolecular interactions for charge transport optimisation,
123 has subsequently been exploited in a series of isoindigo polymers⁸, and a comparison drawn with
124 similar associations observed in biology. Here the polymer alkyl side chains were described as
125 undergoing ‘molecular docking’, the locking of side chains into voids along the polymer chain. Indeed,
126 the collective van der Waals interactions between inert aliphatic side chains are the dominant
127 interaction that governs morphology and inter- and intrachain contacts. Even though the degree of
128 interdigitation exhibited by **pBTTT** is extremely unusual, a close packed and regular alkyl
129 distribution between backbones can act to not only order a material, but also minimize the local free
130 volume such that unwanted species such as H₂O are excluded. If these small molecules were included
131 then they could participate in charge-trapping and lower carrier mobility.

132
133 Intramolecular charge transport can be optimally facilitated when the backbone of a polymer has the
134 least possible amount of intrinsic energetic disorder, in which case it is resilient to torsional
135 fluctuations between adjacent monomer units^{9,10}. Energetic disorder is typically minimized by
136 maximising the energetic barrier to rotation between aromatic repeat units along the backbone.
137 Several design strategies can impart coplanarity of adjacent monomer units in a conjugated backbone.
138 Non-covalent through-space interactions between adjacent rings can act as a barrier to rotation, thus
139 promoting co-planarity. Common examples of this approach include the electrostatic attractions
140 between heteroatoms in close proximity to the bond linking two aromatic rings in the backbone. The S
141 atom on a linking thieno group, despite the presence of two lone pairs of electrons, presents a partially
142 positive charge due to the donation of one lone pair to complete an aromatic ring. As a result,
143 heteroatoms such as O and N, which have available lone pairs of electrons, can participate in strong
144 attractive interactions with S, leading to a more rigid structure.¹¹⁻¹³ For example, in poly(3-
145 alkoxythiophene) the S atom of one ring interacts with the more electronegative O atom in the
146 adjacent ring (Fig. 3a). Other planarizing interactions include H-bonding interactions, which are
147 observed between bis(lactam) building blocks and neighbouring residues. Thus, the crystal structures
148 of small-molecule diketopyrrolopyrrole (**DPP**) and isoindigo derivatives feature O \cdots H-C
149 interactions.^{14,15} The O atom in the electron-deficient lactam core interactions with a proximal H atom
150 to lower rotational disorder and maximize π -orbital overlap between the rings. This concept can be
151 extended to polymers by incorporating DPP and isoindigo monomers into the polymer backbone (Fig.
152 3a).

153
154 Non-covalent interactions can also be exploited to design highly coplanar copolymers with low
155 energetic disorder such as the copolymer poly(indacenodithiophene-*co*-benzothiadiazole) (**IDT-BT**,
156 Fig. 2b)⁹. The dominant planarising interaction in this case is a H-bond between the N atom of the
157 benzothiadiazole and the α -H atom of the adjacent indacenodithiophene. These strong N \cdots H-C
158 interactions outweigh the repulsive steric exchange energies associated with planarity, giving rise to
159 extremely low energetic disorder in this polymer. Despite the high coplanarity, the polymer exhibits a
160 hierarchical structure resembling a curved ribbon, and disordered over larger length scales, but the
161 assembly of side chains promotes intermittent short contacts along the backbone. Thus, although
162 charge is primarily transported in 1D along the backbone, there are occasional hops between chains
163 such that these short contact polymers exhibit very high carrier mobilities.

164

165 The above discussion has described organic polymers for charge transport, but small molecule
166 semiconductors can also serve the same purpose in electronic devices. However, transport properties
167 have been notoriously difficult to optimise through rational design at the molecular level. Crystal
168 packing motifs play a dominant role and are extremely sensitive to even the smallest molecular
169 perturbations. The herringbone and 2D slip-stack arrangements in particular have the required
170 combination of electronic coupling and sufficient isotropy for efficient charge propagation. Two key
171 building blocks have emerged as exemplary aromatic cores: pentacene (and its analogue
172 anthradithiophene (ADT)) and benzothienobenzothiophene (BTBT). The packing motifs of these
173 semiconducting molecules have been manipulated by strategically introducing substituents either on
174 the central core (in the case of pentacene and ADT) or periphery (in the case of BTBT). Both
175 pentacene and ADT can be readily functionalized, with the 6 and 13 positions of pentacene¹⁶ and 5
176 and 11 positions of ADT being the most conveniently substituted. In this way, one can prepare species
177 such as the bis((trialkylsilyl)ethynyl) derivatives **TIPS-pentacene** and **TES-ADT** (Fig. 3b).
178 Introducing the $-C\equiv C-SiR_3$ groups increases solubility in organic solvents, blocks a possible site of
179 oxidative degradation, and also adds a structural template that promotes 2D interdigitated π -stacking.
180 This morphology is favourable in that it can give rise to thin films with higher charge carrier
181 mobilities than most other packing motifs. Replacing the ⁱPr groups in **TIPS-pentacene** with Et
182 groups changes the preferred packing structure to a lamellar 1D slip stack with a much larger charge
183 transport anisotropy. Over the length scale of a transistor device, this leads to much lower charge
184 carrier mobilities. In the case of **TES-ADT**, the inclusion of a peripheral F atom can promote short
185 non-covalent contacts, further enhancing electronic coupling and, consequently, carrier mobility.
186 BTBT has been identified as a suitable aromatic core for charge transport and is most easily
187 substituted at the 2 and 7 positions, for example with linear ¹²C₈H₁₇ chains¹⁷. These chains increase
188 solubility in organic solvents and have a highly calamitic (rod-like) shape that makes **C₈-BTBT** adopt
189 a favourable herringbone packing motif. The short contacts between the conjugated cores of adjacent
190 molecules in the crystal give rise to excellent and relatively isotropic electronic coupling, thus
191 enhancing charge carrier mobility. Historically, the charge carrier mobilities observed in small
192 molecule films have been larger than those in polymer films, and this has been attributed to the former
193 having a lower energetic disorder, narrower density of states, and fewer defects. However, the
194 performances of semiconducting polymers with short intermolecular contacts are catching up, and
195 they generally exhibit lower charge transport anisotropy, which makes them potentially favourable for
196 integrated circuitry.

197

198 [H1] Organic photovoltaics

199 An organic photovoltaic (OPV) device includes a photoactive layer consisting of an electron donor
200 and an electron acceptor. Both these materials can be tailored on a molecular level such that they
201 absorb a large proportion of incident solar irradiation. An appropriate energetic offset between
202 frontier orbitals of the donor and acceptor enables the splitting of excitons into free charge carriers,
203 which can be collected at the separate electrodes. To absorb a large fraction of incident photons, an
204 active layer substantially thicker than the exciton diffusion length is required, which, in turn,
205 necessitates an intermixed donor:acceptor bulk heterojunction (BHJ, FIG. 4a) morphology.¹⁸⁻²⁰
206 Optimizing frontier molecular orbital energies of the donor and acceptor to increase the energetic
207 driving force for charge separation and open circuit voltage (V_{oc}) must be balanced against efficient
208 light absorption. Additionally, the donor:acceptor heterojunction must be judiciously controlled
209 throughout the active layer to ensure efficient charge separation and collection with a high degree of
210 morphological stability.

211

212 We now describe selected pairs of organic donor (FIG. 4b) and acceptor materials (FIG. 4c) in the
213 context of a BHJ. In the extensively studied **P3HT:PCBM** heterojunction the LUMO energy levels
214 are ~ -3.2 and -4.2 eV for **P3HT** and **PCBM**, respectively, providing a large energetic offset to
215 overcome the **P3HT** exciton binding energy (typically 0.3 eV) and drive charge separation through a
216 Channel-I mechanism (Fig. 4a). This driving force, combined with the strong visible light absorption
217 of **P3HT** and the favourable intermixed morphology of the BHJ, means that OPV devices can have
218 power conversion efficiencies over 4%.²¹

219

220 To harvest a greater proportion of the solar spectrum, OPV research rapidly shifted from using **P3HT**
221 to instead designing electron donors with hybridized molecular orbitals from having alternating π -
222 conjugated electron-rich and electron-poor repeat units. This effective and highly modular paradigm
223 has been employed repeatedly to narrow the HOMO–LUMO gap and develop vast numbers of push–
224 pull-type polymers with hybridized molecular orbitals. While a narrower-bandgap donor will absorb a
225 greater proportion of the incoming photons and thus increase the extracted current (J_{sc}), it can
226 compromise either the V_{oc} (shallower donor HOMO leading to smaller LUMO_{acceptor}–HOMO_{donor} gap)
227 or the charge separation (deeper donor LUMO leading to smaller LUMO_{donor}–LUMO_{acceptor} offset)
228 according to Figure 4a. Computational modelling suggests that the compromise between high voltage
229 and efficient light absorption is best negotiated in a **PC₆₀BM**-based device using a donor material
230 with a band gap around 1.5 eV.^{22,23} One such material is **PCPDTBT**, which, despite having a near
231 ideal band gap, performed poorly in bulk heterojunction devices. However, in 2007, the efficiency of
232 a **PCPDTBT:PC₇₀BM** device was nearly doubled from 2.8 to 5.5% by adding a small amount of 1,8-
233 octanedithiol when casting the active layer.²⁴ The dithiol preferentially improves the solubility of one
234 of the photoactive components during film casting, enabling the bulk heterojunction morphology to be
235 optimized and hence facilitating more reliable assessment of new photoactive materials without
236 performance being overshadowed by poor morphology. Thus, by using push–pull-type narrow-
237 bandgap donor polymers in conjunction with fullerene-based acceptors, the field steadily developed to
238 being able to fabricate OPV devices with efficiencies up to ~11%. The donor materials often featured
239 the non-covalent interactions discussed above, which promote polymer aggregation and facilitate
240 phase separation on the exciton diffusion lengthscale.²⁵ From a frontier molecular orbital perspective,
241 the HOMO energies of polymers such as **PTB7** (–5.15 eV), **PTB7-Th** (–5.24 eV) and **PfFBT4T**
242 (–5.34 eV) have been lowered to improve V_{oc} , while the bandgap has been increased slightly to
243 ~1.6 eV. It should be noted that most high-performing PCBM devices are prepared not with **PC₆₀BM**
244 as the acceptor, but using the C₇₀ derivative **PC₇₀BM**, the lower symmetry of which allows stronger
245 visible light absorption and greater channel-II photocurrent generation (Fig. 4a).²⁶

246

247 Polymeric electron donors have dominated the OPV landscape, but there are some notable small-
248 molecule electron donors. The pyridalthiadiazole-based small molecule **p-DTS(PTTh₂)₂** (Fig. 4b;
249 $E_{LUMO} = -3.6$ eV; $E_{HOMO} = -5.2$ eV) absorbs in the broad 500–800 nm region and has a large LUMO–
250 LUMO offset when paired with **PC₇₀BM**.²⁷ Controlling the blend morphology in a two molecule
251 blend is challenging, as evidenced by the performance of **p-DTS(PTTh₂)₂:PC₇₀BM** devices being
252 remarkable sensitive to processing conditions. A 70:30 donor:acceptor weight ratio with 0.25%
253 solvent additive affords a power conversion efficiency of 6.7%. Small deviations from this
254 composition see the performance drop precipitously.

255

256 The difference between the optical energy gap and the observed open-circuit voltage V_{oc} is referred to
257 as the V_{oc} loss. This quantity is substantial for fullerene-based OPV devices that predominantly
258 operate by a channel-I mechanism. Losses in high-performance PCBM cells are typically on the order
259 of 0.8 eV — a value substantially larger than the exciton binding energy.²⁸ Using a non-fullerene
260 acceptor (NFA) addresses this crucial barrier to further improving OPV device efficiencies. Although
261 it is relatively straightforward to design and synthesise NFAs with appropriate HOMO and LUMO
262 energy levels, early work highlighted the difficulties achieving both an intermixed blend morphology
263 and sufficiently high charge carrier mobilities. For example, the high crystallinity of rylene diimides
264 can preclude blending but has been mitigated by using twisted dimer-type acceptor structures. Indeed,
265 the Se-annulated PDI motif in **SdiPBI-Se** can be used to achieve a PCE of 8.4%, and the four-blade
266 propeller-type structure **FTTB-PDI4** gives rise to a higher PCE of 10.6% with a low V_{oc} loss of 0.53
267 V.^{29,30} NFAs are more tunable than fullerenes in terms of frontier orbital energies, with SdiPBI-Se
268 ($E_{LUMO} = -3.9$ eV; $E_g = 2.2$ eV) and **FTTB-PDI4** ($E_{LUMO} = -3.6$ eV; $E_g = 1.9$ eV) being two notable
269 examples. The acceptor strength can be adjusted to match the chosen donor material, and E_g can
270 likewise be tuned to ensure complementary absorption with the donor. The control over frontier
271 orbital energies of NFAs is further emphasized when one notes that their HOMOs and LUMOs are
272 often spatially separated (FIG. 1), meaning that they can be adjusted independently of each other
273 through molecular design. Additionally, NFAs typically have better light absorption than fullerene

274 acceptors, and combined with the efficient hole transfer from acceptor to donor, this provides high
275 channel-II photocurrent generation and high J_{sc} values.

276

277 A recently developed NFA design is a calamitic π -conjugated molecule with a central fused electron-
278 rich (hetero)aromatic core flanked by terminal electron-deficient units such as indanedione or
279 rhodanine. Further modularity in the molecular design can be incorporated by introducing electron-
280 rich or electron-deficient π -conjugated spacers between the core and the flanking groups. **IDTBR**
281 (FIG. 4c), which features an indacenodithiophene core flanked on each side by 2,1,3-benzothiadiazole
282 and rhodanine, is one such calamitic acceptor.³¹ The aromatic groups in its backbone are coplanar,
283 such that **IDTBR** has a relatively narrow E_g (1.6 eV) and a **P3HT:IDTBR** active layer consequently
284 absorbs strongly over the entire visible spectrum to give devices with efficiencies above 6%. In
285 addition to improving the OPV performance of a simple and commercially scalable polymer such as
286 **P3HT**, this result also illustrates that NFAs can be used as the primary low-bandgap light absorber, a
287 role which was hitherto reserved for the donor material. Further improvements towards 8% power
288 conversion efficiency with **IDTBR** has been reported for ternary blends using two complementary
289 NFAs in conjunction with **P3HT**.³² Further, **IDTBR** has an electronic structure ($E_{LUMO} = -3.9$ eV)
290 that is compatible, in terms of LUMO–LUMO offset, with donor polymers such as **PffBT4T**. Indeed,
291 a **PffBT4T:IDTBR**-based device can exhibit a power conversion efficiency of 10% and a very small
292 V_{oc} loss (~ 0.5 V).³³ **ITIC** is another calamitic acceptor with comparable frontier orbital energy levels
293 to those of **IDTBR**.³⁴ Likewise, **ITIC** has been used in several high-efficiency OPV devices, but as
294 with **IDTBR** its optical bandgap ($E_g \approx 1.6$ eV) is comparable to most high-performing donor polymers
295 developed specifically for fullerene-based devices. Thus, to absorb more broadly within the solar
296 spectrum and increase J_{sc} it is beneficial to widen the bandgap of the donor polymer, so as to prevent a
297 large spectral overlap with the NFA and possibly open a pathway for Förster energy transfer from the
298 donor to acceptor. For example, **PBDB-T** (FIG. 4b, $E_{HOMO} = -5.3$ eV; $E_g \approx 1.8$ eV) comprises the
299 weakly electron-deficient benzodithiophenedione unit in conjunction with the well-known electron-
300 rich benzodithiophene motif. Being highly compatible with **ITIC**, this wider bandgap donor has been
301 incorporated into devices, and the power conversion efficiencies of **PBDB-T:ITIC** active layers have
302 gradually improved to over 14%.^{35,36} **PBDB-T** has been modified by replacing alkyl chains with
303 thioalkyls, as well as by fluorination and chlorination. Similarly, **ITIC** has been fluorinated and
304 chlorinated — modifications that make it a better electron acceptor by lowering the energies of both
305 the HOMO and LUMO. The bandgap is slightly narrowed because the lowering is greater for the
306 LUMO, on account of it being more distributed over the ITIC unit. This red-shifted absorption
307 increases the J_{sc} while enhanced intra- and intermolecular interactions concurrently improve the
308 extinction coefficient and charge-transport properties. Thus, the HOMO energy of the dichlorinated
309 derivative **PBDB-T-2Cl** is 0.2 eV lower than that of **PBDB-T**, which makes the former useful in
310 terms of affording OPV devices with high V_{oc} values with the active layer having good oxidative
311 stability on account of the low-lying frontier orbital energies.

312

313 Most recently, the research community has looked beyond linear calamitic motifs to the curved
314 structure **Y6**, a narrow bandgap NFA that absorbs strongly beyond 900 nm.³⁷ The central π -
315 conjugated chromophore in this material is a 2,1,3-benzothiadiazole flanked by thieno[3,2-
316 *b*]thiophene units that are fused onto the benzothiadiazole with *N*-alkylpyrrolo groups. The two alkyl
317 side chains face each other and their interactions give **Y6** its slight twist ($\sim 17^\circ$), which ensures good
318 solubility and favourable control of aggregation. This electron acceptor, paired with a fluorinated
319 derivative of **PBDB-T** as the donor, can afford devices with power conversion efficiencies exceeding
320 15% and V_{oc} values above 0.8 V. The already small V_{oc} loss for this system can be further improved
321 by using a chlorinated analogue of **Y6**, giving devices with efficiency above 16% and V_{oc} loss of only
322 0.53 V.³⁸ It is hypothesised that the much larger dipole moments in these bent NFAs compared to
323 ITIC-type NFAs, and the high electron mobility, contribute to efficient charge separation and fill
324 factors being around 75% — a high value that is desirable.

325

326 The tunability of molecular structure and frontier orbital energies has driven the OPV field over the
327 last decade and related design approaches are being explored to sensitise other PV applications. This
328 is most notable in the development of singlet fission materials that convert one high-energy singlet

329 exciton to two lower energy triplet excitons. In turn, these triplets can generate additional e^-h^+ pairs,
330 for example, in low bandgap Si-based PV devices. With an S_1 singlet exciton energy of 2.4 eV,
331 tetracene can absorb high-energy photons that would otherwise lead to high thermalization losses in
332 Si cells, with subsequent singlet fission converting the singlet exciton into two triplet excitons. The T_1
333 triplet exciton energy of tetracene (~ 1.25 eV) nicely matches the bandgap of Si (1.1 eV). Although it
334 is challenging to efficiently transfer the triplet excitons to the Si cell, this technology holds promise to
335 exceed the Shockley–Queisser limit of 29% efficiency for a single junction PV device.

336

337 [H1] Organic light-emitting diodes

338 Despite organic light emitting diodes (OLEDs) being at an advanced stage of commercialization, their
339 study remains an extremely active area of research in which many fascinating developments have
340 been reported over the last 5–10 years. The fundamental operating principle of an OLED is extremely
341 simple: charges injected from electrodes recombine within an organic layer to form an excited state
342 which decays radiatively. However, spin statistics dictate that recombination of free charges results in
343 a 1:3 ratio of singlet and triplet excited states being generated. The vast majority of OLED research
344 has been targeted at overcoming the non-emissive nature of triplet excited states, a problem that
345 would limit internal quantum efficiency (IQE) to 25% — the fraction of excited states that are singlets.
346 The first successful approach to overcoming this was to move away from fluorescent emitters (1st
347 generation materials, FIG. 5) to phosphorescent compounds (2nd generation). These compounds can
348 emit quickly because they feature heavy metals, which promote intersystem crossing (ISC) of the
349 triplets, as observed for organoplatinum and -iridium complexes (Fig. 5). This allowed all of the
350 electrically generated excited states to be used radiatively such that devices with 100% internal
351 quantum efficiency (with a maximum of 20–25% external quantum efficiency (EQE) due to
352 outcoupling losses) could be prepared. However, problems associated with colour purity and stability
353 (particularly in the blue region) have motivated the development of better OLED materials. The
354 newest OLED materials (3rd generation) exhibit reverse intersystem crossing (RISC) to use triplet
355 states. By lowering the energy gap between the lowest excited singlet and triplet states (ΔE_{ST}), the
356 system has enough thermal energy to undergo RISC and have its triplet state convert into an emissive
357 singlet. This process has fittingly been referred to as thermally-activated delayed fluorescence (TADF)
358 and is a contemporary research topic of intense interest.

359

360 The most commonly used phosphorescent emitters are cyclometallated Ir(III) complexes dispersed
361 within an organic host. It has long been known that the emitting dipole orientation of a dye influences
362 the outcoupling efficiency (EQE/IQE) of OLEDs.³⁹ Despite this, the dipole orientations of
363 phosphorescent dopants have not been studied extensively, presumably due to the lack of any
364 obvious driving force for alignment in (typically amorphous) host materials. However, a recent study
365 using angle-dependent polarized photoluminescence emission spectroscopy shows that certain Ir
366 complexes can be aligned in films.^{40,41} The inherent asymmetry at the surface of a growing film
367 apparently promotes dopant alignment in these otherwise amorphous films. Alongside other
368 investigations into controlling phosphor alignment, external quantum efficiencies in excess of 30%
369 have been reported, and it is projected that efficiencies of up to 60% are possible.^{39,42} Despite decades
370 of research, new strategies for achieving efficient blue emission from Ir complexes are still being
371 sought with very impressive results emerging recently. Isomerizing a UV-emitting *N*-heterocyclic
372 carbene complex of Ir(III) from its *fac* to *mer* form subtly red-shifts its emission such that it exhibits
373 efficient deep blue phosphorescence with $\sim 80\%$ photoluminescence quantum yield (PLQY) and EQE
374 $\sim 15\%$.⁴³ There has recently also been considerable progress in the development of Ir-free
375 phosphorescent emitters, including a new class of cyclometalated Au(III) complexes with tuneable
376 emission spanning sky-blue to red. When deposited as thin films, these materials exhibited high
377 PLQY values of up to 80%, and the OLEDs have excellent stability while maintaining EQEs up to
378 22%.³⁷ An extremely active area of research is the development of near-infrared OLED emitters for
379 security and communication applications. Examples of $\{Pt^{II}[3-(\text{pyrazinyl})\text{pyrazolato}]_2\}$ derivatives
380 emit at 740 nm with a PLQY of 81%, and adopts a highly preferred horizontal dipole orientation such
381 that its OLED devices exhibited an external quantum efficiency of 24%.⁴⁴ The origin of the near-
382 infrared emission has been attributed to the stacking of Pt(II) centres on top of each other in the solid
383 state, enabling metal–metal-to-ligand charge transfer.

384

385 Almost certainly the biggest development in OLED research over the last 10 years has been the
386 observation of TADF from purely organic dyes. This work was pioneered by the group of Adachi,
387 whose seminal publication described a series of purely organic materials such as 2,3,5,6-tetra(N-
388 carbazolyl)benzotrile (Fig. 5) that afford tuneable emission with high PLQYs and OLED EQEs
389 approaching 20%.⁴⁵ This work showed that the simple design concept of spatially separating a
390 molecule's HOMO and LUMO by using a twisted donor-acceptor structure lowers the energy gap
391 between the first excited singlet and triplet states. Thus, triplet states can convert into emissive
392 singlets by RISC, such that the materials exhibit TADF. By tuning the number, twist angle and
393 electron density of donor moieties linked to the acceptor(s), one can obtain a series of compounds that
394 collectively exhibit extremely high PLQY and OLED EQEs from the blue to near infrared.^{46,47,48,49,50}
395 Despite these impressive results, the exact mechanism by which RISC and TADF occur remains the
396 subject of debate. In order to design efficient TADF emitters it is vital to consider both locally excited
397 (LE) and charge-transfer (CT) states.⁵¹ However, the process by which singlet and triplet states
398 interconvert is not clear. 'Hidden' $n-\pi$ mixed states may play an important role in the process or it is
399 also possible that second-order vibronic coupling between the various excited states is required.⁵²⁻⁵⁴
400 The role of intermediate electronic states that mediate the spin-flip through molecular vibrations has
401 been demonstrated using a new model that also complements the notion of non-adiabatic coupling of
402 triplet states promoting ISC.⁵⁵ Therefore, the synthetic strategy of merely minimising the S_1-T_1 energy
403 gap requires refinement. One of the issues with conventional TADF is the requirement of donor-
404 acceptor structures to be highly twisted, which results in broad spectral emission with low oscillator
405 strength. This can potentially be overcome using a "hyperfluorescence" strategy, whereby a fluorescent
406 guest is introduced into a TADF host, albeit at the expense of device simplicity.⁵⁶ It has also been
407 suggested that a 'multi-resonant' strategy, that aims to spatially separate the HOMO and LUMO of a
408 single planar molecule, can afford narrow ΔE_{ST} materials with high oscillator strengths and narrow
409 emission.^{57,58} Indeed, extremely impressive results using this strategy has recently been reported with
410 a blue (469 nm) organoboron TADF-based OLED with an EQE of 34%.⁵⁹

411

412 TADF has also been observed in organometallic systems, with $[Cu^I(NR_2)(N\text{-heterocyclic carbene})]$
413 complexes exhibiting outstanding optoelectronics properties (PLQY = 100%, EQE >25%).^{60,61}
414 Emission in these systems appears to stem from interligand charge-transfer states and, importantly, it
415 appears that (as has also been suggested for organic TADF emitters⁶²) that there is considerable spin-
416 mixing, further indicating that the spin-pure picture of TADF emitters may be simplistic. However, as
417 with phosphorescent OLED emitters, achieving highly stable blue OLEDs with good colour purity
418 has proved extremely challenging.

419

420 [H1] Beyond the state-of-the-art

421 A typical chemical design approach to optimize a semiconductor involves taking the conjugated
422 aromatic units comprising the core or backbone and introducing systematic variations to isolate and
423 study substituent effects on both morphology and frontier molecular orbitals. The results for the new
424 materials are often compared to those in previous publications to justify a new design. In transistor
425 research, unreliable charge carrier mobility values, extracted from invalid model equations and
426 assumptions, have inflated expectations. Moreover, they have led to incorrect structure-property
427 relationships being proposed, with molecular design conclusions reached on tenuous evaluations. This
428 body of erroneous and misleading literature has seriously impeded progress in the development of
429 materials for transistor applications. However, there are some obvious opportunities for further
430 exploration. Incorporating aliphatic chains in these materials is primarily done to impart
431 organosolubility, with a secondary reason being to control the solid-state structure. However, both
432 alkyl chain and lamellar crystallization can come at the expense of conjugated backbone planarity and
433 crystallinity. It is imperative that new semiconductors are designed in a holistic fashion, whereby the
434 self-assembly of the system works with optimum performance rather than against it. It may be
435 possible to deploy side chains in creative new ways to suppress undesirable phonon modes, which
436 have recently been shown to severely affect charge transport.⁶³ Alternatively, removing the alkyl
437 chains altogether should fundamentally improve charge transport. Detaching the side chains in situ,
438 without compromising microstructural order, would increase backbone densification and performance.

439 Although promising in principle, most methods to remove the chains do so at the expense of order,
440 thereby detracting from transport properties. Molecular order has proved to be key in optimising
441 charge transport, so finding ways to further reduce disorder in conjugated systems, or otherwise
442 designing materials with a higher tolerance towards rotational fluctuations, will be essential to
443 improve charge transport. To date, the introduction of labile side chains has proven challenging as it is
444 difficult to predict the solid state packing of molecules and the different vibrational modes associated
445 with a particular unit cell. With improvements in computational power, we have access to material
446 property predictions that are more sophisticated and accurate, such that they can provide important
447 insights into material packing motifs and phonon coupling modes. Thus, not only can we often
448 calculate the many phonon coupling modes in a conjugated system, but, importantly, we can predict
449 and identify the modes most detrimental to charge transport.

450
451 Besides the transport of electronic charge through a solid, other phenomena such as mixed conduction
452 — electronic and ionic charge transport — are also attracting increasing attention due to their
453 potential applications in biological interfacing.^{64,65} In this context, an organic electrochemical
454 transistor (OECT), a three-terminal device that can be gated through an aqueous electrolyte, is
455 emerging as a powerful tool for bioelectronic applications. In an OECT, the active layer exhibits both
456 electronic and ionic mobility throughout the bulk. Development of n- and p-type semiconducting
457 polymers for OECTs therefore necessitates new design rules for tuning the frontier orbitals. For stable
458 operation in aqueous environments, as a first prerequisite, the HOMO of p-type materials must be
459 electrochemically accessible — at a potential lower than that at which H₂O oxidation would take
460 place (1.23 V versus the normal hydrogen electrode). High-performance mixed conductors have much
461 shallower HOMO levels, with E_{HOMO} between -4.4 and -4.6 eV, depending on the measurement
462 technique.^{66,67} HOMO levels in this energy range can be obtained with glycolated polythiophenes
463 similar to poly(3-alkoxythiophene) (FIG. 3), in which the O atoms mesomerically donate electron
464 density to the polymer backbone while the polar nature of the oligoether side chain facilitates ion
465 transport. The development of n-type semiconductors is essential to sense biologically-relevant
466 metabolites and cations, such as Na⁺, K⁺ and Ca²⁺. To be operationally stable in H₂O, the main
467 challenge centres around stabilizing the radical anion forms of the semiconductor towards H₂O and/or
468 O₂.⁶⁸ This stability would dictate materials to have $E_{\text{LUMO}} < -4.0$ eV.^{69,70} At present, the performance
469 of electron-transporting OECT semiconductors lags substantially behind their hole-transporting
470 counterparts. This lag has been tentatively attributed to coulombic charge-pinning from counterions,
471 charge-trapping from H₂O, and other phenomena. Clearly, new molecular designs for electron
472 transport in aqueous environments are required to overcome these limitations.

473
474 To develop organic semiconductors for photovoltaic applications, focus should not be on optimising
475 the electronic and solid-state properties of a single material, but rather on understanding how to
476 deliberately control the morphology of an active layer. This might entail, for example, incorporating
477 multiple materials that are chosen to set up an energy cascade with large CT state energies. While the
478 frontier orbital energy levels and the isolated molecular packing of both donor and acceptor can in
479 general be controlled, there is presently a lack in understanding how functionalization of an organic
480 molecule will affect its solid morphology on microscopic and macroscopic length scales. Using less-
481 diffusive NFAs does help the morphological stability of a BHJ blend but it would be highly
482 advantageous if the tertiary structure could be controlled to a greater extent, for instance by choice of
483 heteroatoms, functional groups and side chains. Ideally, such approaches should also provide a means
484 to 1) generate much thicker photoactive layers without unwanted vertical phase separation and
485 excessive charge recombination and 2) scale up the cell's active area more effortlessly to generate
486 large devices for beneficial practical implications. Over much shorter length scales, being able to
487 control the donor:acceptor interfaces in the blend, for instance through molecular shape and dipole
488 moments, would allow for greater understanding and control of the energy-transfer and charge-
489 transfer processes. Another important aspect that requires further attention is the role of the CT state,
490 how the CT state can be manipulated through chemical design and how this can be used to suppress
491 recombination processes. Recent work indicates that electrostatic potential mapping, for instance,
492 could be a useful and rapid tool to help understand how molecular structure and intermolecular
493 interactions influence the charge separation processes.⁷¹ The recent reports describing **Y6**, a curved

494 NFA structure markedly different from the previous best NFA performers in terms of molecular
495 design, have to a large extent taken the OPV community by surprise. This promising example shows
496 that there is still ample room to improve device performance, and also highlights the lack of unified
497 molecular design criteria. Detailed structure–property relationships of NFAs and the main reasons for
498 their excellent performance continue to be explored. Factors such as their off-axis dipoles, high
499 electron mobilities, facile energy transfer processes and potential for good Förster energy overlap with
500 donors could play important roles. As the OPV research community now embarks on in-depth
501 fundamental studies of devices based on **Y6** and its analogues, further pieces of this puzzle will
502 emerge. This insight will push the device performance closer towards the 20% efficiency mark and
503 hopefully add to the understanding of molecular and frontier energy level design criteria.

504

505 The commercialization of OLED technologies has already been a monumental success. However, we
506 lack a detailed understanding of the exact photophysical processes at play during charge
507 recombination and emission. Moreover, we require a clear relationship between chemical structure
508 and photophysical properties to rationally design new materials and realize progress. It is necessary to
509 further understand the origin of the stability/instability of excited states, in particular in the presence
510 of charges. Identifying degradation pathways may allow us to come up with chemical modifications
511 enhance the stability of emitters. Despite this, present generations of OLED materials are operating
512 close to their theoretical maxima and for a step-change in performance, a new generation of materials
513 must be developed. Some encouraging signs of emerging 4th generation materials that warrant
514 exploration are emerging. For example, there have been recent reports of extremely efficient OLED
515 devices based on radical fluorophores.^{72,73} These compounds, which feature the well-known
516 luminescent tris(2,4,6-trichlorophenyl)methyl (TTM) radical motif, emit from a doublet excited state
517 such that recombination is independent of the excited state spin. However, thus far these materials
518 have only exhibited electroluminescence in the red/near-infrared and it remains to be seen whether it
519 is possible to tune them to cover the entire visible spectrum. Another interesting new approach
520 involves the use of host materials that can undergo singlet fission, which, in principle, could allow for
521 IQEs of 200%.⁷⁴ Yet, such a device fashioned using the emitter [Er^{III}(8-hydroxyquinolato)₃] as the
522 guest in a rubrene singlet fission host gave a very low EQE, likely due to the low PLQY of the Er(III)
523 complex. Thus, in order for this strategy to succeed it will be necessary to not only develop wide
524 band-gap singlet fission hosts but also highly emissive near-infrared emitters capable of harvesting
525 triplet excitons. There have been several recent reports of OLEDs that exploit triplet fusion, whereby
526 two triplets annihilate and produce an emissive singlet.⁷⁵⁻⁷⁷ Although this limits IQE to a maximum of
527 50% (if only triplets are injected), it could allow for low driving voltages and may offer blue emitters
528 with greater photostability than present compounds.

529

530 There is a need to improve the chemistry used to synthesize organic semiconductors. The presence of
531 (often hard to detect) residual impurities can result in batch-to-batch variations or unintentional
532 doping. The availability and compatibility of chemical building blocks dictates the choice of reactions
533 used in synthetic routes. For example, polymerizations often rely on Pd-catalysed cross-couplings,
534 such as the Yamamoto, Suzuki–Miyaura, and Stille reactions. Although these coupling are extremely
535 efficient, their low atom economy and requirement (in the case of the present polyaromatic substrates)
536 for chlorinated solvents does not comply with sustainability requirements. Further, these reactions are
537 not particularly suitable for large-scale production. C–H activation and condensation chemistry
538 circumvent some of these problems by shortening the synthetic pathway and making extensive
539 functionalization of monomers obsolete.⁷⁸ The narrow scope and restrictions on what building blocks
540 are accessible leave ample room for improvement. Developing new chemical polymerisation
541 protocols that allow for control over molecular weight and polydispersity whilst reducing chemical
542 defects (that might occur on, for example, homocoupling or partial oxidation) will be an integral to
543 advance the quality of synthesised materials.

544

545 [H1] References

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742

743 [H1] ToC blurb

744 Many present and emerging electronic devices make use of organic semiconductors in view of their
745 readily tuneable atomic and electronic structures. This Review describes the importance of analytical
746 and computational tools in studying the molecules as well as their hierarchical self-assemblies, in
747 which the motion of charges and excited states govern device properties.

748

749 Subject terms

750 Conjugated polymers URI /639/638/455/954

751 Electronic materials URI /639/638/298/917

752 Excited states URI /639/638/440/949

753

754 Captions

755 Fig. 1 | **Manipulating frontier orbital distributions and energies.** A series of conjugated aryl
756 molecules differing in aromatic units and substituent functionality is shown to exhibit contrasting
757 distributions and energies of their highest occupied molecular orbital (HOMO) and lowest unoccupied
758 molecular orbital (LUMO). Ground state geometries and HOMO wavefunction distributions were
759 obtained using density functional theory with the B3LYP method and def2-SVP basis set, using
760 Grimme's D3 dispersion correction and the BJ damping function. Time-dependent density functional
761 theory, along with the ground state coordinates, was used at the same level of theory to calculate the
762 LUMO wavefunction distributions.

763

764 Fig. 2 | **Schematic illustrations and chemical structures of conjugated thiophene-derived**
765 **polymers. a** | The 3D packing arrangement of **pBTTT** enables electron transport across and between
766 its crystalline domains⁷. **b** | In contrast, **IDT-BT** exists as disordered chains, through which electrons
767 can move⁹. The chains intermittently contact another chain or region, to/from which the electrons can
768 move. The arrows illustrate a possible optimal pathway for electron transport. R represents alkyl side
769 chains.

770

771 Fig. 3 | **Species that may find applications in organic field effect transistors. a** | Chemical
772 structures of poly(3-alkoxy)thiophene, diketopyrrolopyrrole and isoindigo, with attractive planarizing
773 interactions highlighted in green and orange. **b** | Chemical structures of high-performance molecular
774 polyaromatic semiconductors **TIPS-pentacene**, **TES-ADT** and **C₈-BTBT**. R depicts alkyl side
775 groups.

776

777 Fig. 4 | **Donor:acceptor bulk heterojunctions and some typical semiconducting components. a** |
778 Energy diagrams depicting the donor–acceptor electronic band alignment and photocurrent generation
779 through a channel-I or II mechanism. **b** | Archetypical electron donors, which evolved from the early
780 poly(3-hexylthiophene) P3HT to the more elaborate structures on the right. **c** | Archetypical electron
781 acceptors. R describes solubilising side groups, such as linear and branched alkyl chains.

782

783 Fig. 5 | **The evolution of molecular organic light emitters.** 1st generation emitters rely on
784 fluorescence between singlet states, with subsequent developments leading to the development of 2nd
785 generation emitters, in which intersystem crossing (ISC) from singlet to triplet states is followed by
786 phosphorescence. Examples of the most recent paradigm, the 3rd generation emitters, exhibit
787 thermally-activated delayed fluorescence, in which ISC is followed by reverse intersystem crossing
788 (RISC).

789

790 **BOX 1 | Energy levels in an isolated organic molecule and a molecular crystal or polymer.**

791 Isolated organic semiconductor moieties have discrete HOMO and LUMO energy levels, which are
792 broadened into electronic bands — the valence and conduction band, respectively — when the
793 moieties aggregate, either in terms of individual molecules in a solid or moieties connected as part of
794 a polymer. The optical band gap E_g is the difference in energy between the highest energy of the
795 valence band and the lowest energy of the conduction band. The IP is the energy required to remove
796 one electron from the top of the valence band, whereas the EA is the energy released by adding one
797 electron from the vacuum level to the bottom of the conduction band.

798