Bright short-wavelength infrared organic light-emitting devices

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Organic LEDs that emit light in the short-wavelength infrared (SWIR) region, which spans the 1–2 μm region, are attractive for applications in biosensors, biomedical imaging and spectroscopy, and surveillance. However, fabrication of such devices with high radiance has not yet been achieved owing to an intrinsic limitation imposed by the energy-gap law, which leads to extremely low emission efficiencies. Here, we report that acceptor–donor–acceptor-type molecules with high coplanarity, rigid π-conjugated backbones, an extremely small reorganization energy and an electron–phonon coupling factor are capable of simultaneously providing a strongly suppressed non-radiative recombination rate and a high operation stability at high current density. We achieve electrically driven SWIR organic LEDs with an irradiance of up to 3.9 mW cm⁻² (corresponding to 7% of direct sunlight infrared irradiance). These findings should open a wide avenue to a new class of organic SWIR light sources for a broad range of applications.
generally involve several key considerations\textsuperscript{13,14}, such as extending the conjugation length, reducing bond length alternation (corresponding to greater $\pi$-electron delocalization), the introduction of appropriate donor–acceptor charge-transfer units and the use of triplet\textsuperscript{15} or doublet excitons\textsuperscript{16}. As a result, organic emitters that are available nowadays for NIR OLEDs include mainly organometallic phosphorescent complexes\textsuperscript{17,18}, organic ionic dyes\textsuperscript{19}, conjugated polymers\textsuperscript{20}, organic compounds containing donor–acceptor charge-transfer chromophores\textsuperscript{21,22,23}, thermally activated delayed fluorescent materials\textsuperscript{24} and doublet emitters\textsuperscript{25}. In 2020, Wei et al. reported state-of-the-art phosphorescent NIR OLEDs by exploiting a series of 5-(2-pyridyl)pyrimidine Pt(II) complexes, achieving an EL emission maximum at 930 nm, with an external quantum efficiency (EQE) of 2.14% and a remarkable maximum radiant exitance of 13.06 mW cm\textsuperscript{-2} (ref. \textsuperscript{26}). Yu et al. demonstrated high-performance fluorescent NIR OLEDs based on anthracene-core emitters, which exhibit EL peaks at 838 nm and 916 nm with EQE values of 0.58% and 0.07%, while the maximum radiant exitance is 2.8 mW cm\textsuperscript{-2} and 0.29 mW cm\textsuperscript{-2}, respectively\textsuperscript{27}. More recently, progress in fluorescent NIR OLEDs has been made by Minotto et al., who achieved an EQE of 1.1% with an EL emission maximum at 850 nm and a maximum radiant exitance of 1.9 mW cm\textsuperscript{-2} (ref. \textsuperscript{28}). However, previous studies have shown that OLEDs emitting at longer wavelengths (for example, beyond 1,000 nm and extending into the SWIR region) always suffer from severe non-radiative recombination loss, leading to low EQE values of the order of 0.01% (refs. \textsuperscript{29,30}). In 2009, Qian et al. reported a series of pure organic emitters based on a benzo[3,4-$b$]thiadiazole derivative that emitted at wavelengths beyond 1,000 nm (ref. \textsuperscript{31}). Non-doped devices based on a chromophore featuring triphenylamine derivatives as the acceptor group exhibited a state-of-the-art EQE of 0.28% and an EL peak at 1,080 nm, with a maximum radiant exitance around 0.06 mW cm\textsuperscript{-2}. Although the radiant exitance and EQE of an OLED based on a different chromophore were too low for practical applications, its EL peak at 1,220 nm was one of the longest emission wavelengths for pure organic emitters reported so far, demonstrating the promising potential of organic chromophores as SWIR emitters for further development. Ever since the recent emergence of a new class of aromatic fused-ring electron acceptors with an acceptor–donor–acceptor (A–D–A) structure, the development of organic solar cells has entered into a new era, featuring the coincidence of efficient charge separation and low voltage losses\textsuperscript{32}. Owing to the strong intramolecular charge-transfer effect and the rigid planarity configuration of the fused rings, the $\pi$-electron delocalization in these A–D–A-type organic semiconductors is enhanced, producing a reduction in the bandgap and a greater oscillator strength that increases the NIR absorption coefficient. Moreover, A–D–A-type organic semiconductors show several additional great merits that are essential for minimizing energy losses in organic solar cells. These include a sharp optical absorption edge, a suppressed non-radiative recombination rate, low energetic disorder and a high luminescence (radiative recombination) yield, which play an important role in obtaining a high photovoltage\textsuperscript{33}. According to the reciprocity relationship that exists between light absorption and emission\textsuperscript{34}, such organic semiconductors that are ideal for solar cells are likewise ideal for LEDs.

**Photophysical properties and numerical simulations.** To further illustrate their potential as a new type of SWIR emitter, the absorption and photoluminescence (PL) spectra of the three molecules were measured. As shown in Fig. 2a–c, the thin-film spectra of the three molecules exhibit sharp absorption bands with a dominant peak slightly above the optical gap and a low-energy shoulder adjacent to it. Owing to its overwhelmingly high oscillator strength, transition from the ground state (S\textsubscript{0}) to the first excited state (S\textsubscript{1}) induces an intense absorption peak, which, consequently, surpasses the intensities of other transitions. Following Kasha's rule, fast thermalization to the first excited state (S\textsubscript{1}) selects the electronic transition of interest for the generation of strong electronic couplings between the donor and acceptor moieties. In conjunction with the alternating electron-withdrawing and electron-releasing moieties that incur an intramolecular charge-transfer effect\textsuperscript{26}, the enhanced wavefunction delocalization and the extended planarity of the A–D–A molecules ensure minimized optical bandgap energies ($E_g$) of 1.37, 1.27 and 1.17 eV for Y11, IDSe-4Cl and COTIC-4F, respectively (Supplementary Fig. 2), which is envisaged to lead to SWIR emissions beyond 1,000 nm. More importantly, the significant spatial overlaps ($O_{\text{sp}}$) between the NTO-hole and NTO-electron give rise to very large oscillator strength ($f$) values of 2.3, 3.2 and 3.0 for Y11, IDSe-4Cl and COTIC-4F, respectively\textsuperscript{35}, corresponding to their high radiative recombination rates, as discussed below.

**Results and discussion**

**Computational results.** Before attempting to exploit A–D–A-type organic semiconductors for SWIR emitter applications, density functional theory (DFT) and time-dependent DFT (TD-DFT) approaches at the oB97XD/6-31G(d,p) level with the optimally tuned $\omega$ parameter were used to study the structural regularity and excited-state properties for three typical narrow-bandgap molecules with low photon energy loss in organic solar cells, that is, Y11 (ref. \textsuperscript{36}), IDSe-4Cl (Supplementary Methods) and COTIC-4F (ref. \textsuperscript{37}) (see Fig. 1a–c for chemical structures and the Methods section for computational details). Our DFT calculation results displayed a small dihedral angle of 14° for Y11, whereas nearly planar structures with negligible torsion in their relaxed geometries were observed for IDSe-4Cl and COTIC-4F (Supplementary Fig. 1). The success of this design strategy was confirmed via the extended emission exciton wavefunctions, as shown by the calculated natural transition orbitals (NTOs) that describe the first singlet ($S_1$) excited states (see Fig. 1d). The NTO hole and electron wavefunctions of the $S_1$ excitons are spread over the whole $\pi$-conjugated backbones, implying strong electronic couplings between the donor and acceptor moieties. In conjunction with the alternating electron-withdrawing and electron-releasing moieties that incur an intramolecular charge-transfer effect\textsuperscript{38}, the enhanced wavefunction delocalization and the extended planarity of the A–D–A molecules ensure minimized optical bandgap energies ($E_g$) of 1.37, 1.27 and 1.17 eV for Y11, IDSe-4Cl and COTIC-4F, respectively (Supplementary Fig. 2), which is envisaged to lead to SWIR emissions beyond 1,000 nm. More importantly, the significant spatial overlaps ($O_{\text{sp}}$) between the NTO-hole and NTO-electron give rise to very large oscillator strength ($f$) values of 2.3, 3.2 and 3.0 for Y11, IDSe-4Cl and COTIC-4F, respectively\textsuperscript{39}, corresponding to their high radiative recombination rates, as discussed below.

\[
\frac{I_{\text{Emission}}(h\nu)}{(h\nu)^3} \propto f \times \text{FCWD}(h\nu)
\]

(1)

\[
\text{FCWD}(h\nu) = \frac{\exp\left(-\frac{E_g - h\nu - \beta_k T}{kT}\right)}{\sqrt{4\pi k_B T}} \sum_{j=0}^{\infty} \frac{\Gamma_j}{\Gamma}
\]

(2)

in which $k_B$ is the Boltzmann constant and $T$ is the temperature. Here, FCWD($h\nu$) is further governed by three vibrational parameters: the low-frequency reorganization energy $\lambda$, that describes the conformational changes of the molecule and its surroundings upon excitation; the energy of the high-frequency vibrational mode $h\nu_v$.
in which \( \bar{\nu}_v \) is the average of the frequencies of atomic vibrations within the molecule; and the electron–phonon coupling factor \( S \), which is related to the high-frequency reorganization energy \( \lambda_h \), results from atomic displacements upon charging to the aforementioned mean phonon energy \( \hbar\bar{\nu}_v \) by \( S = \lambda_h/(\hbar\bar{\nu}_v) \). The lineshape of the reduced emission spectra where the emission spectra are divided by \( (\hbar\nu)^3 \) are therefore intrinsically modulated by these vibrational parameters through equation (2).

Careful fitting of the measured PL spectra via equations (1) and (2) enabled the extraction of vibrational parameters for our molecules, as shown in Fig. 2d–f, with details provided in Supplementary Note 2. Very low \( \lambda_h \) values ranging from 0.045 to 0.06 eV are obtained for these molecules, which correspond to their narrow linewidths. The observations are also consistent with the noticeably reduced PLQY values are included in this figure for direct comparison.

The PLQY data show a dramatic decrease as the bandgap is lowered, followed by the electronic coupling \( V_c \), approximated by the generalized Mulliken–Hush method \(^{41,42} \) (Supplementary Note 1). The photoluminescence quantum yield (PLQY) can eventually be determined via PLQY = \( k_r/N \), where \( k_r \) is the rate constant of radiative recombination. The calculated PLQY values for a set of representative parameters are plotted against the bandgap in Fig. 2g. The PLQY data show a dramatic decrease as the bandgap is lowered, following the energy-gap law, leading to a lower PLQY for narrow-bandgap molecules. The results of experimentally determined PLQY values are included in this figure for direct comparison. Nevertheless, further numerical simulations show that the reduced \( \lambda_h \), \( \hbar\bar{\nu}_v \), and \( S \) values of the molecules reported herein significantly suppress the rate constant for non-radiative recombination.

\[
\bar{\nu}_v = \frac{\lambda_h}{\hbar \bar{\nu}_v} = \frac{\lambda_h}{\hbar \lambda_S} \approx \frac{\lambda_h}{\hbar \lambda_r} = \frac{\lambda_h}{\hbar \lambda_s}
\]

\[
k_{nr} = \frac{2\pi}{\hbar} V_c^2 FCWD (0)
\]
is impacted by several potential factors (for example, a reduction in PLQY for the three molecules is very different, which is related to their molecular packing in the films. As demonstrated in previous investigations, the aggregation effect on the emissive efficiency could be an effective molecular-design strategy to lower the mean photon energy $\hbar\nu$, in A–D–A molecules, as discussed below. Under these circumstances, A–D–A molecules with conjugation extension and/or enhanced planarity and rigidity in their $\pi$-conjugated backbones, as well as increased non-bonding interactions between molecular fragments that enable reduced reorganization energies, are indeed ideal candidates that are capable of enhancing the long-wavelength emission and the emission efficiency simultaneously. To make further improvements in the PLQY, other approaches, such as heavy-atom substitution (for example, selenium substitution, as introduced in our IDSe-series molecules) or halogenation for retarding high-frequency vibration modes, could be an effective molecular-design strategy to lower the mean phonon energy $\hbar\nu$, in A–D–A molecules, as discussed below.

Although the $k_{nr}$ values for the series of A–D–A-type organic semiconductors extracted from experimentally determined PLQY (Supplementary Table 1) and time-resolved PL decay transients (Supplementary Fig. 6) increase with decreasing bandgap, this is much less pronounced compared with the prediction of the

( Supplementary Fig. 4), whereas an enhanced oscillator strength $f$ is beneficial for an increased rate constant for radiative recombination, eventually giving rise to higher PLQY values for the molecules (calculated values of 0.1–10% for bandgaps ranging from 1.1 to 1.3 eV). It is worth noting that the PLQY values of Y11, IDSe-4Cl and COTIC-4F in dilute solutions are measured to be 17.3%, 3.26% and 3.28%, respectively, which show a noticeable increase along with their broadened energy gap, which is also predicted by the proposed model (Supplementary Fig. 5). These results demonstrate that aggregation of the studied molecules in films plays a role in reducing their emissive efficiencies. Interestingly, the extent of decrease in PLQY for the three molecules is very different, which is related to their molecular packing in the films. As demonstrated in previous investigations, the aggregation effect on the emissive efficiency is impacted by several potential factors (for example, a reduction of the effective reorganization energy due to exciton delocalization, or the suppression of non-adiabatic electron–vibration coupling).

Fig. 2 | Optical properties and photophysical studies of representative A–D–A molecules. a–c, Absorption (Abs.) and PL spectra of the SWIR emitters Y11 (a), IDSe-4Cl (b) and COTIC-4F (c) as solid films, measured in air at room temperature. d–f, Normalized reduced emissions for the respective SWIR emitters deduced from the measured PL through equation (1), the corresponding curves fitted by multiple Gaussian peaks, and the emission spectra modelled using equation (2), with the extracted parameters as input also being shown. g, The modelled PLQY data using specific photophysical parameters extracted from Y11, IDSe-4Cl and COTIC-4F plotted as a function of the optical gap, where their experimentally measured PLQY values are shown as scattered dots for comparison.
The chemical structure of the molecules is fixed at 0.8. The electronic coupling $S_{Vc}$ is related to variation in the oscillator strength ($V_{c}$ values for a set of representative A-D-A-type molecules and a fullerene derivative as denoted data points for non-radiative and radiative recombination rate constants extracted from analysis of the time-resolved PL measurements and PLQY for each emitter (Supplementary Table 1). The PLQY measurements were carried out under ambient conditions.

This modelling study rationalizes and fundamentally explains why reducing $h\nu$ by 0.02 eV or lowering $S$ by 0.3 correspond to nearly an order of magnitude enhancement in PLQY, as illustrated in Supplementary Fig. 4i,j.

**Device characterization and demonstrations.** The analyses above suggest that A-D-A-type organic semiconductors show good potential for realizing high-performance SWIR OLEDs. To validate our findings, we fabricated electroluminescent devices using narrow-bandgap molecules as emitters, including Y11, IDS-4Cl and COTIC-4F and other representative narrow-bandgap A-D-A-type molecules (with the chemical structures and the corresponding absorption spectra shown in Supplementary Figs. 7 and 8, respectively). The device architecture employed was ITO/PEDOT:PSS/ emissive layer/PDINO/Ag (ITO, indium tin oxide; PEDOT:PSS, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate; PDINO, (N,N-dimethylammonium N-oxide)propyl perylene diimide; Ag, silver). The OLED performance characteristics, including
current density–radiance–voltage ($J$–$R$–$V$), EL spectra and EQE dependence on the current density (EQE–$J$), are shown in Fig. 4 and Supplementary Fig. 9, while the key parameters are summarized in Table 1. The influence of doping on the EL properties was also investigated in OLEDs based on an emitting layer containing a typical host material blended with the SWIR emitters at various doping concentrations, with the device characteristics of the optimized COTIC-4F and IDSe-4Cl devices shown in Supplementary Fig. 10 and the corresponding device parameters summarized in Supplementary Table 2. The EL spectra of the COTIC-4F devices undergo a remarkable blueshift upon doping, with peaks at 1,200 nm for the COTIC-4F neat film, 1,060 nm for the 70 wt% film, 1,030 nm for the 50 wt% film and 1,010 nm for the 30 wt% film, where a similar trend is also observed in the IDSe-4Cl devices. The blueshift in the EL spectra can be attributed to the polar surrounding effect that leads to a gradual decrease in the surrounding polarizability with a decreasing doping concentration of emitters with good planarity29. It is noteworthy that the maximal EQE for the doped COTIC-4F device is 0.059%, which is approximately twice that of the best non-doped COTIC-4F device (0.031%), while the doped IDSe-4Cl devices show a decreased EQE of 0.079% compared with the that for non-doped device (0.13%), which is probably as a result of the different variation of charge-transport properties between the emitting layers, as evidenced by the change in the turn-on voltage $V_{on}$ (Supplementary Table 2). The EL spectra of the devices demonstrate tuning with the peak ranging from 810 to 1,230 nm (Fig. 4a).

It is worth noting that OLEDs based on i-IDSe-4Cl (with an emission peak at 843 nm) and Y11 (a peak at 945 nm) show a maximum EQE of 0.54% and 0.33%, respectively (Table 1), which are among the highest efficiencies reported in fluorescent NIR OLEDs29. Moreover, these devices exhibit a high maximum radiant exitance of 8–14 mW cm$^{-2}$, which is twice that of the best fluorescent emitter29 and comparable to state-of-the-art phosphorescent NIR OLEDs with similar EL spectra (Supplementary Fig. 11)22. More importantly, the broad tunability of the A–D–A-type organic semiconductors has enabled bright SWIR EL that spans 1,000 to 1,300 nm and beyond, which is extremely rare in organic material systems. Among them, devices based on IDSe-4F and IDSe-4Cl show the best performance (Table 1), which have EQE values of 0.12% and 0.13% with EL peaks at 1,080 nm and 1,110 nm, respectively. These two molecules are analogues of the reported ultranarrow-bandgap A–D–A-type conjugated molecules46 in which indacenodiselenophene (IDSe) is used as the electron-donating core to achieve redshifted absorption and large extinction coefficients47. Besides, a long branched alkoxy group was introduced to the inserted thiophene unit to provide good solubility for improved film quality in OLEDs. It is important to note that the EQE values of IDSe-4F and IDSe-4Cl are sevenfold higher than that of their molecular analogue TTT-C20-4F (~0.017%, Table 1), highlighting the importance of retarding the high-frequency vibration modes through heavy-atom substitution.

The superior device performance is also evident in the current density–radiance–voltage ($J$–$R$–$V$) characteristics, as shown...
Under any voltage above 0 V, a diffusion current due to recombination of diffusion-driven and thermally generated charge carriers is dominated by the diffusion of charge carriers, rather than by the gradient of the carrier concentrations starting to flow, following an exponential dependence on the applied voltage. According to the mechanism, it was demonstrated that once charge recombination is dominated by the diffusion of charge carriers, rather than by the drift current, while the accumulation of majority carriers takes place at the same time, emissive Langevin recombination can become apparent even when at subgap voltages. In our devices, barrier-free hole injection into the emissive layer leads to hole accumulation at the active layer/cathode interface, while a relatively small built-in potential gives rise to the establishment of a positive drift current at low forward bias (Supplementary Fig. 12). It is equally important to note that the recombination rate \( k_{\text{Rec}} \) in the diffusion-dominated regime is inversely proportional to an exponential dependence on the bandgap via \( k_{\text{Rec}} = \gamma N_e \exp \left( -\frac{E_g}{k_B T} \right) \left( \exp \frac{\phi}{k_B T} - 1 \right) \), where \( \gamma \) is the bimolecular recombination coefficient and \( N_e \) is the effective density of states in the conduction band. Therefore, the recombinaton rate in our low-bandgap devices is sufficiently high to fulfill the condition for diffusion-dominated recombination to occur, leading to the EL emission at subgap voltages. The conclusion of diffusion-dominated current in our devices is further supported by the calculated diffusion current using the Shockley equation and numerical drift-diffusion simulations (Supplementary Fig. 13a), both of which use the same set of extracted charge mobility data as input parameters (Supplementary Fig. 13b–d). With the validation of the diffusion-dominated current description, the bandgap of the emitters contributes to the exponential part of the current while their charge-transport properties contribute to the linear part of the current.

It is noteworthy that all devices can operate up to a high current density of 2,000–3,000 mA cm\(^{-2}\) (Fig. 4c and Supplementary Fig. 9), which was challenging to realize in previous NIR/SWIR OLEDs. The detailed physical picture that leads to such a high current density tolerance is far from clear; however, it is likely to stem from the short exciton lifetime of the emitters (55–600 ps, Supplementary Table 1), which are beneficial for preventing the accumulation of

| No. | Emitter | \( E_g \) (eV) | 0–0 emission peak (nm) | 0–1 emission peak (nm) | PLQY (\%)\(^a\) | \( V_{\text{em}} \) (V)\(^b\) | Maximum radiance (W sr\(^{-1}\) m\(^{-2}\))\(^b\) | Maximum radiant exitance (mW cm\(^{-2}\))\(^b\) | Maximum EQE (\%)\(^b\) |
|-----|---------|-------------|----------------------|----------------------|--------------|----------------|------------------------|------------------------|---------------|
| 1   | BTA3    | 1.79        | 720                  | 750                  | 22.8 ± 4.5   | 1.60 ± 0.05   | 19.6 (16.6 ± 3.8)     | 6.16 (5.22 ± 1.2)     | 0.43 (0.36 ± 0.067) |
| 2   | i-IDSe  | 1.28        | 1,000                | 1,080                | 1.51 ± 0.21  | 1.02 ± 0.076  | 12.2 (10.7 ± 1.58)    | 3.8 (3.37 ± 0.50)     | 0.12 (0.97 ± 0.013) |
| 3   | IDSe-4F | 1.26        | 1,025                | 1,110                | 1.12 ± 0.18  | 0.95 ± 0.055  | 12.4 (10.7 ± 1.25)    | 3.9 (3.36 ± 0.39)     | 0.13 (0.10 ± 0.017) |
| 4   | IDSe-4Cl| 1.37        | 953                  | 1,015                | 0.75 ± 0.20  | 1.08 ± 0.075  | 5.45 (4.78 ± 0.55)    | 1.8 (1.51 ± 0.17)     | 0.054 (0.047 ± 0.008) |
| 5   | i-IDSe-4Cl| 1.05  | 1,050                | 1,120                | 0.26 ± 0.12  | 0.91 ± 0.049  | 2.89 (2.19 ± 0.50)    | 0.91 (0.69 ± 0.16)    | 0.031 (0.026 ± 0.007) |
| 6   | Y6      | 1.7        | 945                  | 1,040                | 3.97 ± 1.07  | 1.07 ± 0.075  | 17.2 (14.2 ± 3.22)    | 5.4 (4.46 ± 1.01)     | 0.25 (0.20 ± 0.041) |
| 7   | Y11     | 1.37       | 945                  | 1,035                | 8.13 ± 0.30  | 1.01 ± 0.035  | 27.3 (23.7 ± 4.78)    | 8.6 (7.96 ± 1.11)     | 0.33 (0.28 ± 0.070) |
| 8   | IDSe-Th | 1.37       | 953                  | 1,015                | 0.75 ± 0.20  | 1.08 ± 0.075  | 5.45 (4.78 ± 0.55)    | 1.8 (1.51 ± 0.17)     | 0.054 (0.047 ± 0.008) |
| 9   | IDSe-4F | 1.28       | 1,000                | 1,080                | 1.51 ± 0.21  | 1.02 ± 0.076  | 12.2 (10.7 ± 1.58)    | 3.8 (3.37 ± 0.50)     | 0.12 (0.97 ± 0.013) |
| 10  | IDSe-4Cl| 1.26       | 1,025                | 1,110                | 1.12 ± 0.18  | 0.95 ± 0.055  | 12.4 (10.7 ± 1.25)    | 3.9 (3.36 ± 0.39)     | 0.13 (0.10 ± 0.017) |
| 11  | Y-2W-F  | 1.035      | 1,140                | 1,07 ± 0.082         | 1.53 (1.25 ± 0.16) | 0.48 (0.39 ± 0.050) | 0.48 (0.39 ± 0.050) | 0.06 (0.005 ± 0.001) |
| 12  | SiOTIC-4F| 1.24      | 1,050                | 1,120                | 0.26 ± 0.12  | 0.91 ± 0.049  | 2.89 (2.19 ± 0.50)    | 0.91 (0.69 ± 0.16)    | 0.031 (0.026 ± 0.007) |
| 13  | Y-2W-Th | 1.055      | —                    | 1.08 ± 0.075         | 0.26 (0.24 ± 0.04) | 0.08 (0.075 ± 0.012) | 0.08 (0.075 ± 0.012) | 0.06 (0.005 ± 0.001) |
| 14  | COTIC-4F| 1.17       | 1,125                | 1,200                | 0.38 ± 0.14  | 0.78 ± 0.041  | 2.81 (2.43 ± 0.39)    | 0.88 (0.75 ± 0.12)    | 0.031 (0.024 ± 0.006) |
| 15  | TTT-C20-4F| 1.15   | —                    | 1.11 ± 0.075         | 1.84 (1.70 ± 0.16) | 0.59 (0.54 ± 0.050) | 0.59 (0.54 ± 0.050) | 0.017 (0.016 ± 0.002) |

\(^a\)Measured in solid films and under ambient conditions. Average values ± standard deviation were obtained from four measurements. \(^b\)Values shown in parentheses are averages over fifteen devices for each emitter.
formed excitons and thus alleviating their concomitant loss, such as via Auger recombination and exciton–exciton annihilation at high carrier injection. Moreover, our non-doped devices promise sufficient recombination sites where injected carriers can recombine, thus avoiding saturation at low current density. In addition, the driving voltage values for the high current density (for example, 1,000 mA cm\(^{-2}\)) in our devices are extremely low (2.2 V for SiOTIC-4F/COTIC-4F, 3.2 V for Y11/Y6 and 3.0 V for IDSe-4F/IDSe-4Cl devices, see Supplementary Fig. 9j,f and Fig. 4b, respectively), which generate smaller Joule heating when compared with other reported OLEDs and thus sufficiently decrease additional exciton dissociation. Moreover, this high current density corresponds to a carrier density of around \(10^{18}\) cm\(^{-3}\), which is a threshold for lasing under electrical excitation\(^4\). Interestingly, with increasing current density, the EQE values for all devices except those based on larger bandgap materials (for example, Y11 and i-IDSe-4Cl) demonstrate a remarkable increase, which ultimately gives rise to a high SWIR radiance. This dependence of EQE on current density is particularly striking as it implies that radiative recombination can compete with non-radiative recombination at high current densities in the OLEDs. One possible interpretation for this unusual dependency is that it corresponds to a trap-filling process with increasing voltage that not only shifts the recombination zone away from the electrode but also eliminates the non-radiative trap-assisted recombination, leading to an EQE enhancement of more than a factor of two in most devices. The injection-dependent EL spectra shown in Supplementary Fig. 14 are consistent with a recent study by Blom and colleagues, who reported that a voltage-dependent EL is a fingerprint of trap-assisted recombination\(^5\), and thus confirms the interpretation that radiative recombination dominates over competing trap-assisted recombination with increasing current density. In this manner, the A–D–A-type organic semiconductors possess the potential to fundamentally overcome the SWIR lasing boundary set by the high-excitation-threshold requirement and efficiency roll-off at high current density.

To demonstrate the potential of our technology, we fabricated large-area SWIR OLEDs based on IDSe-4Cl/IDSe-4F. Figure 4d shows a photograph of a typical IDSe-4Cl device with a peak emission wavelength at 1,110 nm and a SWIR radiation power of \(\sim 0.6\) mW at a current density of 22 mA cm\(^{-2}\), which shows a remarkable emission uniformity over the substrate area with a size of 15 × 15 mm. The large-area device possesses a high maximum SWIR output power of \(\sim 8.8\) mW, which is comparable to 10 mW as seen for InGaAs-based LEDs. These results demonstrate the promise of our devices as a cost-efficient flat-panel light source for applications in portable spectrometers, information-secured...
Displays and night-vision target identification. To provide visualization for these applications, we set up an optical wireless communication system (see Methods for the setup and Supplementary Fig. 15 for the simplified block diagram) in which our SWIR OLEDs are integrated as the transmitter for a free-space data link. Transmitting audio signals or pulsed signals is achieved through the modulation of infrared light, while an InGaAs photodiode was used as the receiver for audio signal recovery. As shown in Supplementary Fig. 15, there is no obvious distortion in the received signals, indicating that our system provides sufficient transmission capacity. Owing to the bright radiation and the fast switching ability, the application of our SWIR OLEDs makes light-fidelity (or Li-Fi) communication possible and more flexible. We further demonstrate the real-time transmission of audio signals and pulsed signals through biological tissue (for example, meat or fish slices) (Supplementary Videos 1 and 2). We further demonstrate that SWIR OLEDs hold great promise for the inspection of semiconductor wafer and chip quality. Since the absorption edge is ~1,100 nm for multi-crystalline silicon and ~1,050 nm for single-crystalline silicon, our IDSe-4Cl device is more advantageous in that its emission is peak located at 1,110 nm compared with a visible-light source. Indeed, as shown in Fig. 5a,b, the SWIR light source shows considerable optical transmission, whereas the wafer is opaque to the visible-light source. The emission from the IDSe-4Cl OLEDs can penetrate the wafer when illuminated from below and reveal more details, making these OLEDs ideal for industrial applications, such as in the detection of pinholes and cracks in wafers. Snapshot images of the microchip yielded by SWIR irradiance from our devices are shown in Fig. 5c, with the images obtained from visible-light illumination included in Fig. 5d for comparison. The features of the microcircuit and details of defects or cracks can be clearly observed in the SWIR image, whereas part of visible-light image is obscure. In addition, the Y11 device exhibits good operation stability, and shows a half-life operation lifetime (T50, the time taken for the radiance to decay to half its initial value) of at least 1,000 h (Supplementary Fig. 16) at a high current density of 100 mA cm⁻² when evaluated under continuous operating conditions and in a glovebox with encapsulation. Other devices based on the IDSe-4F, IDSe-4Cl and COTIC-4F emitters also show comparable lifetime values of 1,000 h (Supplementary Fig. 16a). It is worthy of note that the COTIC-4F device shows a longer T50 of over 500 h when tested in air compared with 300–400 h for other emitters. These findings on large-area devices with high brightness and good stability open up a pathway toward low-cost, portable SWIR OLED light sources for emerging applications.

Conclusion

In summary, we demonstrate OLEDs with bright SWIR emission using finely tuned A–D–A-type molecules as emitters. The resultant OLEDs exhibited very favourable device performance values, including a notable radiance and efficiency in the SWIR region, a very low turn-on voltage at subgap voltages and an even higher efficiency at a high current density of the order of around 1000 cm² W⁻¹. We found that the impressive performance of these SWIR OLEDs is essentially due to the excellent photophysical properties of the A–D–A–type molecules, in which their coplanarity, π-conjugated backbone rigidity, extremely small reorganization energies and electron–phonon coupling factors, combined with the heavy-atom substitution that retards high-frequency vibration modes, contributed to significantly suppressed non-radiative recombination rates and improved PLQY values. Furthermore, given their large oscillator strength and their ability to operate at high current density, these A–D–A-type molecules hold the potential to fulfill electrically pumped SWIR lasers. Benefiting from the semi-transparency of biological tissue to SWIR radiation, their high radiation power and the absence of toxic heavy metals in their make-up, our devices provide a promising outlook for a wide range of emerging applications (Supplementary Fig. 17), such as next-generation optoelectronic devices, wearable biosensors, implantable bioelectronics, IoT (Internet of Things) connectivity and biological imaging.

Online content

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References

1. Tang, C. W. & VanSlyke, S. A. Organic electroluminescent diodes. Appl. Phys. Lett. 51, 913–915 (1987).
2. Burroughes, J. H. et al. Light-emitting diodes based on conjugated polymers. Nature 347, 539–541 (1990).
3. Qian, G. et al. Simple and efficient near-infrared organic chromophores for light-emitting diodes with single electroluminescence emission above 1000 nm. Adv. Mater. 21, 111–116 (2009).
4. Zampetti, A., Minotto, A. & Cacialli, F. Near-infrared (NIR) organic light-emitting-diode (OLEDs): challenges and opportunities. Adv. Funct. Mater. 29, 1807623 (2019).
5. Zheng, Y. & Zhu, X. Recent progress in emerging near-infrared emitting materials for light-emitting diode applications. Org. Mater. 2, 253–281 (2020).
6. Konstantatos, G. et al. Ultrasonic solution-cast quantum dot photodetectors. Nature 442, 180–183 (2006).
7. Lu, H., Carroll, G. M., Neale, N. R. & Beard, M. C. Infrared quantum dots: progress, challenges, and opportunities. ACS Nano 13, 939–953 (2019).
8. Murphy, C. J. Optical sensing with quantum dots. Anal. Chem. 74, 520A–526A (2002).
9. Smith, A. M., Mancini, M. C. & Nie, S. Second window for in vivo imaging. Nat. Nanotechnol. 4, 710–711 (2009).
10. Wilson, R. H., Nadeau, K. P., Jaworski, F. B., Tromberg, B. J. & Durkin, A. J. Review of short-wave infrared spectroscopy and imaging methods for biological tissue characterization. J. Biomed. Opt. 20, 030901 (2015).
11. Dao, S. et al. Fluorescence imaging in vivo at wavelengths beyond 1,500 nm. Angew. Chem. Int. Ed. 54, 14758–14762 (2015).
12. Bruns, O. T. et al. Next-generation in vivo optical imaging with short-wave infrared quantum dots. Nat. Biomed. Eng. 1, 0056 (2017).
13. Minotto, A. et al. Towards efficient near-infrared fluorescent organic light-emitting diodes. Light. Sci. Appl. 10, 18–27 (2021).
14. Wu, J. When group-III nitriles go infrared: new materials and properties. J. Appl. Phys. 106, 011101 (2009).
15. Krier, A., Chub, D., Krier, S. E., Hopkinson, M. & Hill, G. Light sources for wavelengths >2µm grown by MBE on InP using a strained relaxed buffer. IEEE Proc. Optoelectron. 145, 292–296 (1998).
16. Someya, T., Bao, Z. & Malliaras, G. The rise of planar bioelectronics. Nature 540, 379–385 (2016).
17. Tessler, N., Medvedev, V., Kazes, M., Kan, S. & Banin, U. Efficient near-infrared polymer nanocrystal light-emitting diodes. Science 295, 1506–1508 (2002).
18. Qi, J., Qiao, W. & Wang, Z. Y. Advances in organic near-infrared materials and emerging applications. Chem. Rec. 16, 1531–1548 (2016).
19. Ho, C. L., Li, H. & Wong, W. Y. Red to near-infrared organometallic phosphorescent dyes for OLED applications. J. Organomet. Chem. 751, 261–285 (2014).
20. Xu, X. et al. Efficient radical-based light-emitting diodes with doublet emission. Nature 563, 536–540 (2018).
21. Tao, R. et al. High-efficiency near-infrared organic light-emitting devices based on an iridium complex with negligible efficiency roll-off. J. Mater. Chem. C 1, 6446–6454 (2013).
22. Wei, Y. C. et al. Overcoming the energy gap law in near-infrared OLEDs by exciton–vibration decoupling. Nat. Photonics 14, 570–577 (2020).
23. Suzuki, H. Infrared electroluminescence from an organic ionic dye containing no rare-earth ions. Appl. Phys. Lett. 80, 3256–3258 (2002).
24. Chen, M. et al. Microm wave photon photo- and electroluminescence from a conjugated polymer. Appl. Phys. Lett. 84, 3570–3572 (2004).
25. Minotto, A. et al. Efficient near-infrared electroluminescence at 840 nm with metal-free small-molecule/polymer blends. Adv. Mater. 30, 1706584 (2018).
26. Qian, G. et al. Band gap tunable, donor-acceptor–donor charge-transfer heteroquinoid-based chromophores: near infrared photoluminescence and electroluminescence. Chem. Mater. 20, 6208–6216 (2008).

760
27. Yao, L. et al. Highly efficient near-infrared organic light-emitting diode based on a butterfly-shaped donor-acceptor chromophore with strong solid-state fluorescence and a large proportion of radiative excitons. Angew. Chem. Int. Ed. 53, 2119–2123 (2014).

28. Kim, D. H. et al. High efficiency electroluminescence and amplified spontaneous emission from a thermally activated delayed fluorescent near-infrared emitter. Nat. Photonics 12, 98–104 (2018).

29. Yu, Y. et al. Near-infrared electroluminescence beyond 800 nm with high efficiency and radiance from anthracene cored emitters. Angew. Chem. Int. Ed. 59, 21578–21584 (2020).

30. Tregnago, G., Steckler, T. T., Fenwick, O., Andersson, M. R. & Cacialli, F. Thia- and selenadiazole containing polymers for near-infrared light-emitting diodes. J. Mater. Chem. C 3, 2792–2797 (2015).

31. Lin, Y. et al. An electron acceptor challenging fullerenes for efficient polymer solar cells. Adv. Mater. 27, 1179–1174 (2015).

32. Liu, S. et al. High-efficiency organic solar cells with low non-radiative recombination loss and low energetic disorder. Nat. Photonics 14, 300–305 (2020).

33. Rau, U. Reciprocity relation between photovoltaic quantum efficiency and electroluminescent emission of solar cells. Phys. Rev. B 76, 085303 (2007).

34. Lee, J. et al. Bandgap narrowing in non-fullerene acceptors: single atom substitution leads to high optoelectronic response beyond 1000 nm. Adv. Energy Mater. 8, 1801212 (2018).

35. Roncali, J. Molecular engineering of the band gap of π-conjugated systems: facing technological applications. Macromol. Rapid Commun. 28, 1761–1775 (2007).

36. Shuai, Z. G. & Peng, Q. Organic light-emitting diodes: theoretical understanding of highly efficient materials and development of computational methodology. Natl. Sci. Rev. 4, 224–239 (2017).

37. Benduhn, J. et al. Intrinsic non-radiative voltage losses in fullerene-based organic solar cells. Nat. Energy 2, 17053 (2017).

38. Perdigón-Toro, L. et al. Excitons dominate the emission from PM6:Y6 solar cells, but this does not help the open-circuit voltage of the device. ACS Energy Lett. 6, 557–564 (2021).

39. Jortner, J. Temperature dependent activation energy for electron transfer between biological molecules. J. Chem. Phys. 64, 4860–4867 (1976).

40. Gould, I. R. et al. Radiative and nonradiative electron transfer in contact radical-ion pairs. Chem. Phys. 176, 439–456 (1993).

41. Azzouzi, M. et al. Nonradiative energy losses in bulk-heterojunction organic photovoltaics. Phys. Rev. X 8, 031055 (2018).

42. Wilson, I. S. et al. The energy gap law for triplet states in Pt-containing conjugated polymers and monomers. J. Am. Chem. Soc. 123, 9412–9417 (2001).

43. Cave, R. J. & Newton, M. D. Generalization of the Mulliken–Hush treatment for the calculation of electron transfer matrix elements. Chem. Phys. Lett. 249, 15–19 (1996).

44. Zhu, W. et al. Crystallography, morphology, electronic structure, and transport in non-fullerene/non-Indacenodithienothiophene polymer: Y6 solar cells. J. Am. Chem. Soc. 142, 14532–14547 (2020).

45. Zhang, G. et al. Delocalization of exciton and electron wavefunction in non-fullerene acceptor molecules enables efficient organic solar cells. Nat. Commun. 11, 3943 (2020).

46. Yao, H. et al. Design, synthesis, and photovoltaic characterization of a small molecular acceptor with an ultra-narrow band gap. Angew. Chem. Int. Ed. 56, 3045–3049 (2017).

47. Intemann, J. J. et al. Molecular weight effect on the absorption, charge carrier mobility, and photovoltaic performance of an indacenodithienophene-based ladder-type polymer. Chem. Mater. 25, 3188–3193 (2013).

48. Li, Y. et al. Universal electroluminescence at voltages below the energy gap in organic light-emitting diodes. Adv. Optical Mater. 8, 2101149 (2021).

49. Liu, X. K. et al. Metal halide perovskites for light-emitting diodes. Nat. Mater. 20, 10–21 (2021).

50. Kuik, M. et al. 25th Anniversary Article: Charge transport and recombination in polymer light-emitting diodes. Adv. Mater. 26, 512–531 (2014).

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Methods

Materials. The A–D–A-type molecules Y11, SIOTC-4F and COTIC-4F were obtained as commercial chemicals from 1-Material, and Y6 and BTA3 were purchased from Solarna. The three twisted small molecules i-IDSe, i-IDSe-4Cl, and i-IDSe-4F were prepared using a synthetic route employed in ref. 1. Perylene diimide functionalized with amino N-oxide (PDINO) was purchased from Sigma-Aldrich. PEDOT:PSS in aqueous solution was purchased from H.C. Starck. All purchased chemicals were used as received without additional purification. Unless otherwise stated, all other A–D–A-type molecules were synthesized in the laboratory using a route described in the Supplementary Methods.

Computational methods. To study the electronic-structure properties of the molecules Y11, IDSe-4Cl and COTIC-4F (discussed in the main text), we carried out quantum-chemical calculations on them. In our calculations, all the long alkyl chains attached to their \( \pi \)-conjugated backbones were replaced by methyl groups, which is a standard procedure for studying electronic structures of single molecules. Molecular aggregation definitely impacts the electronic and optical properties in solid-state films. Many studies have demonstrated that long alkyl chains significantly impact the aggregation structures of the molecules, similar to what is observed in the present work. The initial geometries of these three molecules were optimized using the range-separated functional B97XD (with a default range-separation parameter \( \omega \) of 0.2 bohr\(^{-1} \)) and the 6-31G(d,p) basis set. An iteration procedure\(^{32,33} \) was used to non-empirically tune the \( \omega \) parameter with the implicit consideration of the dielectric environment via the polarizable continuum model; the dielectric constant \( \varepsilon \) was chosen to be 4.5, which is a representative value for polar organic semiconductor materials. The TD-DFT approach was used to study the excited-state properties. All quantum-chemical calculations were performed using the Gaussian 16 Rev A03 program\(^{32} \). The overlaps between the NTO electron and hole wavefunctions describing the S\(_1\) excited states were quantified using the Multimfn program\(^{33} \).

Optical absorption and photoluminescence characterization. The absorption spectra of the solid-state films were measured using an ultraviolet-visible-NIR spectrophotometer (UV3600, Shimadzu). For measurement of the steady-state PL of solid films, semiconductor lasers were used for excitation, where the wavelength was 530 nm (for PC\(_{71}\)BM), 635 nm (for BTA3, ITIC, IT-M, IT-4F and i-IEICO-4F) or 852 nm (for Y6, Y11, IDSe-Th, IDSe-4F and IDSe-4Cl, SIOTC-4F and COTIC-4F). To measure the PL from solutions, a 635 nm laser was employed to excite the Y11 solution, and an 852 nm laser was used for IDSe-4Cl and COTIC-4F excitation. Calibrated spectrometers (QE Pro and NIR Quest 512, Ocean Optics), which were equipped with a cooled Hamamatsu CCD (charge-coupled device) array (−20 °C) in conjunction with an integrating sphere, were operated as a spectral acquisition system. To avoid self-absorption, an integrating sphere with a diameter of 20.32 cm was used to measure the PL from solutions. To minimize the scattering of incident laser, a longpass filter with a cutoff wavelength at 750 nm or 860 nm was placed between the sample and detector. All PL experiments were carried out under ambient conditions of 25 °C.

Photoluminescence quantum yield measurements. The absolute PLQY values for emitters with a emission between 300 and 950 nm were measured using an integrating-sphere-coupled spectrometer (QE Pro) and further verified using a commercial absolute PLQY measurement system (C11347-11, Hamamatsu Photonics), while for an emission above 950 nm the devices were determined using an integrating sphere and a calibrated spectrometer (NIR Quest 512) as the ratio of the number of photons re-emitted to the number of photons absorbed.

Measurement of time-resolved photoluminescence spectra. The time-resolved PL spectra of the emitters were acquired under ambient conditions of 25 °C using a fluorescence lifetime spectrometer via a time-correlated single-photon-counting technique (Hydroarhap 400, PicoQuant). The samples were excited using a femtosecond Ti:sapphire pulsed laser (Coherent) with a pulse duration of 120 fs, a fluence of ~0.2 J cm\(^{-2} \) per pulse and a repetition rate of 80 MHz. The PL data were collected using a single-photon-counting photomultiplier tube detector. A longpass filter with a cutoff wavelength at 715 nm or 780 nm was placed before the detector to minimize the scattering of incident laser. The time-resolution of the photomultiplier tube detector (PDB-C613-2, Lunainc Photonics), where the initial radiant exitance was calibrated using a spectrometer (QE Pro) with a calibrated silicon photodetector. The EL spectra for devices with emission peaks past 700 nm and 1,000 nm were recorded using a spectrometer (QE Pro) with a calibrated silicon photodetector. The EL spectra for devices with emission peaks past 1,000 nm were recorded using a spectrometer (NIR Quest 512) equipped with an InGaAs line photodetector (calibrated from 900 nm to 1,700 nm).

SWIR photographs and videos. Photographs and videos of the SWIR light source were obtained using a SWIR camera (LD-SW601725-CTEG2-L (Leading Optoelectronics) or RT-A25M10-ARTCAM (Andover Optical)) whose detection range was between 950 nm and 1,700 nm with a pixel resolution of 25 μm. Microscopic photographs were taken using a transfective polarizing microscope (XP4A, SHMIL) equipped with a visible-light CCD, and the SWIR photographs were recorded by switching the self-activated CCD to the SWIR camera.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request. Source data are provided with this paper.

References

51. Wang, W. et al. Achieving efficient polymer solar cells based on near-infrared absorptive backbone twisted non-fullerene acceptors through a synergistic strategy of indacenodiselenophene fused-ring core and chlorinated terminal group. ACS Appl. Energy Mater. 5, 1322–1330 (2022).
52. Li, C. et al. Non-fullerene acceptors with branched side chains and improved molecular packing to exceed 18% efficiency in organic solar cells. Nat. Energy 6, 605–613 (2021).
53. Jiang, K. et al. Alkyl chain tuning of small molecule acceptors for efficient organic solar cells. Joule 3, 3020–3033 (2019).
54. Cui, L.-S. et al. Fast spin-flip enables efficient and stable organic solar cells. Joule 6, 636–642 (2020).
55. Frisch, M. J. et al. Gaussian 16 revision C.01 (Gaussian, Inc., 2016).
56. Lu, T. & Chen, F. MultiFln: a multifunctional waveform analyzer. J. Comput. Chem. 33, 580–592 (2012).
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Author contributions
Y.X., Hongbin Wu and C.G. conceived the idea. Y.X. and W.L. fabricated the SWIR OLEDs devices. C.G., Haimei Wu and WW. designed and synthesized the i-IDSe- and IDSe-series A–D–A-type emitters. Y.X. performed the theoretical calculations and the numerical simulations. X.-K.C. performed the theoretical calculations and provided feedback on the manuscript. Y.X., W.L. and W.D. performed the device characterization and optical absorption measurements. W.D. and W.L. performed the time-resolved PL decay measurements. Y.X. and W.D. performed the recombination-rate calculations. W.L. and Y.X. acquired the SWIR EL photographs. Y.S. set up the optical communication system. W.L. and Y.X. carried out optical communication demonstration, wafer-quality inspection and operational lifetime tests. X.Z. and J.P. discussed the results and commented on the manuscript. Hongbin Wu, Y.X., C.G., W.D., W.L. and X.-K.C. contributed to the writing of the manuscript. All authors discussed the experiments and results. Hongbin Wu, C.G. and Y.C. supervised the project and advised on device optimization.

Competing interests
The authors declare no competing interests.

Additional information
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