We have designed and synthesized three N-annulated perylene diimide (PDI) compounds containing sterically bulky alkyl-substituted benzyl moieties (PDI-X, where $X = 1, 2, 3$) with photoluminescence quantum yield (PLQY) in the solid-state $> 20\%$. The PDI molecules show PLQY of $\sim 0.8$ in solution and $\sim 0.2$ as neat films. Organic light-emitting diodes (OLEDs) have been fabricated using these new PDI molecules as light emitters with the active layer being solution processed from non-halogenated solvents. The OLED devices had brightness of $\sim 2000$ cd m$^{-2}$ and low turn-on voltage of $\sim 3$ V, among the best for PDI based red colored OLEDs.

Perylene diimide (PDI) based materials have been actively explored in the context of fluorescence labels, organic semiconducting devices, and light harvesters. The PDI chromophore has key processability. The high photoluminescence quantum yield visible region, high photothermal stability, and solution properties such as tunable photon absorption and emission in the context of fluorescence labels, organic semiconducting devices, and light harvesters. The PDI chromophore has key processability.

Efforts have been made to increase the PLQY of PDI materials in the solid-state. Zhang and coworkers synthesized PDI molecules showing PLQY near 30% in neat films and an optical quantum efficiency of 0.6%.\textsuperscript{11} The performance of OLEDs depends not only on the PLQY of the emitting layer but charge transport, radiative exciton formation efficiency, and light outcoupling efficiency,\textsuperscript{12} thus completely isolating the PDI chromophore is not an option. A way to increase PLQY without sacrificing electrical performance is to control the aggregation of the PDI units via the formation of dimers, trimers, tetramers.\textsuperscript{13} Such larger oligomers and/or starburst derivatives can reduce co-facial $\pi-\pi$ stacking and limit ACQ.\textsuperscript{14}

Recently, the Welch group has reported on a series of N-annulated PDI dimers with controlled aggregation tendencies\textsuperscript{15} and green solvent processability\textsuperscript{16} that have found utility in both organic solar cells\textsuperscript{17–20} and OLEDs.\textsuperscript{21,22} These compounds are readily made on scale, are highly soluble in common organic processing solvents, and exhibit a range of optoelectronic properties. N-Annulation destabilizes the frontier molecular orbital energy levels changing the PDI electronic structure\textsuperscript{23} while the pyrrolic N-position can be readily functionalized.\textsuperscript{24} We have shown that an N-annulated PDI dimer with bulky 2-ethylhexyl sidechains (tPDI$_2$N-EH) can function as an effective light emitter in OLEDs\textsuperscript{21} and our hypothesis was that increasing the bulk of the side-chain would lead to greater PLQY in the film and subsequent increased OLED device performance.

Herein, we report the synthesis and characterisation of air stable red-light-emitting N-annulated PDI dimers substituted at pyrrolic N-atom position with 2,4,6-trimethylbenzyl, 2,4,6-trisopropylbenzyl, and 3,5-di-tert-butylbenzyl side-chains. The target structures tPDI$_2$N-trimethylbenzyl (PDI-1), tPDI$_2$N-trisopropylbenzyl (PDI-2), and tPDI$_2$N-di-tert-butylbenzyl (PDI-3) are shown in Fig. 1. The benzyl side chains with sterically bulky alkyl substituents can lead to different intermolecular interactions as compared to alkyl side chains, with the possibility of different electronic influences on the dimeric PDI core. The PDI molecules. Kozma and coworkers appended large naphthyl moieties to the PDI chromophore and were able to achieve PLQY $\sim 23\%$ in neat films and developed OLEDs based on these materials with moderate external quantum efficiency (EQE) of 0.6%.\textsuperscript{11} The performance of OLEDs depends not only on the PLQY of the emitting layer but charge transport, radiative exciton formation efficiency, and light outcoupling efficiency,\textsuperscript{12} thus completely isolating the PDI chromophore is not an option. A way to increase PLQY without sacrificing electrical performance is to control the aggregation of the PDI units via the formation of dimers, trimers, tetramers.\textsuperscript{13} Such larger oligomers and/or starburst derivatives can reduce co-facial $\pi-\pi$ stacking and limit ACQ.\textsuperscript{14}
dimers are easily processed into uniform films from non-
halogenated solvents. The UV-vis absorption and PL spectra of
the PDI molecules in diluted solution were recorded and PLQYs
were calculated. The absolute PLQY of PDI molecules dispersed
into neat films were measured by an integrating sphere. Finally,
OLED devices reported here show enhanced performance com-
pared to previously reported PDI dimers. Complete synthesis
and characterization are presented in the ESI.†

To investigate the influence of different substituted benzyl
side chains on the photophysical properties of the PDI deriva-
tives, the UV-vis absorption and emission spectra of PDI-1, PDI-2
and PDI-3 in o-xylene solution and as thin films were measured
(Fig. 2 and Table 1). In the o-xylene solution, the absorption
spectra of all PDI molecules are identical and demonstrate the
two characteristic maxima of the PDI chromophore. All
dimers have high PLQY of ~0.7 in solution with similar PL
spectra and emission maxima at ~580 nm. The high PLQY of
these compounds is attributed to the bulky-side chains which
inhibits aggregation resulting in partial isolation of PDI dimer
core. For films cast from o-xylene, the absorption spectra
of all PDI molecules are slightly red-shifted and broadened
compared to the solution indicating that the PDI dimers are
weakly aggregated. All PDI molecules in the film have PLQY of
20–25% which is high for PDI-based light emitting materials.

A multi-stack device structure was used to fabricated
OLEDs31 (ITO) was used as the anode. Poly(3,4-ethylenedioxythiophene):poly(4-
styrenesulfonic acid) (PEDOT:PSS) and polyvinylcarbazole (PVK) were
used as the hole injection and transport layers, respectively. Zinc
oxide (ZnO) was used as an electronic transport layer with silver (Ag)
as the top cathode. The PDI molecules were used individually in
the emitting layer in combination with the polyfluorene polymer
PFO (i.e. poly(9,9-di-octylfluorenyl-2,7-diyi)) to assist with hole
transport.21

PEDOT:PSS films were formed by spin-casting aqueous
solution of PEDOT:PSS on top of cleaned glass/ITO and then
annealed at 150 °C for 30 min in air. PVK was spin-coated from
toluene on top of the PEDOT:PSS and annealed at 120 °C. Of
note the PVK film is resistant to o-xylene solvent and thus
allows for good formation of the emitting layer films on top. The
emitter layer was spin-coated on top of the PVK film from
o-xylene solutions of PFO:PDI molecules (1:9 w/w ratio). ZnO
nanoparticles in methanol were spin-coated on top and
annealed at 60 °C for 30 min in air. The emitting layer films
were found to show good tolerance to methanol solvent (Fig. S1
and S2, ESI†). The Ag top electrode deposited via thermal
evaporation (Fig. 3).

The device parameters of PDI-based OLEDs are summarized
in Table 2. All PDI-based OLEDs had similar performance with
a maximum external quantum efficiency (EQE) of ~0.7%,
luminous efficiency (LE) of 0.6 cd A⁻¹, power efficiency (PE) of
~0.3 lm W⁻¹ and a maximum of luminous (Lmax) of 2400 cd m⁻²

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**Table 1** Optical data for PDI 1–3 in solution and as neat films

|          | Absorption (nm) | Emission (nm) | Stokes shift (cm⁻¹) | PLQY (%) |
|----------|-----------------|---------------|---------------------|----------|
|          | Onset           | 0–0          | 0–1 Max             | FWHM     |          |
| PDI-1    |                 |               |                     |          |
| Solution | 543             | 530          | 495                 | 586      | 84       | 1803     | 76       |
| Film     | 564             | 533          | 496                 | 640      | 97       | 3067     | 20       |
| PDI-2    |                 |               |                     |          |
| Solution | 543             | 530          | 493                 | 591      | 90       | 1947     | 65       |
| Film     | 584             | 532          | 494                 | 642      | 101      | 3221     | 25       |
| PDI-3    |                 |               |                     |          |
| Solution | 546             | 532          | 494                 | 584      | 76       | 1674     | 74       |
| Film     | 572             | 532          | 494                 | 650      | 83       | 3412     | 25       |

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**Fig. 2** Absorption (ABS) and emission (PL) spectra of all PDI molecules in o-xylene solutions and neat films processed from o-xylene solutions.
and low turn-on voltage ($V_{\text{on}}$) of $\sim$3 V. Notably, the electroluminescence (EL) spectra of all PDI molecules are similar with a deep red maximum at $\sim$650 nm with the CIE (international commission on illumination) coordinates of ($x = 0.66; y = 0.33$) (Fig. 4). The EQE is a critical parameter of a OLED device that describes the ratio between the number of emitted photons and injected charge carriers which has been expressed by equation $\text{EQE} = \gamma \eta_{\text{sc}} q \eta_{\text{out}}^{32-35}$ where $\gamma$ is the charge carrier balance factor; $\eta_{\text{sc}}$ is the singlet–triplet factor; $q$ is the effective quantum yield of the emitter material and $\eta_{\text{out}}$ is the out-coupling efficiency of the emitted light. For theoretical evaluation of EQE the $\gamma$ value is often assumed to be unity, $\eta_{\text{sc}}$ equal 0.25 for fluorescent emitters, $q$ equals the PLQY of EL not considering the emitting dipole orientation factor and the Purcell effect; $\eta_{\text{out}}$ can be estimated as $1/(2n^2)$ for isotropic emitters, where $n$ is the refractive index of the organic EL. $^{37}$ Here, the theoretical EQE is estimated at 1% based on a 20% PLQY and $n \sim 1.5$. $^{38}$ The OLED devices had a maximum EQE ranging from 0.4% to 0.7% for each different PDI molecule. Clearly by varying the sidechain of the PDI molecule, slight changes in OLED device performance are obtained. Compared to the literature these PDI based OLEDs have much improved performance. $^{11,12}$

Conclusion

A series of $N$-annulated perylene diimides with sterically bulky alkyl-substituted benzyl side chains were designed, synthesized, and used as emitters in OLED devices. These PDI dimers demonstrated high PLQY in the solution ($\sim$80%) and as neat films ($\sim$20%). The PDI molecules were used as emitting layers and solution processed from the non-halogenated solvent o-xylene. All OLED devices based on the PDI molecules showed good performance with EQE $\sim$ 0.7%, high brightness of 2400 cd m$^{-2}$ with deep red maximum EL spectra of $\sim$650 nm, and CIE coordinates of ($x = 0.66; y = 0.33$). Future work is set to explore the utility of such molecules in complete roll-to-roll processed OLED devices.

Conflicts of interest

There are no conflicts to declare.

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