

# Synthesis and utilization of perylene-based *n*-type small molecules in light-emitting electrochemical cells†

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We report the synthesis of a soluble perylene-based small molecule for use as an *n*-type emissive material for organic optoelectronic device applications, and demonstrate the material in a light-emitting electrochemical cell configuration.

Light-emitting electrochemical cell (LEC) device operation involves *in situ* redistribution of ions under an applied bias with subsequent electrochemical doping of the  $\pi$ -conjugated material at the electrodes.<sup>1</sup> A variety of primarily *p*-type, or partially oxidized, materials have been utilized for LECs.<sup>2–6</sup> Common reported materials include poly(*p*-phenylene vinylene) (PPV)-based emissive polymers, among others. While these materials have been shown to be successful in LECs, there is growing evidence that the use of materials that are relatively easy to oxidize but are difficult or impossible to reversibly reduce could introduce asymmetry in the location of the emissive, or junction, region.<sup>7–10</sup> The use of more *n*-type materials that are more easily and reversibly reduced could be advantageous in balancing doping effects in this device architecture.

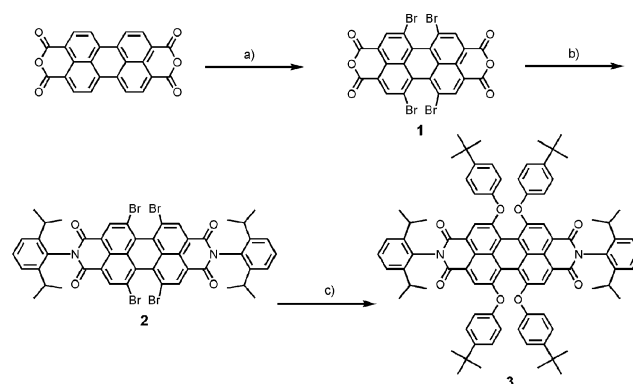
In addition to improving the electrochemical effects in these materials, *n*-type materials, such as perylene-based compounds, could offer additional advantages in organic optoelectronic devices through enhanced stability to ambient conditions that cause device degradation due to oxidation of the emissive material. In particular, perylenetetracarboxylic diimide (PDI)-based materials are increasingly attractive *n*-type materials due to efficient emission characteristics, high molar extinction coefficients, as well as high thermal, chemical, and photostability.<sup>11–13</sup> “Color tuning” for light-emitting applications can also be achieved by rational alterations of PDI at the terminal imide as well as the bay region (1,6,7,12 substitution).<sup>12</sup> Potential applications include photovoltaic devices, dye lasers, and molecular switches.<sup>11</sup> In this communication, we report the synthesis of a perylene-based compound modified for device applications (processability, solid-state fluorescence) and demonstrate its utility as the emissive material in an LEC.

Substitution at the terminal and bay region of PDI modifies both the solubility and processability of the resultant material and significantly influences the photophysical properties of the product.<sup>14–17</sup> A 2,6 diisopropyl phenyl group is appended at the terminal imide, primarily to enhance solubility.<sup>14,15</sup> To more directly disrupt  $\pi$ – $\pi$  interactions that influence solubility and

lead to fluorescent quenching in the solid state, the bay region is tetra-substituted with 4-*tert*-butylphenoxy groups.<sup>16,17</sup> These substitutions offered the desired molecule 1,6,7,12-tetra-(4-*tert*-butylphenoxy)-*N,N'*-bis(2,6-diisopropylphenyl)perylene-3,4,9,10-bis(dicarboximide).<sup>18</sup>

The synthesis to obtain our target PDI molecule is outlined in Scheme 1. Bromination of 3,4,9,10 perylene tetracarboxylic dianhydride afforded a product that could not be purified or analyzed by NMR due to its poor solubility in organic solvents. Würthner and co-workers reported that the tetrabromo product was difficult to obtain in high yield because a mixture of di-, tri-, and tetrabromo product formation.<sup>19</sup> Alternatively, Qui *et al.* reported elevated temperatures and extended time led to a majority of the tetrabromo product being formed.<sup>20</sup> Utilizing the approach of Qui *et al.*, we took the product forward after filtration and washing. This product was subsequently condensed with 2,6-diisopropylaniline in propionic acid to afford the diimide (**2**). Based on the integration ratios of the crude NMR sample of **2**, the tetrabrominated species was the major product (>90% yield) in the first step. The condensation product **2** was obtained in moderately low yield (33%) after column chromatography and recrystallization. Further reaction with base and *t*-butylphenol led to **3** in 23% yield. Since compounds **2** and **3** exhibited significant solubility in methylene chloride, purification using silica was possible. However, both **2** and **3** had di- and tri-substituted impurities making purification a challenge, leading to lower overall yields.

The target molecule, **3**, showed solubility in methylene chloride, chloroform, and a 50 : 50 mixture of chloroform



**Scheme 1** Synthesis of perylene-3,4,9,10-tetracarboxylic dianhydride. (a) Br<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, 110 °C, 168 hours, > 50% yield; (b) 2,6-diisopropylanilinepropionic acid, 140 °C, 17 hours, 33% yield; (c) 4-*t*-butylphenol, CaH<sub>2</sub>, NMP, 20 hours, 23% yield.

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and acetonitrile. Solutions of **3** were made in both chloroform and chloroform–acetonitrile (50 : 50) with no notable differences in the solution absorption spectra. The absorption spectra of thin films of **3** were slightly blue-shifted relative to solution spectra. Solution absorption spectra were collected in a  $10^{-4}$  to  $10^{-6}$  M concentration range, and a molar absorptivity of  $44000 \text{ M}^{-1}\text{cm}^{-1}$  was measured in chloroform. Absorbance spectra of thin films of **3** showed a maximum at 568 nm, consistent with the range of previously reported substituted perylene compounds.<sup>11,14,16,17,21</sup> Photoluminescence spectra showed an emission maximum at 613 nm giving a Stokes shift of 45 nm (Fig. 1). The optical band gap of 2.0 eV was calculated from the onset of absorption at 618 nm. This agrees with the observed photoluminescence and the band gap measured using cyclic voltammetry.

To determine the band gap of **3**, electrochemistry experiments were performed (see ESI†). As previously reported in the literature for perylene-based compounds,<sup>16,21–23</sup> we observe a quasi-reversible, one-electron oxidation wave and two quasi-reversible, one-electron reduction waves. Our data is consistent with the mechanism for the two-electron reduction previously proposed.<sup>11</sup> The half wave oxidation potential ( $E_{1/2}$ ) of the perylene compound *versus*  $\text{Ag}/\text{Ag}^+$  was +0.9625 V. Using  $E_{[\text{vacuum}]} = E_{\text{Ag}/\text{Ag}^+} + 4.66 \text{ V}$ , a HOMO of 5.6 eV is calculated. The half wave reduction potential ( $E_{1/2}$ ) of the perylene compound *versus*  $\text{Ag}/\text{Ag}^+$  was –1.0 V. Using  $E_{[\text{vacuum}]} = E_{\text{Ag}/\text{Ag}^+} + 4.66 \text{ V}$ , a LUMO of 3.66 eV is calculated. This correlates to a band gap of 1.96 eV, which is in good agreement with the optically calculated band gap. The LUMO level is much lower than the typical PPV derivatives often employed in LECs, indicating that in relative terms, **3** is an *n*-type material. The lower lying LUMO level may lead to enhanced stability of the perylene film in comparison to PPV-based films. This is supported by observed, quasi-reversible reduction waves. In contrast to PPV-based materials where only the oxidation wave is observable, both oxidation and reduction waves can be measured for **3** (see ESI† for CV data).

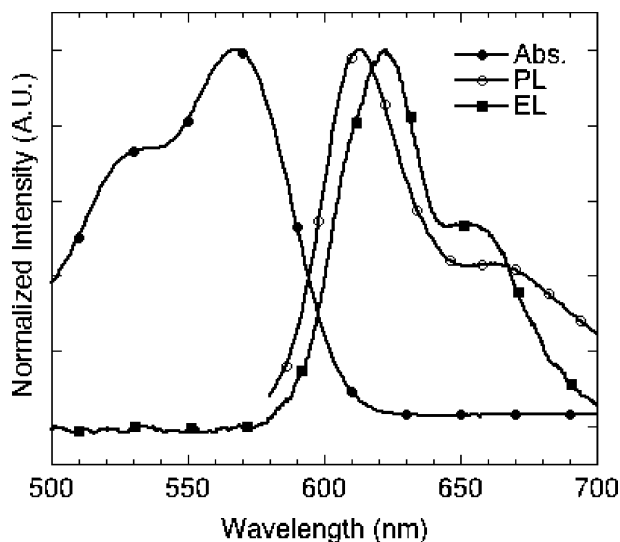


Fig. 1 Target PDI molecule, **3**, absorption, photoluminescence, and electroluminescence spectra.

LECs were fabricated in a single-layer device architecture by spin-casting a mixture of **3**, PEO, and LiTf in chloroform to a thickness of 200 to 500 nm onto patterned ITO glass substrates. Solution composition was **3**, PEO, and LiTf in a 10 : 2 : 2 weight ratio at approximately 1% total weight in chloroform. The films were annealed on a hot plate under an inert atmosphere at 80 °C for 1 h. Gold top electrodes were deposited by thermal evaporation at  $10^{-7}$  torr following overnight drying under vacuum. All device testing took place in a dry nitrogen glovebox using a Keithley 2400 Sourcemeter. Electroluminescence measurements were taken using a calibrated Ocean Optics USB2000 fiber optic spectrometer. After applying an initial bias of +8 to +10 V, the current reached equilibrium and emission was observed. Red emission could be observed by the eye in a lighted lab. The electroluminescence spectrum obtained (Fig. 1), exhibited a  $\lambda_{\text{max}}$  of emission at 622 nm. The electroluminescence and photoluminescence spectra are similar with the exception of a more defined shoulder on the electroluminescence spectra at approximately 660 nm.

The use of perylene-based, *n*-type small molecules as the emissive material in LECs has been demonstrated. The bay- and imide-substituted PDI, 1,6,7,12-tetra(4-*tert*-butylphenoxy)-*N,N'*-bis(2,6-diisopropylphenyl)perylene-3,4,9,10-bis(dicarboximide) (**3**) was synthesized in useable yields. The material demonstrates good solubility and high photoluminescence in the solid state. LEC devices fabricated with **3** have shown red light emission indicating that devices utilizing PDIs are possible. We expect that improvements in device performance will be likely with continued optimization of film and device parameters. Studies to determine the effects of using an *n*-type material in an LEC with regards to doping symmetry and environmental stability are ongoing.

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