

# Journal of Materials Chemistry C

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## ARTICLE

## Utilization of phenanthroimidazole based fluorophore in light-emitting electrochemical cells

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Madayanad Suresh Subeesh,<sup>a</sup> Kanagaraj Shanmugasundaram,<sup>a</sup> Chozhidakath Damodharan Sunesh,<sup>a</sup> Yong Sun Won,<sup>b</sup> Youngson Choe\*<sup>a</sup>

A facile, small-molecular, highly soluble phenanthroimidazole derivative has been synthesized and characterized. The synthesized compound shows strong luminescence in solution and exhibit good thermal stabilities. Single crystal X-ray crystallography studies were carried out. Correlation between X-ray structures, photophysical properties and the performance in light-emitting electrochemical cells (LECs) are described. Yellowish green emission was achieved by applying the target compound in a LEC device configuration. The constructed prototype device performance was promising with a maximum brightness of 125 cd/m<sup>2</sup>. The results suggest that phenanthroimidazole derivative can also function as an active material in LEC devices.

dures, structure tunability and amenability towards purification techniques.<sup>12–14</sup> Thus, it is

### Introduction

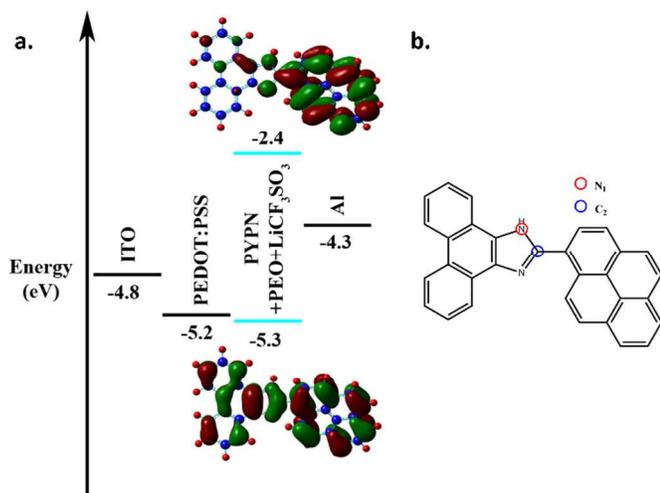
Light-emitting electrochemical cells (LECs) are considered to be the future generation of lighting sources.<sup>1</sup> When compared to any other solid state lighting devices, simple device architecture and air stable electrodes makes LECs impressive.<sup>2</sup> In addition, LECs operate under a unique electrochemical doping mechanism,<sup>1</sup> which makes it simple and cost-effective among electroluminescent devices ever reported. Furthermore, its compatibility towards various solution processing techniques proposes LEC as an excellent device for industrial scale up. The state-of-the-art devices of luminescent materials are currently confined under two major classes of luminescent materials, the conjugated polymers<sup>3</sup> and ionic transition metal complexes.<sup>4</sup> In particular, much research has been focused on cationic iridium complexes. Even though several iridium based devices have had separately achieved significant milestones like high brightness,<sup>5</sup> color purity<sup>6</sup> and long life time,<sup>7</sup> an ideal single system possessing all these qualities still remains a challenge. Moreover, rare (0.001 ppm)<sup>8</sup> and expensive nature<sup>9</sup> of iridium may increase the cost of future industrial scale up. Devices based on cheap and earthly abundant copper can be an alternative to iridium, but low color tunability of ionic copper complex keeps this class of materials less explored.<sup>10</sup> On the other hand, tedious work-up procedure for the synthesis and purification of conjugated polymers hinder further advances in polymer light emitting electrochemical cells (PLECs).<sup>11</sup> All these facts lead to the conclusion that more improved devices can only be achieved by opening up the library of emitters for LECs. Recent reports on non-ionic small molecules as an active material in LECs attracts much attention due to its wide range of synthetic proce-

dures, structure tunability and amenability towards purification techniques.<sup>12–14</sup> Thus, it is

utterly important to develop potential fluorescent small molecules which can perform its role as an emissive material in LECs. The utility of organic small molecules as a functional layer in electroluminescent devices can be well understood, considering the exceptional performance of recently reported non doped OLEDs.<sup>15–20</sup> Even though a wide variety of luminescent small molecules have been reported so far, the proper choice of reasonable emitters for LEC application still remains difficult. An ideal emitter shall have considered to possess the characteristics such as an easy solution processibility, stability towards temperature, color tunability, and enhanced charge transporting abilities. Moreover, the deeply appreciated factor will be the cost effectiveness of the material. The so far reported small molecule light emitting electrochemical cells (smLECs) were based on molecules synthesized by profound and complex reaction steps,<sup>12,13</sup> which are not ideal for future advances. We believe that further development in this area can be made possible only with a small and easily modifiable class of luminescent molecules. Considering all these aspects, the authors designate a phenanthroimidazole derivative as the luminescent material for LEC devices in this study.

Phenanthroimidazole derivatives are well known for its extraordinary photophysical property, thermal stability, and balanced charge transporting capabilities.<sup>15,16,18–20</sup> Most appealing feature of this type of luminophores are the presence of different bonding structures of two nitrogen atoms, which makes structure tuning effortless. Reports on simple and concentration independent white and red emitting imidazole derivatives<sup>21–23</sup>

pinpoint the potential of this class of compounds to replace any other reported luminophores for solid state lighting. Along with all these factors, the high yield facile synthetic procedure adds much to the versatility of these compounds in a wide variety of applications.<sup>24–28</sup>



**Figure 1** (a) Schematic representation of energy levels of materials used in LEC devices with DFT calculated electronic distribution of 2-(pyren-1-yl)-1H-phenanthro[9,10-d]imidazole (PYPN). (b) Chemical structure of target compound (PYPN).

Herein, a LEC device based on a strongly luminescent phenanthroimidazole derivative as an active material was introduced. The device structure was literally similar to the conventional non-doped PLECs.<sup>1</sup> A schematic representation of energy levels of materials used in this particular LEC device is given in figure 1. In contrast to ionic compounds based LECs, free ions are inevitable for electrochemical doping and the formation of PN junction in smLECs, which can be a limiting factor of non-ionic small molecules as emitters in LECs. However, for the smooth functioning of the former demands additional ions in the form of ionic liquids.<sup>29</sup> Hence, herein too, the active layer consists of a tricomponent blend of this organic molecule along with polyethylene oxide (ion transporting polymer) and lithium triflate (inorganic salt). The present study demonstrates a correlation of the structural, photophysical, electrochemical, and EL properties of target compound.

## Experimental part

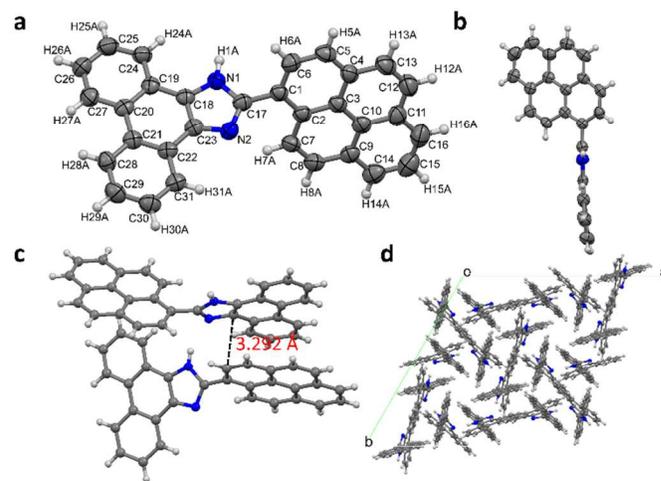
### Materials and methods

Phenanthrene-9,10-dione (Alfa Aesar), pyrene-1-carbaldehyde (TCI),  $\text{LiCF}_3\text{SO}_3$  (Aldrich), Poly ethylene oxide (PEO,  $M_w = 3 \times 10^5$  g/mol, Aldrich) and poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS, Clevis P VP AI 4083, Heraeus) were used as received. All other chemicals and solvents were used as received from commercial suppliers without further purification.

Nuclear magnetic resonance (NMR) spectra were measured using  $[\text{D}_6]\text{DMSO}$  as solvent with a Varian unity Inova 500 MHz FT-NMR spectrometer. Mass spectra were recorded on Agilent, Q-TOF 6530 MS/MS system. Absorption spectra were carried out using 8453 UV-visible Agilent spectrophotometer. Photoluminescence spectra were performed with an F-7000 FL spectrophotometer. The solution photoluminescence quantum yield measurements were carried out in

dichloromethane solutions ( $10^{-7}$  M) with diphenyl anthracene as standard ( $\Phi_F = 0.9$  in cyclohexane). X-ray single-crystal diffraction data were collected on a Bruker SMART CCD area detector diffractometer. Thermo gravimetric analyses (TGA) were performed on a Netzsh TG 209 at a heating rate of  $20^\circ\text{C min}^{-1}$ . Differential scanning calorimetric (DSC) measurements were performed on a TA Instruments Q200 KBSI. The samples were initially heated to a rate of  $10^\circ\text{C min}^{-1}$  to melt and then quenched. Glass transition temperatures ( $T_g$ ) and crystallization temperatures ( $T_c$ ) were obtained by heating the quenched sample at a heating rate of  $10^\circ\text{C min}^{-1}$ . Thin film thickness was measured using an interferometer. Voltammetric measurements were performed in a potentiostat/galvanostat (Iviumstat) voltammetric analyzer using  $10^{-3}$  M solution of  $\text{CH}_2\text{Cl}_2$  at a scan rate of  $50\text{ mVs}^{-1}$ . The electrolytic cell consists of a glassy carbon as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl as the reference electrode. The supporting electrolyte was 0.1 M tetra butyl ammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) in  $\text{CH}_2\text{Cl}_2$  and the redox potentials were measured against ferrocenium/ferrocene ( $\text{Fc}^+/\text{Fc}$ ) couple as internal standard. Density functional theory calculation was performed at the B3LYP/6-31G (d) level.

Electroluminescent devices were fabricated using indium tin oxide (ITO) patterned glass substrates. The initial cleaning of substrate was done by subsequent ultra-sonic treatment with detergent, acetone, ethanol and isopropyl alcohol. Prior to the deposition of active layer, an 80 nm layer of PEDOT:PSS was deposited and annealed at  $120^\circ\text{C}$  for 1 h under vacuum. For the deposition of active layer approximately 1.6 % (by mass) tricomponent blend solution of tetrahydrofuran and cyclohexanone in the ratio 1:0.57 were prepared and kept stirring for 12 h at  $T = 45^\circ\text{C}$ . Blend solution was prepared by mixing corresponding master solutions of PYPN (tetrahydrofuran), PEO (cyclohexanone) and lithium triflate (cyclohexanone) to obtain a weight ratio 1:0.1:0.185 (PYPN:PEO: $\text{LiCF}_3\text{SO}_3$ ). Sequentially active layer was spin coated from blend solution at 2000 rpm for 20 s and annealed at  $120^\circ\text{C}$  for 1 h under vacuum to obtain a yellowish green transparent film. Al cathodes (100 nm) were deposited on top of the active layer by thermal evaporation through a shadow mask under high vacuum. Current density and luminescence versus voltage characteristics were measured using a Keithley 2400 source meter calibrated with silicon photodiode. An avantes luminescence spectrometer was used to measure the electroluminescence spectrum and CIE coordinates.

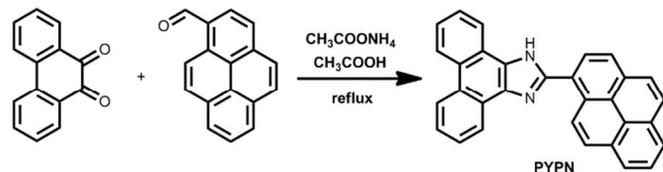


**Figure 2** (a) ORTEP diagram for PYPN atom-labeling scheme. Thermal ellipsoids are plotted at the 50 % level. (b) Twisted conformation of PYPN.

mation. (c)  $\pi$ - $\pi$  interaction between adjacent molecules. (d) Packing along c-axis.

### Synthesis and characterization

#### 2-(pyren-1-yl)-1H-phenanthro[9,10-d]imidazole (PYPN).



**Scheme 1** Synthetic route to 2-(pyren-1-yl)-1H-phenanthro[9,10-d]imidazole (PYPN).

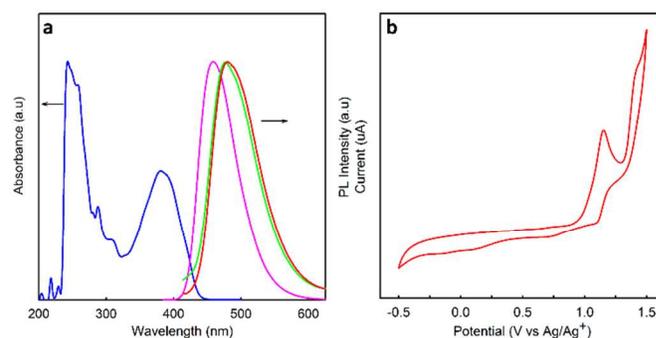
The compound was synthesized by refluxing phenanthrene-9,10-dione (1 g, 4.8 mmol), pyrene-1-carbaldehyde (1.11 g, 4.8 mmol) and ammonium acetate (4.53 g, 58.7 mmol) in glacial acetic acid for 12 h under nitrogen atmosphere. After cooling to room temperature, the separated solid was filtered off, washed with water, ether and dried to give a yellowish green solid. Purification of the obtained solid was done by double recrystallization in acetone water mixture. Resultant yellowish green needle shaped crystals were filtered, washed with cold acetone-water mixture, diethyl ether and dried under vacuum. Yield after crystallization: 1.2 g (60%).  $^1\text{H}$  NMR (300 MHz;  $[\text{D}_6]\text{DMSO}-d_6$ ;  $\text{Me}_4\text{Si}$ )  $\delta_{\text{H}}$  [ppm]: 13.8 (s, 1H), 9.57 (d,  $J = 8\text{ Hz}$ , 1H), 8.87 (d,  $J = 7.1\text{ Hz}$ , 1H), 8.66 (d,  $J = 8\text{ Hz}$ , 1H), 8.49 (d,  $J = 8\text{ Hz}$ , 1H), 8.26-8.35 (m, 4H), 8.11 (m, 4H), 7.63-7.77 (m, 5H).  $^{13}\text{C}$  NMR (50 MHz;  $[\text{D}_6]\text{DMSO}$ ) 149.86 (s), 131.81 (s), 131.39 (s), 130.83 (s), 129 (s), 128.87 (s), 128.75 (s), 127.79 (d), 127.09 (s), 126.24 (d), 125.92 (s), 125.25 (d), 124.87 (s), 124.24 (s). TOF-MS: Found: 419.15 ( $\text{M}-\text{H}^+$ ). Calcd for  $\text{C}_{31}\text{H}_{18}\text{N}_2$ : 418.15. Elemental analysis calcd (%) for  $\text{C}_{31}\text{H}_{18}\text{N}_2$ : C, 88.97; H, 4.34; N, 6.69; Found: C, 89.17; H, 4.43; N, 6.55.

### Results and discussion

A one pot Debus-Radziszewski method<sup>30</sup> was used for the synthesis of targeted molecule 2-(pyren-1-yl)-1H-phenanthro [9,10-d] imidazole (PYPN) scheme 1. The target compound exhibited solubility in most of the organic solvents, especially in THF and DMF. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of PYPN in THF. The molecular structure of PYPN was determined by X-ray structural analysis; an ORTEP drawing of PYPN is shown in Fig. 2 (a), in which the phenanthroimidazole and pyrene adopted a twisted configuration with an interplanar dihedral angle *ca.* 60°. It was observed that molecules are arranged in a face-to-face  $\pi$ - $\pi$  stacking with the phenanthroimidazole and pyrene moieties facing each other giving an interplanar distance of 3.3 Å (Fig. 2 (c)). Albeit their twisted molecular orientation, the planar fused rings and unsubstituted nitrogen ( $\text{N}_1$ ) may increase the intermolecular interactions in the solid state.

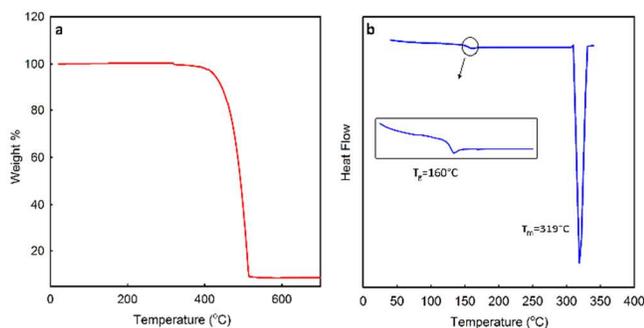
The absorption and photoluminescence (PL) spectra were measured in  $10^{-5}\text{ M}$  anhydrous THF. An intense absorption band was observed around 260 nm, which is intrinsic among phenanthroimidazole derivatives.<sup>31</sup> And a less intense broad band found at 380 nm can be designated to the delocalized  $\pi$ - $\pi^*$  transition of the phenanthroimidazole.<sup>18</sup> The solution emission maxima of PYPN is centered around 458 nm giving a reasonable Stokes shift (difference between the lowest energy band in the absorption spectrum and the highest energy band in the emission spectrum) of about 77 nm in solution (Fig. 3 (a)) and a photoluminescence quantum yield of 0.6 in solution.<sup>32</sup>

Thin film photoluminescence quantum yield for PYPN was measured to be 0.3. The optical band gap ( $E_g$ ) in solution calculated from the onset of absorption spectra was 2.84 eV. In the as-spun thin solid film, PYPN shows an emission maxima *ca.* 477 nm, which was 19 nm red shifted from its solution photoluminescence. After annealing the film at 120 °C for 1 h, emission band was further red shifted to about 3 nm from its unannealed thin film emission. As mentioned earlier, this larger red shift can be explained by their strong intermolecular interactions in the solid state.<sup>33</sup> Incorporating long branched alkyl spacers or aliphatic bulky groups to the  $\text{N}_1$  position of PYPN shall be one possible approach to eliminate this issue without sacrificing its high solubility.<sup>36,37,41</sup>



**Figure 3** (a) Absorption spectra of PYPN in solution (blue), PL in solution (pink), PL of as-spun thin film (green), PL of annealed thin film (red). (b) Cyclic voltammogram of PYPN.

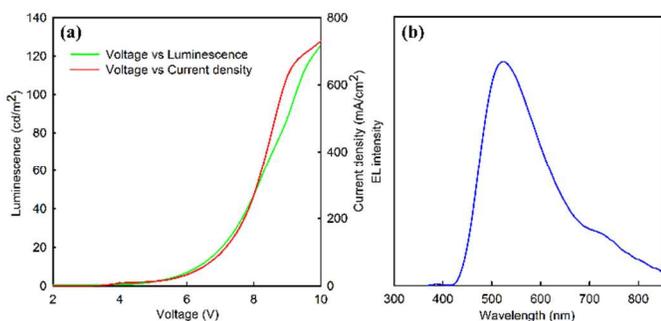
The highest occupied molecular orbital (HOMO) energy level of PYPN was determined using electrochemistry experiments. All the experiments were carried out in anhydrous dichloromethane solution, having a concentration of 0.1 M  $\text{Bu}_4\text{PF}_6$  as the electrolyte. The energy levels were estimated using ferrocene/ferrocenium ion ( $\text{Fc}/\text{Fc}^+$ ) reference redox system under a scan rate of 50 mV/s (Fig. S2). The compound under study was dissolved in an electrolyte solution to obtain a concentration of  $10^{-3}\text{ M}$ . The target compound exhibited an oxidation onset at 0.99 V versus  $\text{Ag}/\text{Ag}^+$  in dilute solution (Fig. 3). The corresponding HOMO energy level was calculated to be -5.3 eV using the formula  $E_{\text{HOMO}} = -4.32 - E_{\text{onset}}(\text{Ox})$ . The lowest occupied molecular orbital (LUMO) energy level was calculated to be -2.4 eV by adding the optical band gap ( $E_g$ ) to the calculated HOMO value. To better understand the electronic structures of target compound, a density functional theory (DFT) calculation was performed. Analogous to the previously reported similar class of compounds, PYPN shows a scattered distribution of HOMO throughout the phenanthroimidazole core and  $\text{C}_2$  substituent<sup>20</sup> (Fig. 1 (a)). On the contrary LUMO exhibit a well segregated geometry over pyrene moiety. This partial segregation of HOMO and LUMO may be effective in decreasing dipolar quenching of fluorescence in the solid state.<sup>34</sup>



**Figure 4.** (a) TGA and (b) DSC thermograms of PYPN

Thermal properties of PYPN were investigated by TGA and DSC under an inert nitrogen atmosphere. As expected, PYPN exhibited a high decomposition temperature ( $T_d$ ) which is defined as the temperature at which the material shows a 5% weight loss, were measured to be 426 °C (Fig. 4). It is noteworthy that direct incorporation of bulky groups like pyrene to the phenanthroimidazole core can make no difference in the thermal stability of phenanthroimidazole derivatives. Melting point ( $T_m$ ) of PYPN was observed upon heating up to 319 °C. The glass transition temperature ( $T_g$ ) was found to be 160 °C on a second heating process but does not show any crystallization temperatures ( $T_c$ ) up to its melting point.

To evaluate the electroluminescent properties of PYPN, LEC devices were fabricated. The spin casted solution of active layer was a tri component blend of PYPN, polyethylene oxide and lithium triflate in the weight ratio 1:0.1:0.185 (PYPN:PEO:LiCF<sub>3</sub>SO<sub>3</sub>). The total weight percentage of the solution was approximately 1.6 % in a mixture of THF and cyclohexanone (1:0.57). The constructed device structure was ITO/PEDOT:PSS (80 nm)/Active layer (90 nm)/Al (100 nm). All the spin coating process as well as device characterizations were carried out in the presence of ambient air and moisture. The electroluminescent spectrum of PYPN shows a yellowish green emission *ca.* 521 nm (Fig. 2 (b)) with CIE coordinates (0.38, 0.49). As expected from single crystal study as well as thin film photoluminescence measurements, EL spectra exhibited a red shift compared to PL spectra in solution. But the red shift was even stronger than what observed in its thin film PL (as-spun film and annealed film). At this point we turned our attention to unveil the real cause of this red shifted emission on the bias. By analyzing a series of thin film PL measurements of PYPN (detailed thin film PL experiments were explained in ESI †) including and excluding lithium triflate suggest that, spectral shifts have nothing to do with the mode of excitation or any other mechanism related to LEC, but merely dependent on the presence of lithium triflate in thin film. It was found that heat treated films incorporating lithium triflate exhibits a PL spectra more similar to its EL emission, which may be due to replacement of neutral solvent molecules by ions in the solid state. Bathochromic emission shifts for cationic metal complexes with and without ionic liquids were previously reported by several groups.<sup>35–37</sup> But in those instances, intrinsic ionic complexes were used, and hence a direct comparison would be meaningless. Our ongoing work is targeted at unveil the mechanism behind this red shift occurred in here and is beyond the scope of this work.



**Figure 5** (a) Current density (red), luminescence (green) versus voltage for ITO/PEDOT:PSS/PYPN:PEO:LiCF<sub>3</sub>SO<sub>3</sub>/Al (b) electroluminescence spectrum of fabricated device.

The current density and luminescence versus voltage characteristics (Fig. 2 (a)) illustrates a typical LEC behavior with a delayed turn on voltage at 4.3 V ( $V_{on}$ , defined as the voltage required to give a luminescence of 1 cd/m<sup>2</sup>), due to the initial difficulty of charge injection and slow movement of ions in the active layer followed by a swift rise at 6 V. From the J-V curve it is well understood that PYPN has a good charge transporting nature. But low brightness at high current density again confirms that PYPN have a strong tendency to aggregate in the solid state. However, by systematic tuning of structure, the inherent charge transporting quality of the material can be well utilized for developing doped as well as non-doped improved LEC devices in the very near future.<sup>38</sup>

## Conclusions

In summary, a highly soluble, thermally stable and strongly luminescent phenanthroimidazole derivative was developed through a facile synthetic procedure. Single layer yellowish green LEC devices were fabricated using phenanthroimidazole as an active material in the emissive layer. Even in the presence of ambient air and moisture, the constructed device exhibited a peak brightness of about 125 cd/m<sup>2</sup> at 9.9 V. This is an important achievement because, reports on facile fluorescent small molecules capable of functioning as an active material in LECs opens up the possibilities to positively change the concept about emitters that can be used for LEC devices.<sup>10,14</sup> Despite the strong red shift, a critical amount of devoted research is needed for developing improved LEC devices based on this class of compounds.

## Acknowledgements

This research has been supported by Basic Science Research program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-2013R1A1A4A03009795) and Brain Korea 21 Plus project.

## Notes and references

<sup>a</sup> Department of Polymer Science and Chemical Engineering, Pusan National University, Busan 609-735, South Korea.

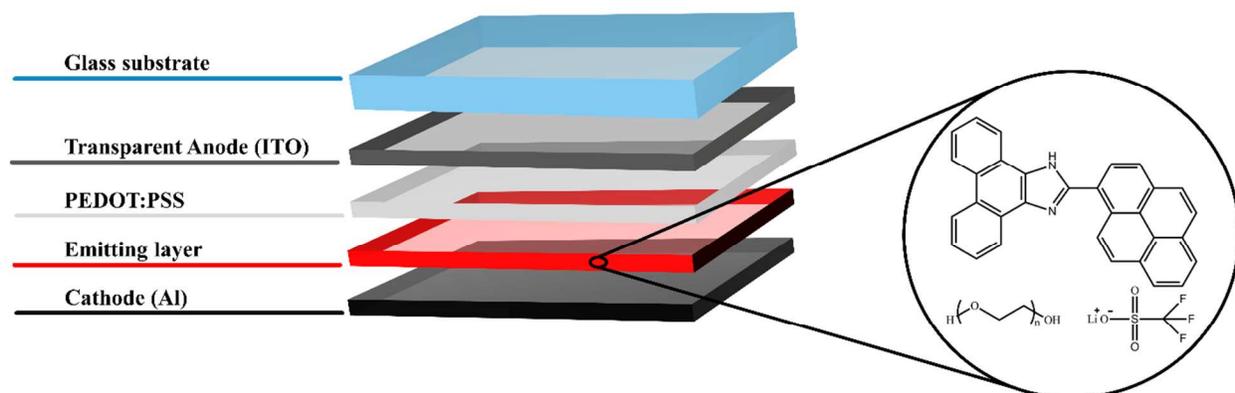
<sup>b</sup> Department of Chemical Engineering, Pukyong National University, Busan, South Korea.

† Electronic supplementary information (ESI) available: Fluorescence spectra and crystal structural data CCDC reference number 1041210.

- Q. Pei, G. Yu, C. Zhang, Y. Yang and A. J. Heeger, *Science*, 1995, **269**, 1086–1088.
- S. B. Meier, D. Tordera, A. Pertegás, C. Roldán-Carmona, E. Ortí and H. J. Bolink, *Mater. Today*, 2014, **17**, 217–223.
- Q. Pei, Yang, G. Yu, C. Zhang and A. J. Heeger, *J. Am. Chem. Soc.*, 1996, **118**, 3922–3929.
- J. Slinker, D. Bernards, P. L. Houston, H. D. Abruna, S. Bernhard and G. G. Malliaras, *Chem. Commun.*, 2003, 2392–2399.

5. M. K. Nazeeruddin, R. T. Wegh, Z. Zhou, C. Klein, Q. Wang, F. De Angelis, S. Fantacci and M. Grätzel, *Inorg. Chem.*, 2006, **45**, 9245–9250.
6. H.-C. Su, H.-F. Chen, F.-C. Fang, C.-C. Liu, C.-C. Wu, K.-T. Wong, Y.-H. Liu and S.-M. Peng, *J. Am. Chem. Soc.*, 2008, **130**, 3413–3419.
7. G. E. Schneider, A. Pertegas, E. C. Constable, C. E. Housecroft, N. Hostettler, C. D. Morris, J. A. Zampese, H. J. Bolink, J. M. Junquera-Hernandez, E. Orti and M. Sessolo, *J. Mater. Chem. C*, 2014, **2**, 7047–7055.
8. N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Butterworth-Heinemann, Oxford 2<sup>nd</sup> edn., 1997.
9. <http://www.metalprices.com/FreeSite/metals/ir/ir.asp>
10. R. D. Costa, D. Tordera, E. Orti, H. J. Bolink, J. Schonle, S. Graber, C. E. Housecroft, E. C. Constable and J. A. Zampese, *J. Mater. Chem.*, 2011, **21**, 16108–16118.
11. D. Xiang, Q. Shen, S. Zhang and X. Jiang, *J. Appl. Polym. Sci.*, 2003, **88**, 1350–1356.
12. Z. B. Hill, D. B. Rodovsky, J. M. Leger and G. P. Bartholomew, *Chem. Commun.*, 2008, 6594–6596.
13. S. Tang, W.-Y. Tan, X.-H. Zhu and L. Edman, *Chem. Commun.*, 2013, **49**, 4926–4928.
14. S. Kervyn, O. Fenwick, F. Di Stasio, Y. S. Shin, J. Wouters, G. Accorsi, S. Osella, D. Beljonne, F. Cacialli and D. Bonifazi, *Chem. A Eur. J.*, 2013, **19**, 7771–7779.
15. Y. Zhang, S.-L. Lai, Q.-X. Tong, M.-F. Lo, T.-W. Ng, M.-Y. Chan, Z.-C. Wen, J. He, K.-S. Jeff, X.-L. Tang, W.-M. Liu, C.-C. Ko, P.-F. Wang and C.-S. Lee, *Chem. Mater.*, 2012, **24**, 61–70.
16. Y. Yuan, J.-X. Chen, F. Lu, Q.-X. Tong, Q.-D. Yang, H.-W. Mo, T.-W. Ng, F.-L. Wong, Z.-Q. Guo, J. Ye, Z. Chen, X.-H. Zhang and C.-S. Lee, *Chem. Mater.*, 2013, **25**, 4957–4965.
17. J. Huang, J.-H. Su, X. Li, M.-K. Lam, K.-M. Fung, H.-H. Fan, K.-W. Cheah, C. H. Chen and H. Tian, *J. Mater. Chem.*, 2011, **21**, 2957–2964.
18. Y. Zhang, S.-L. Lai, Q.-X. Tong, M.-Y. Chan, T.-W. Ng, Z.-C. Wen, G.-Q. Zhang, S.-T. Lee, H.-L. Kwong and C.-S. Lee, *J. Mater. Chem.*, 2011, **21**, 8206–8214.
19. Z. Wang, P. Lu, S. Chen, Z. Gao, F. Shen, W. Zhang, Y. Xu, H. S. Kwok and Y. Ma, *J. Mater. Chem.*, 2011, **21**, 5451–5456.
20. S. Zhuang, R. Shanguan, H. Huang, G. Tu, L. Wang and X. Zhu, *Dye. Pigment.*, 2014, **101**, 93–102.
21. S. Park, J. E. Kwon, S. H. Kim, J. Seo, K. Chung, S.-Y. Park, D.-J. Jang, B. M. Medina, J. Gierschner and S. Y. Park, *J. Am. Chem. Soc.*, 2009, **131**, 14043–14049.
22. W. Li, W. Lin, J. Wang and X. Guan, *Org. Lett.*, 2013, **15**, 1768–1771.
23. K. Benelhadj, J. Massue, P. Retailleau, G. Ulrich and R. Ziessel, *Org. Lett.*, 2013, **15**, 2918–2921.
24. W. Lee, Y. Yang, N. Cho, J. Ko and J.-I. Hong, *Tetrahedron*, 2012, **68**, 5590–5598.
25. Y. Zhang, D. Yu and G. Feng, *RSC Adv.*, 2014, **4**, 14752–14757.
26. W. Lin, L. Long, L. Yuan, Z. Cao and J. Feng, *Anal. Chim. Acta*, 2009, **634**, 262–266.
27. S. Liao, Z. Zhang, Q. Wu, X. Wang and W. Mei, *Bioorg. Med. Chem.*, 2014, **22**, 6503–6508.
28. J. G. Lombardino and E. H. Wiseman, *J. Med. Chem.*, 1974, **17**, 1182–1188.
29. A. Pertegás, D. Tordera, J. J. Serrano-Pérez, E. Orti and H. J. Bolink, *J. Am. Chem. Soc.*, 2013, **135**, 18008–18011.
30. C. Yumusak, M. Abbas and N. S. Sariciftci, *J. Lumin.*, 2013, **134**, 107–112.
31. K. Skonieczny, A. I. Ciuciu, E. M. Nichols, V. Hugues, M. Blanchard-Desce, L. Flamigni and D. T. Gryko, *J. Mater. Chem.*, 2012, **22**, 20649–20664.
32. Y.-N. Yan, W. Pan and H.-C. Song, *Dye. Pigment.*, 2010, **86**, 249–258.
33. D. F. Eaton, *Pure Appl. Chem.*, 1988, **60**, 1107.
34. H. Lee, Y. I. L. Park, B. Kim, J.-H. Lee and J. Park, *Opt. Mater. Express*, 2014, **4**, 924–933.
35. K. R. Justin Thomas, M. Velusamy, J. T. Lin, C.-H. Chuen and Y.-T. Tao, *Chem. Mater.*, 2005, **17**, 1860–1866.
36. C. Rothe, C.-J. Chiang, V. Jankus, K. Abdullah, X. Zeng, R. Jitchati, A. S. Batsanov, M. R. Bryce and A. P. Monkman, *Adv. Funct. Mater.*, 2009, **19**, 2038–2044.
37. C.-W. Chang, H.-Y. Tsai and K.-Y. Chen, *Materials.*, 2014, **7**, 5488–5506.
38. Y.-M. Wang, F. Teng, Y.-B. Hou, Z. Xu, Y.-S. Wang and W.-F. Fu, *Appl. Phys. Lett.*, 2005, **87**, 233512-3.
39. L. He, L. Duan, J. Qiao, R. Wang, P. Wei, L. Wang and Y. Qiu, *Adv. Funct. Mater.*, 2008, **18**, 2123–2131.
40. H. J. Bolink, L. Cappelli, S. Cheylan, E. Coronado, R. D. Costa, N. Lardies, M. K. Nazeeruddin and E. Orti, *J. Mater. Chem.*, 2007, **17**, 5032–5041.
41. Y.-N. Yan, D.-Y. Lin, W.-L. Pan, X.-L. Li, Y.-Q. Wan, Y.-L. Mai and H.-C. Song, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, 2009, **74**, 233–242.

# Graphical Abstract



Phenanthroimidazole derivative as a facile emitter in light emitting electrochemical cells (LECs).