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Thia- and selena-diazole containing polymers for near-infrared light-emitting diodes†

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We report the optical characterization of near-infrared (NIR) emitters for polymer light-emitting diode (PLEDs) applications based on the copolymerization of a phthalimide-thiophene host polymer with a low-gap emitter containing the bisthienyl(benzotriazolothiadiazole) unit. We investigate different loadings of the low-gap emitter (in the range 1–3% by weight) and the substitution of a sulphur atom with a selenium atom to further extend the emission in the NIR up to 1000 nm. PLEDs based on copolymers with 1% loading give the best efficiency (0.09%) and show an almost pure NIR EL (95% in the NIR) peaking at 895 nm.

Over the last few years near-infrared (NIR) organic light-emitting diodes (OLEDs) have generated considerable interest for their potential application in the medical, telecommunication and defence fields.[1,2] Interestingly, the peculiarity of light emission in the NIR region (700–2500 nm) can be combined with the major advantages of OLEDs such as the solution processing, the low-cost fabrication and the possibility of using flexible, conformable or even stretchable substrates.[3,4] Given the importance of NIR optoelectronics, different organic compounds have been explored as red and NIR emitters, such as small molecules,[5–7] metal–organic complexes[8,9] and conjugated polymers,[10,11] whilst inorganic nanoparticles[12] and materials "improperly" but commonly indicated as perovskites[13] have been used as NIR emitters in solution processed LEDs with organic charge transport layers. Furthermore, different strategies have been employed to reduce emission quenching and aggregation effects of low-gap emitters and/or promote energy transfer to NIR moieties, *e.g.* by blending the NIR emitters with wider gap polymers,[14,15] by diluting them in a matrix by co-evaporation,[16,17] by exploiting cyclic or linear molecular π-systems with appropriate ligands to inhibit aggregation[18] or *via* charge-transfer excitons at the organic semiconductors heterojunction with a proper gap between the energy levels for the emission to fall in the NIR.[19] Among these strategies, inclusion of donor–acceptor–donor (DAD) low-gap units in wider gap host polymers *via* copolymerization has been demonstrated as a valid approach.[20,21] In particular, benzothiadiazole and both its homo- and hetero-annulated derivatives have been extensively investigated[22–24] in conjunction with different host polymers for efficient NIR emission.[21,25–27] A promising route to extend further the emission in the near-infrared region is the replacement of the sulphur atom in the benzothiadiazole unit with selenium. In fact, benzoselenodiazole units have been reported to reduce the polymer energy gap and lead to a red-shift of the absorption and emission spectra compared to the sulphur-containing unit.[28–33] The efficiency of NIR emitters is generally lower than that of visible emitters, owing to more efficient non-radiative quenching of the excited states which follows from the smaller number of vibrational quanta needed to dump the energy of excited states in vibrational deactivation processes. Polymers for light-emitting diodes (PLEDs) with emission beyond 850 nm have been reported with external quantum efficiencies (EQEs) of only 0.02–0.05%,[26,34] although recently we reported an EQE of 0.27% for a NIR PLED emitting at 885 nm.[25] In this and earlier reports we found that using ambipolar host polymers such as phthalimide-thiophene[25] and F8BT[14,18,35] can yield high EQEs for NIR emission. Following from the success of using phthalimide-thiophene host polymers, in this study we look at modifications to the host polymer structure and the NIR emitting moiety to shift the emission further into the NIR whilst maintaining high EQEs.

We present NIR emitters (see Fig. 1a) based on a phthalimide-thiophene host polymer (**P1**) copolymerised with a low-gap DAD moiety based on the bisthienyl(benzotriazolothiadiazole) unit at different loadings, 1% and 3% (**P2** and **P3**, respectively) calculated with respect to the host polymer portion for the initial ratio of reactants. To lower the energy gap, we also exchanged a sulphur

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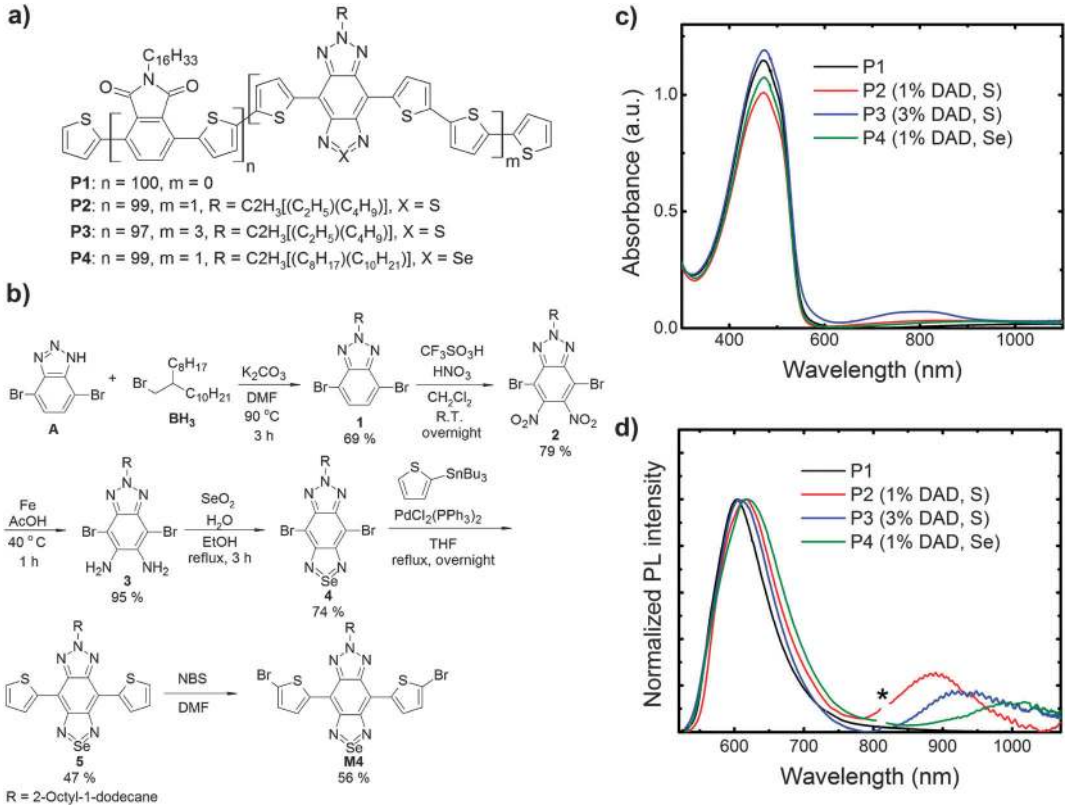

Fig. 1 (a) Chemical structure of the wide-gap host polymer (**P1**) and the copolymers (**P2**, **P3** and **P4**). **P2** and **P3** differ in the DAD loading (1% and 3% respectively). The DAD unit in **P2** and **P4** differs in the substitution of a sulphur atom for a selenium atom to lower the energy gap. (b) Synthesis of monomer **M4** (**P4** precursor). (c) Absorption spectra of the polymers thin films (100 nm) over fused silica glass. We report in the legend the percentage of DAD moieties and the type of atom (S or Se) in the DAD segment. (d) PL of polymers thin films, the "*" indicates the monochromator 2nd-order transmission of the excitation wavelength (λ_{ex} = 405 nm).

atom in the thiadiazole for a selenium atom (**P4**). Note that the branched alkyl side chains of the DAD unit for the **P4** copolymer is longer than those of the **P2** and **P3** copolymers. It should also be noted that the phthalimide-thiophene host polymer used in this study has a straight alkyl chain ($C_{16}H_{33}$) as the solubilizing group whereas a phthalimide-thiophene host with branched side-chains ($CH(C_8H_{17})_2$) was used for NIR OLEDs in our previous study.[25] In the past study we showed that a straight side-chain phthalimide-thiophene copolymers showed higher and more balanced ambipolar field-effect mobilities, increased order and higher photoluminescence quantum efficiencies than its branched side-chain analogue, but in this paper we report the use of these straight-chain phthalimide-thiophene copolymers as host materials for OLEDs for the first time. In particular, we found a relatively high EQE (0.09%) for **P2** with an electroluminescence (EL) at 895 nm characterized by a high spectral purity (>95% in the NIR). We also show that the substitution of the sulphur atom in the thiadiazole unit of the DAD with a selenium atom (**P4**) red-shifts the emission to a band peaking at 990 nm, also yielding one of the most efficient PLEDs reported to date at such a long wavelength.[26]

For polymer **P4**, the synthesis of the bisthienyl(benzotriazolo-selenadiazole) (**M4**) emitter can be seen in Fig. 1b. Initially, 4,7-dibromo-1*H*-benzo[*d*][1,2,3]triazole was alkylated with 2-octyl-1-bromododecane using K_2CO_3 in DMF yielding **1** in 69%. Next, an improved nitration using triflic acid and fuming nitric acid in DCM resulted in the formation of **2** (79%),[36] which upon reduction using iron in acetic acid gave **3** in 95%. Ring closing with SeO_2 yielded **4** in 74%. Stille coupling of **4** and 2-tributylstannylthiopene resulted in **5** (47%), which was then brominated to yield **M4** (56%).

Following our previous work, the synthesis of the copolymers (**P1–P4**) were carried out *via* Stille polymerization and worked up in a similar manner (see ESI†).[25] Polymers **P1** and **P2** had number average molecular weights of 8.1 and 9.5 kg mol^{-1}, which are similar to our previous results for these type of polymers.[25] Polymers **P3** and **P4** had slightly higher number average molecular weights of 15.1 and 12.1 kg mol^{-1}. All polymers were thermally stable with 1% weight loss occurring at temperatures >300 °C (under N_2). For this study square-wave voltammetry was used to determine the HOMO/LUMO levels of the polymers. **P1** has a HOMO of −6.05 eV and a LUMO of −3.45 eV (Fig. S1, ESI†). These values are very similar to what we reported previously for the same polymer with either a different end-capping unit or no end-capping.[25] Due to the small loadings of the NIR-emitting segments, square-wave voltammetry of polymers **P3–P4** showed no signal from the low gap segments as we saw previously for polymers with similar loadings.[25] Likewise, based on previous studies of

similarly structured compounds in the literature, we estimated the HOMO/LUMO levels of the NIR-emitting segments to be $\sim -5.1/-4.0 \pm 0.1$ eV for segment **M3**[23] and a slightly narrower HOMO/LUMO gap for segment **M4**. Since the HOMO/LUMO levels of these segments lie within the HOMO/LUMO levels of the host polymer **P1**, this ought to allow for energy transfer to the NIR-emitting segments.[37–39]

We report the absorption spectra of the polymer films in Fig. 1c, in which we note that the host polymer (**P1**) absorption band is centred at 470 nm. As expected, all the copolymers display the host polymer absorption peak. In addition, **P3** (the copolymer with 3% b.w. content of DAD) clearly shows a band at 790 nm that is not visible in the host polymer, and that we thus assign to the DAD moiety. The DAD absorption is not clearly distinguishable in the other copolymers (**P2** and **P4**) due to the lower content (1% b.w.) of such a moiety. However the solution spectra show the absorption feature of the DAD unit peaking at 756 nm, 767 nm and 859 nm for **P2**, **P3**, and **P4** respectively (see Fig. S2, ESI†). We report the PL spectra of the polymers in Fig. 1d. Emission from the host polymer (**P1**) features a band at 605 nm, and as intended, the copolymers also show an emission band in the NIR region, peaking at 895 nm (**P2**), 927 nm (**P3**) and 1000 nm (**P4**), respectively. We attribute such bands to states delocalised over the DAD segments. Emission from the host polymer is still visible in the PL spectra of the copolymers, thereby suggesting that energy transfer (ET) from the host segment to the DAD is not complete. This is consistent with the fact that the spectral overlap between the host polymer emission and the DAD unit absorption is not optimal as the emission of **P1** is not centred on the DAD unit absorption (this is detailed by the shaded area in Fig. 2a). We also expect a red-shift of the lower energy band when increasing the DAD loading[21] as a result of aggregation. Similarly, we expect an even more significant red-shift when substituting S with Se, owing to a lower LUMO energy level,[40,41] as also suggested from the solution spectra in Fig. S2 (ESI†). Whereas this is appealing for the purpose of achieving an as pure as possible NIR emission, any red-shift should also lead to a less efficient energy transfer from **P1**, which is undesired. Both expectations (red-shift and less-efficiency ET, leading to lower NIR intensity) are confirmed by the trends observed in Fig. 1d. In fact, we observe that the percentage of the PL in the NIR (*i.e.* taken for wavelengths >700 nm) are 31% (**P2**), 24% (**P3**) and 21% (**P4**), respectively. Upon increasing the DAD loading from 1% (**P2**) to 3% (**P3**), we notice a red-shift of the DAD unit PL emission from 895 nm (**P2**) to 927 nm (**P3**). We attribute such a red-shift to aggregation of the DAD moieties.[21] The exchange of sulphur with selenium in the benzothiadiazole also shifts the DAD unit emission further from 895 nm (**P2**) to 1000 nm (**P4**). Indeed, the introduction of benzoselenadiazole moieties is thus confirmed as a successful approach to lower the polymer energy gap and enable emission up to 1000 nm.

We also found the films PLQE efficiency (in the 500–1100 nm range) to drop from 14.8% for the host polymer **P1**, to 1.4% for **P2**, 1.0% for **P4**, and below our 1% sensitivity limit for **P3**. As mentioned, such a reduction is entirely expected as a result of both the reduction of the energy gap, and because of quenching/aggregation (*e.g.* in the comparison **P2** *vs.* **P3**). To investigate further the energy transfer between the host polymer and the DAD unit, we measured the PL lifetime decays of the host polymer emission (at 610 nm) for all the samples, and we report the results in Fig. 2b. The lifetimes of the host polymer **P1** can be fitted with a mono-exponential that returns a 1.65 ns time constant. The copolymers show a drop in the lifetime to 0.50 ns for **P2** and to 0.32 ns for **P4** whereas the lifetime of **P3** is below the detection limit of the apparatus.[42] We note that such reduction in the lifetime follows the PL quenching of the host polymer by the presence of the DAD unit. The quenching is stronger when using Se instead of S and when increasing the concentration of the DAD unit.

We also incorporated the copolymers into PLEDs with ITO/PEDOT:PSS anodes and Ca/Al cathodes. We report the EL spectra of the devices above in Fig. 3a. Whereas the host polymer shows essentially a single band (albeit with a main peak at 560 nm and a shoulder at 605 nm), the EL from the copolymers is predominantly in the NIR and peaking at 895 nm for **P2**, 939 nm for **P3** and ~990 nm for **P4**. Although relatively noisy, it is possible to note that the emission of **P4** shows a shoulder at 807 nm. The percentage of NIR (>700 nm) EL is 95% (**P2**), 87% (**P3**) and 88% (**P4**), respectively. Even though the host polymer emission is also present to some extent in the EL

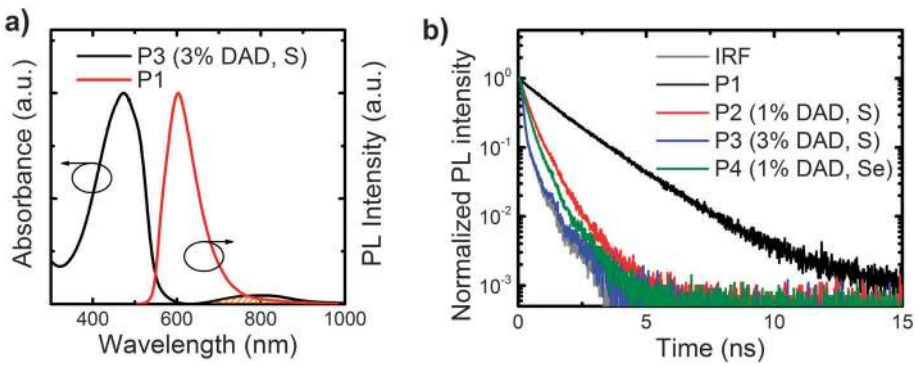

Fig. 2 (a) Normalized absorption spectrum of **P3** superimposed on the normalized emission spectrum of **P1**. The overlap between the absorption of the DAD unit and the **P1** emission is highlighted in orange. (b) PL time decay for thin films (100 nm thick on fused silica glass) of polymers **P1**, **P2**, **P3** and **P4** taken at 610 nm, following excitation at 371 nm. The instrument response function (IRF) is also reported.

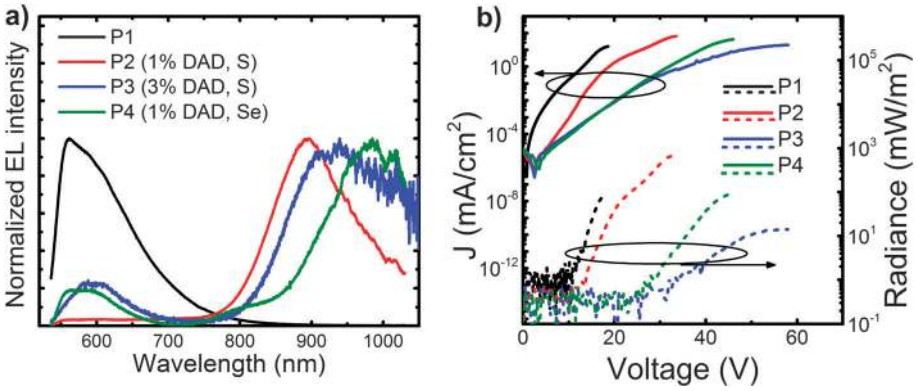

Fig. 3 (a) EL of the polymers taken at 20 V (**P1**), 33 V (**P2**), 60 V (**P3**) and 42 V (**P4**). (b) PLEDs characteristics: current density and radiance *versus* voltage. The active layer thickness is ~100 nm and the device area is 3.5 mm^2.

of the copolymers, it is largely suppressed in EL compared to the PL (and in fact nearly completely suppressed in **P2** devices). Such suppression (compared to the PL) is due to the energy-selective injection and trapping and transport of charges *via* the NIR moieties, and subsequent formation of excitons at such sites (which effectively act as traps). Residual visible EL from **P3** is thus easily reconciled by taking into account the relatively high voltage needed for such a spectrum (60 V) that would also enable some degree of charge injection and transport *via* the host. Additionally, we note that spectra in Fig. 3a are normalised, thereby amplifying the visible spectral region for those devices that are less efficient in the NIR (as suggested by the higher noise levels of **P3** and **P4** spectra compared to that of **P2**).

Finally, we report a summary of the PLEDs characteristics in Table 1, and the current–radiance–voltage characteristics in Fig. 3b. We find that the best results are obtained for the devices incorporating the low-content S-based DAD units (1%, **P2**), for which we achieve a maximum EQE of 0.091%, an irradiance of 291 mW m^{-2} (measured at 20 mA cm^{-2}), and most importantly, with nearly pure NIR emission peaking at 895 nm (95% > 700 nm). These results are among the best reported in the literature for a single active layer NIR PLED at such a long wavelength.[14,18,21,25,26] Regrettably, although perhaps not surprisingly, at 3% DAD loading the external quantum efficiency decreases significantly (from 0.09 to 0.006%), whereas the turn-on voltage (V_{on}) increases from 14.3 V for **P2** (1% DAD) to 28.1 V for **P3** (3% DAD). The increased driving voltage is easily attributed to an increased number of traps, related to the higher concentration of DAD units, which have a lower energy gap compared to **P1**. In addition we attribute the EQE reduction to the expected aggregation of the DAD units, which is also corroborated further by the previously-discussed PL red-shifts. A similar trend has also been reported by some of us for other low-gap polymers copolymerized with a wide-gap host.[21,35] Interestingly by comparing **P2** and **P4**, we are also able to get an insight into the influence of the exchange of a sulphur atom for selenium as a strategy to achieve NIR emission at longer wavelengths. We notice again that such a substitution leads to a decreased EQE and an increased V_{on}. However we point out that despite a disappointing V_{on}, not only is Se substitution a better approach for increasing the wavelength of the emission than increasing DAD loading, but it also gives one of the most efficient devices at ~1 μm reported to date for a polymer.

We can also compare **P2** to our previously reported polymer, where the only difference is that in the previous study a branched alkyl chain ($-CH(C_8H_{17})_2$) was used on the host polymer where as in this study we used the straight alkyl chain ($C_{16}H_{33}$).[25] We can see that in this study, NIR PLEDs constructed from **P2** suffer from slightly higher turn-on voltages, and a factor of 3 lower EQE (0.09% *vs.* 0.27%). Thus, in comparing these two host polymers, it is surprising that the increased order, luminescence and higher (and more balanced) mobility provided by the straight alkyl chain ($C_{16}H_{33}$) on the host polymer, as characterized previously,[25] did not result in the best host polymer for NIR PLEDs. Interestingly, the emission for the PLED based on **P2** is at 895 nm, which is red-shifted 10 nm compared to the previous study using the branched alkyl chain (885 nm). This supports the idea that lower order in the previous system likely prevented some aggregation of the NIR-emitting segments, resulting in higher performance. Even though the lower and unbalanced mobilities of the branched

Table 1 Summary of PLEDs performance

Polymer	Max EQE (%)	V_{on}[a] (V)	Radiance[b] (mW m^{-2})	NIR PL peak (nm)	% PL in NIR[c]	NIR EL peak (nm)	% EL in NIR[c]
P1	0.037 ± 0.008	9.0 ± 0.8	98 ± 13	—	—	—	—
P2	0.091 ± 0.004	14.3 ± 2.9	291 ± 9	890	31	895	95
P3	0.006 ± 0.002	28.1 ± 1.1	16 ± 2	927	24	939	87
P4	0.018 ± 0.004	23.5 ± 1.5	58 ± 10	1000	21	990	88

[a] Intercept of the *I–V* curve with the *x*-axis in a semi-log plot. [b] Measured at 20 mA cm^{-2}. [c] Defined as $\lambda > 700$ nm.

alkyl side-chains would have suggested higher resistance in the devices, we observe no significant differences in the operating voltages of devices when compared to the devices using linear side-chain host polymers.[25] This suggests that charge trapping on the low gap DAD segments is the dominant source of resistance in these devices.

Conclusions

In summary, we have characterised the NIR emission of low-gap DAD units copolymerized with a wider gap phthalimide-thiophene polymer. PLEDs based on copolymers with 1% DAD loading give the best efficiency (~0.09%) and EL peaking at 895 nm. We show that the copolymerization is a successful strategy to obtain almost pure NIR EL (up to 95% of the overall emission) for benzothiadiazole-based polymers. By varying the loading of the DAD moieties it is possible to shift the emission further into the NIR however at a cost of lowered PLED efficiency because of increased aggregation. As an alternative and effective approach to shift the emission into the NIR (up to 1000 nm) we report the use of Se containing materials, that produce a lower impact on PLEDs EQE and driving voltage when compared to S-based copolymers with a higher DAD loading. We have also demonstrated that in using the phthalimide-thiophene copolymer as a host polymer for NIR PLEDs, the more disordered system using the branched alkyl chain ($CH(C_8H_{17})$ *vs.* $C_{16}H_{33}$) results in better performing NIR PLEDs. In addition, we consider that there should be significant margins of improvements for the spectral purity by further engineering the chemical design of these copolymers so as to provide lower-energy-gap host units, and thus ensure better spectral overlap, and more efficient energy transfer to the NIR moieties.

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42 Please note that the decays reported in Fig. 2b have not been deconvolved to remove the instrumental response, therefore do not look mono-exponential, but we have used an algorithm taking into account such a response to fit the data with a mono-exponential, which returns fits with a $\chi^2 < 1.3$.