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# PAPER

# Colour tuning of blue electroluminescence using bipolar carbazole–oxadiazole molecules in single-active-layer organic light emitting devices (OLEDs)†

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A synthetically versatile strategy has been employed for luminescence colour tuning in a new series of bipolar carbazole–2,5-diaryl-1,3,4-oxadiazole hybrid molecules 1–7. Their syntheses, solution absorption and emission properties and cyclic voltammetric data are reported. Calculations using DFT (density functional theory) establish that they possess molecular orbitals which favour bipolar charge-transport. Single-active-layer organic light emitting devices (OLEDs) have been fabricated by thermal evaporation using the bipolar compounds as the emitters in the architecture ITO:PEDOT-PSS:X:Ca/AI (X = 1-7). The structure–property relationships within the series of compounds are assessed with emphasis on the OLED performance and emission colour. The HOMO–LUMO gap has been varied by systematic modifications of the molecular subunits of 1–7, allowing the colour of the electroluminescence to be tuned from deep blue (CIE x, y 0.157, 0.079) through to green (CIE x, y 0.151, 0.096). These materials are very attractive for further development due to the combination of good processability of the molecules, their bipolar structure, colour tunability and efficient performance of OLEDs using a simple device architecture.

# Introduction

Organic light emitting devices (OLEDs) are attracting great attention within academia and industry due to their emerging applications in full-colour flat panel displays<sup>1-3</sup> and solid-state lighting technologies.<sup>4,5</sup> Much work with phosphorescent and fluorescent OLEDs has concerned multilaver structures which can afford very bright and efficient devices by using an emitter layer in combination with additional hole-transport and electron-transport layers. However, there are limitations in the practical applicability of multilayer devices as they require tedious sequential layer-by-layer fabrication procedures. Exciplex formation at the interfaces of the stacked organic layers can reduce operating lifetimes and result in broad red-shifted emission.6a,b This has led to the search for small molecules in which the HOMO and LUMO levels can be adjusted for efficient injection and transport of both holes and electrons (i.e. bipolar molecules).<sup>6c,d</sup> These can serve as emitters in single-active-layer

OLEDs that do not need additional charge injection layers. Moreover, they do not require doping into host molecules – a strategy which presents problems of dopant–host phase separation. The devices with bipolar fluorophores are, therefore, easier to fabricate and manufacturing costs are reduced.<sup>7–15</sup> Molecules with comparable hole- and electron-transporting abilities are also termed ambipolar.<sup>9,15</sup>

Carbazole (Cz) is a popular electron donor component for optoelectronic materials: it is easy to functionalise, thermally very stable and has good hole-transporting ability.<sup>16,17</sup> On the other hand, oxadiazole (OXD) derivatives – more specifically 2,5-diaryl-1,3,4-oxadiazoles – are widely used as versatile electron-transporting materials.<sup>18-20</sup>

The aim of the present work is to study the series of fluorescent Cz–OXD donor–acceptor dyad molecules 1–7 in which the bipolar characteristics and HOMO–LUMO levels are systematically varied by chemical modification and to exploit them as emitters in OLEDs. We use a simple device architecture comprising a single-active-layer, without additional layers for charge injection or transport. Compound 1 has been reported in a recent communication.<sup>21</sup> The Cz–OXD dyads 1–7 are structurally different from those reported by Thomas *et al.*<sup>22</sup> and Guan *et al.*,<sup>23</sup> and the Cz–OXD–Cz triad systems studied by Ma *et al.*<sup>24,25</sup> Furthermore, these authors<sup>22–25</sup> did not report systematic variations in order to probe structure–property relationships.

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# **Results and discussion**

#### Molecular design, synthesis and characterisation

Molecules 1-7 (Chart 1) each possess a donor carbazole and an acceptor diaryloxadiazole unit. 9,9-Dihexylfluorene was chosen as the spacer component in 1-6 as fluorene derivatives are highly fluorescent<sup>26</sup> and serve as efficient  $\pi$ -conjugating units.<sup>27</sup> The hexyl chains at the C(9) position of fluorene improve the solubility of the molecules in organic solvents. The molecular structures in the series 1-7 were systematically varied in the following ways to probe structure-property relationships. (i) The acceptor diaryIOXD was changed, with phenylene (1), pyridyl (2) and thienyl (3) units in the backbone to modify the HOMO and LUMO levels of this portion of the molecules. (ii) The electron donor ability and electrochemical stability of the carbazole unit was enhanced with the attachment of dimethoxy substituents (4) and tert-butyl substituents (5). (iii) The number of fluorene units was changed from one (1-5) to two (6) to none (7) to probe the effects of the conjugation length of the spacer.

The synthetic route to 1-3 is shown in Scheme 1. Crosscoupling of  $8^{21}$  with the halo-diarylOXD derivative 9,<sup>28</sup> 10 or 11 under palladium-catalysed Suzuki–Miyaura conditions gave 1-3, respectively, in 72–84% yields.

The synthesis of 4 and 5 is shown in Scheme 2. Copper-catalysed C–N cross-coupling of  $12^{29}$  with the appropriate carbazole derivative gave 13 and 14 in 93 and 78% yields, respectively. Palladium-catalysed cross-coupling of 13 or 14 with 15 then gave the final products 4 and 5.

The synthesis of bifluorene derivative **6** from  $16^7$  is shown in Scheme 3.

Compound 7 was synthesised by a Buchwald–Hartwig C–N coupling reaction (Scheme 4).



Scheme 1 *Reagents and conditions*: (i) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, NaOH (aq), THF, reflux, 15 h (1, 78%; 2, 72%; 3, 84%).

#### Cyclic voltammetry studies

Electrochemical measurements for 1–7 are presented in Table 1 and cyclic voltammograms are shown in the ESI<sup>†</sup>. All compounds showed oxidation waves due to the electrondonating carbazolyl groups. Compounds 4 and 5 with substituents at the 3- and 6-positions of the carbazolyl groups revealed reversible oxidation waves at 0.48 and 0.75 V, respectively, whereas compounds 1-3, 6 and 7 showed irreversible oxidation waves at high sample concentrations. The latter waves appear more 'reversible' as the sample concentrations are lowered and at faster scan rates. A carbazolyl group couples with a second carbazolyl group on oxidation via the 3- (or 6-) positions and thus a dimer is formed:<sup>30</sup> this process cannot occur with 4 and 5. This process is favoured on increasing the concentration of the sample and the length of time the sample is in the oxidised state. The dimer contains a redox centre with a lower oxidation potential so a second cathodic wave is observed at ca. +0.55 V in 1-3, 6 and 7. A second irreversible oxidation wave in compound 4 is probably due to the oxidation of the electron-donating methoxy group.

Compound 6, which has a bifluorenyl link, showed a second oxidation wave that is only 0.23 V higher than the first oxidation



Chart 1 The structures of bipolar molecules 1–7 studied in this work.



Scheme 2 Reagents and conditions: (i) 3,6-dimethoxycarbazole or 3,6-ditert-butylcarbazole, CuI, 1,10-phenanthroline,  $K_2CO_3$ , DMF, 120 °C, 40 h, (13, 93%; 14, 73%); (ii) 15, Pd(PPh\_3)\_2Cl\_2, NaOH (aq), THF, reflux, 15 h (4, 73%; 5, 77%).

wave. Fig. 1 shows the CV traces for  $\mathbf{6}$  at high and low sample concentrations. The second oxidation may take place at one of the fluorene units, presumably the unit furthest from the oxidised carbazolyl group, and this fluorene redox process has a degree of reversibility.

Reversible reduction waves at -2.19 and -2.28 V were observed for the pyridylene and thienylene compounds, 2 and 3, respectively. No reduction waves were present within the THF solvent window for 1 and 4–7. The reduction processes in 2 and 3 are likely to occur at the pyridylene and thienylene units, respectively.

#### Photophysical studies

Absorption data for 1–7 in cyclohexane and acetonitrile solutions are summarised in Table 2. All compounds have strong bands at 345–370 nm and additional bands are observed at 312 nm for 4, 321 nm for 5 and 285 nm for 7. The extinction coefficients for these bands correlate with the number of fluorene units present,  $\varepsilon = 47\ 000-63\ 000$  for 1–5,  $\varepsilon = 100\ 000$  for 6 and  $\varepsilon = 27\ 000$  for 7. There are significant solvatochromic shifts on going from cyclohexane to acetonitrile solutions for 2, 4, 5 and 7 and negative solvatochromism is observed for these compounds. Such solvatochromism, typically found for zwitterions, indicates that for these compounds their ground states are more polar than their excited states.

Emission data for 1–7 in cyclohexane and acetonitrile solutions are listed in Table 3. Blue emission bands with vibronic structures with high fluorescence quantum yields ( $\Phi_f$ ) in the range of 0.80 to 0.99 were observed in cyclohexane for all compounds. While compounds 1–6 have blue emission maxima between 383 nm (for 1) and 412 nm (for 3), the deep blue emission maximum for 7 is at 358 nm. The modifications on the parent molecule 1 result in red shifts of the emissions for 2–6. Compound 7 is blue shifted relative to 1; thus the absence of a fluorene unit increases the energy gap between the excited and ground state in 7 compared to 1.

The trend in the positive solvatochromic shifts in the emissions listed in Table 4 follow the trend in the negative solvatochromic



Scheme 4 *Reagents and conditions*: (i) carbazole, Pd(OAc)<sub>2</sub>, P'Bu<sub>3</sub>·HBF<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, toluene, reflux, 24 h (54%).

Table 1 Electrochemical measurements for 1-7

	$E_{1/2}(\operatorname{Ox1})^a$	$E_{\rm c}{}^{ab}$	$E_{1/2}(\mathrm{Ox2})^a$	$E_{1/2}(\operatorname{Red})^c$
1	$0.86^{d}$	0.54		
2	$0.89^{d}$	0.57		-2.19
3	$0.85^{d}$	0.56		-2.28
4	0.48		$1.19^{e}$	
5	0.75			
6	$0.80^{d}$	0.54	$1.03^{d}$	
7	$1.00^{d}$	$0.50^{f}$		

<sup>*a*</sup> Scan between 1.5 V and -0.5 V vs. ferrocenium/ferrocene couple (FcH<sup>+</sup>/ FcH = 0.0 V) in DCM. <sup>*b*</sup> From cathodic wave of the 'dimer' formed after oxidation. <sup>*c*</sup> Scan between -0.5 V and -2.5 V vs. FcH<sup>+</sup>/FcH (0.0 V) in THF. <sup>*d*</sup> Estimated from 'reversible wave' at low sample concentration. <sup>*e*</sup> Irreversible wave, anodic wave value given. <sup>*f*</sup> Third cathodic wave observed at -0.40 V after oxidation.

effects observed in the absorption data. Fig. 2 shows the emission bands for 4 and 6 in solvents of different polarities. Compounds 2, 4, 5 and 7 display the largest solvatochromic effects, whereas the smallest solvatochromic shift is observed for compound 6with two fluorene units. Compound 3, containing a thiophene unit, has the second smallest solvatochromic shift. The charge transfer character in the excited states of 2, 5, 7 and especially 4 must be relatively strong, whereas the CT character in 6 and 3 is weaker. The Stokes shifts in cyclohexane solutions for compounds **1–6** are consistent in the range of  $2040-3010 \text{ cm}^{-1}$ , whereas for 7 it is small at 720 cm<sup>-1</sup>. The excited state geometry in 7 must be quite similar to its ground state geometry and thus there is a substantial blue shift in its emission compared to 1. Small geometry rearrangements are likely in the excited states for 1-6 and presumably involve the fluorene units present in these molecules.

Thin films of compounds 1–7 were obtained by thermal evaporation and showed broad featureless emissions with the maxima values listed in Table 3. The emission maxima are consistently red-shifted by 2870–3550 cm<sup>-1</sup> (Table 4) compared to emission maxima from cyclohexane solutions. The PLQY values ( $\Phi_{\rm f}$ ) are between 0.17 and 0.38 for thin films and low compared to the PLQY values in cyclohexane solutions. They indicate that devices, which are 'solid state' in nature, from 1–7



Scheme 3 Reagents and conditions: (i) ICl, DCM, RT, 1 h, 87%; (ii) 8, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, NaOH (aq), THF, reflux, 15 h (91%).



Fig. 1 Cyclic voltammograms showing two oxidation waves for 6 in low (left) and high sample concentrations.

Table 2	Absorption	ı data for	1-7
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	Abs cyclohexane/ nm (cm <sup>-1</sup> )	Extinction coefficient ( $\varepsilon$ ) cyclohexane (M <sup>-1</sup> cm <sup>-1</sup> )	Abs acetonitrile/ nm (cm <sup>-1</sup> )	Solvatochromic shift/cm <sup>-1</sup>
1	345 (28 986)	61 510	344 (29 070)	-84
2	363 (27 548)	63 180	353 (28 329)	-745
3	370 (27 027)	56 710	370 (27 027)	0
4	363 (27 548)	46 660	351 (28 490)	-942
	312 (32 051)	60 450	311 (32 154)	
5	353 (28 329)	57 770	350 (28 571)	-242
	321 (31 153)	43 360	321 (31 153)	
6	357 (28 011)	99 540	358 (27 933)	78
7	349 (28 653)	26 520	339 (29 498)	-845
	339 (29 498)	30 770	331 (30 211)	
	285 (35 088)	34 560	291 (34 364)	
	284 (35 211)	51 560	284 (35 211)	

Table 3 Emission data for 1-7

	$\lambda_{\max}$ cyclohexane <sup><i>a</i></sup> /nm (cm <sup>-1</sup> )	$\lambda_{max}$ acetonitrile <sup>b</sup> / nm (cm <sup>-1</sup> )	$\lambda_{max}$ thin film <sup>c</sup> / nm (cm <sup>-1</sup> )	$\lambda_{\max} EL^d/$ nm (cm <sup>-1</sup> )	PLQY cyclohexane <sup><math>e</math></sup> ( $\Phi_{\rm f}$ )	PLQY thin film <sup><math>f</math></sup> ( $\Phi_{\rm f}$ )
1	383, 405 (26 110, 24 691)	464 (21 552)	430 (23 256)	435 (22 988)	0.88	0.38
2	392, 415 (25 510, 24 096)	505 (19 802)	450 (22 222)	453 (22 075)	0.99	0.36
3	412, 435 (24 272, 22 988)	472 (21 186)	467 (21 413)	484 (20 661)	0.86	0.17
4	402, 424 (24 876, 23 585)	583 (17 153)	465 (21 505)	470 (21 277)	0.80	0.17
5	395, 417 (25 316, 23 981)	498 (20 080)	450 (22 222)	453 (22 075)	0.96	0.20
6	400, 420 (25 000, 23 810)	439 (22 779)	450 (22 222)	447 (22 371)	0.99	0.21
7	358, 377 (27 933, 26 525)	439 (22 779)	410 (24 390)	415 (24 096)	0.95	0.29

<sup>*a*</sup> Excitation at the lowest energy  $\lambda_{abs}$  of the compound in cyclohexane. <sup>*b*</sup> Excitation at the lowest energy  $\lambda_{abs}$  of the compound in acetonitrile. <sup>*c*</sup> Excitation wavelengths ( $\lambda_{ex}$ ) for **1** at 350 nm, for **2**, **3** and **4** at 370 nm and for **5**, **6** and **7** at 340 nm. <sup>*d*</sup> Electroluminescence (EL) data from devices, see Table 7 for details. <sup>*c*</sup> Photoluminescence quantum yields (PLQY) measured in cyclohexane solution using an integrating sphere with excitation  $\lambda_{ex}$  at the lowest energy  $\lambda_{abs}$  of the compound in cyclohexane. Estimated errors  $\pm 5\%$ . <sup>*f*</sup> PLQY data obtained using an integrating sphere as described in the literature;<sup>31</sup> estimated errors  $\pm 5\%$ .

would have EQE values more closely related to PLQY values from thin films than to the higher PLQY values from cyclohexane solutions. Atomic force microscope (AFM) images of films of 1–7 revealed a granular-type morphology with grain sizes of 125–278 nm ( $\pm 10\%$ ). Details are given in the ESI<sup>†</sup>.

#### Molecular orbital computations

Ground state ( $S_0$ ) geometry optimisations were carried at the B3LYP/6-31G\* model chemistry without symmetry constraints. Ethyl groups were used instead of hexyl groups in compounds 1–7 to reduce computational efforts and these model geometries

are denoted by the suffix **a**, *i.e.* 1a-7a. Electronic structure calculations on these geometries 1a-7a show that the HOMOs are located, as expected, at the carbazolyl groups as shown in the molecular orbitals for 1a and 6a (Fig. 3). Fig. 4 summarises the energy levels of the HOMO and LUMO along with selected orbitals that are close to the HOMO or LUMO in energies. There is excellent agreement between the trend in HOMO energies for 1a-7a and the trend in the oxidation potentials for 1-7 (Table 5). The second oxidation waves observed in the cyclovoltammograms for 4 and 6 are also in accord with the relatively high HOMO+1 energies in 4a and 6a. While the second oxidation wave observed experimentally in 4 is assigned to the

Table 4 Stokes, solvatochromic and phase shift data for 1-7

	Stokes shift cyclohexane (cm <sup>-1</sup> ) <sup>a</sup>	Stokes shift acetonitrile $(cm^{-1})^b$	Solvatochromic shift $(cm^{-1})^c$	Film-solution shift $(cm^{-1})^d$	EL-solution shift $(cm^{-1})^e$	Film-EL shift (cm <sup>-1</sup> )
1	2880	7520	4560	2850	3120	270
2	2040	8530	5710	3290	3440	140
3	2760	5840	3090	2860	3610	750
4	2670	11 340	7720	3370	3600	230
5	3010	8490	5240	3100	3240	140
6	3010	5150	2220	2780	2630	-150
7	720	6720	5150	3550	3840	290

<sup>*a*</sup> Difference between the lowest energy  $\lambda_{abs}$  and the highest energy  $\lambda_{em}$  in cyclohexane. <sup>*b*</sup> Difference between the lowest energy  $\lambda_{abs}$  and  $\lambda_{em}$  in acetonitrile. <sup>*c*</sup> Difference between the highest energy  $\lambda_{em}$  in cyclohexane and  $\lambda_{em}$  in acetonitrile. <sup>*d*</sup> Difference between the highest energy  $\lambda_{em}$  in cyclohexane and  $\lambda_{em}$  as thin film. <sup>*e*</sup> Difference between the highest energy  $\lambda_{em}$  in cyclohexane and  $\lambda_{em}$  as device. <sup>*f*</sup> Difference between the highest energy  $\lambda_{em}$  as thin film and  $\lambda_{em}$  as device.



Fig. 2 Emission spectra for 4 (left) and 6 (right) showing solvatochromism in different solvents.



Fig. 3 Selected molecular orbitals for 1a (left) and 6a (right) contours drawn at  $\pm 0.04$  (e bohr<sup>-3</sup>)<sup>1/2</sup>.

dimethoxycarbazolyl group, the corresponding observed wave in **6** is due to oxidation at the fluorene ring next to the oxadiazole ring where the HOMO-1 for **6a** is depicted in Fig. 3.

The two reduction waves observed only for 2 and 3 are in accord with the lowest LUMO energies calculated for 2a and 3a in the series 1a-7a. These LUMOs are located on the heteroaromatic rings. The heteroaromatic linkers in 2 (electron

accepting) and **3** (increased conjugation) and the electrondonating OMe and butyl groups at the carbazolyl groups in **4** and **5** lower the HOMO–LUMO gap compared to **1** according to Fig. 4.

The characters of LUMO and LUMO+1 are the phenylene rings next to the oxadiazole ring for **1a–5a** and **7a**, rather than the oxadiazole unit itself as viewed in Fig. 3 for **1a**. The



Fig. 4 Molecular orbital energy diagram for the important orbitals in 1a-7a.

diaryloxadiazole unit as a whole is a relatively strong  $\pi$ -electron acceptor. The LUMO+1 in **6a** is located on the fluorene unit near the carbazolyl group rather than on the phenylene ring with the butyl group. Thus **6a** has a different orbital make-up where the two fluorene units contribute to the LUMO+1 and HOMO-1 of **6a** in Fig. 3.

The different solvatochromic effects observed for 1–7 can be linked to the amount of carbazolyl character in the HOMO, as evident from Table 5. The largest carbazolyl group contribution to the HOMO at 86% is for 4a and the smallest at 61% is for 6a. The carbazolyl group contributions to the LUMOs in 1a–7a are negligible thus low energy charge transfer transitions are expected in 1–7.

Table 5Comparison of calculated HOMO energies for 1a-7a vs.observed oxidation potentials, and carbazolyl character in HOMO vs.observed solvatochromic shifts

	HOMO (calc., eV)	HOMO $(obs., V)^a$	Carbazolyl contribution in HOMO (calc., %)	Emission solvatochromic shift (cm <sup>-1</sup> ) <sup>b</sup>	Absorption solvatochromic shift (cm <sup>-1</sup> ) <sup>b</sup>
	5.00	5.04	50	15.00	0.0
la	-5.28	-5.26	73	4560	-80
2a	-5.28	-5.29	73	5710	-780
3a	-5.26	-5.25	63	3090	0
4a	-4.89	-4.88	86	7720	-940
5a	-5.14	-5.15	77	5240	-240
6a	-5.22	-5.20	61	2220	80
7a	-5.45	-5.40	81	5150	-850
<sup>a</sup> F	or <b>1–7</b> , bas	ed on <i>E</i> (H0	OMO) = -4.4	$V - E_{1/2}(Ox1).$	<sup>b</sup> For <b>1–7</b> .

 Table 6
 TD-DFT
 data for 1a–7a and comparison with observed absorption maxima

	Calc. abs. (nm)	Oscillation strength (f)	Transitions	Obs. abs (nm)
1a	394	0 741	$\pi(C_z) > \pi^*(C_zH_z)$	345
2a	424	0.681	$\pi(C_2) > \pi^*(C_5H_3N)$	363
3a	421	0.995	$\pi(Cz) > \pi^*(C_4H_2S)$	370
4a	436	0.423	$\pi(Cz) > \pi^*(C_6H_4)$	363
	348	1.459	$\pi$ (fluorene) > $\pi$ *(C <sub>6</sub> H <sub>4</sub> )	312
5a	407	0.659	$\pi(Cz) > \pi^*(C_6H_4)$	353
	344	1.534	$\pi$ (fluorene) > $\pi^*(C_6H_4)$	321
6a	397	1.544	$\pi(Cz) > \pi^*(C_6H_4)$	357
7a	378	0.482	$\pi(Cz) > \pi^*(C_6H_4)$	349
	303	0.591	$\pi(C_6H_4'Bu) > \pi^*(C_6H_4)$	285

TD-DFT computations were carried out on 1a-7a to predict the absorption maxima and the nature of the transition bands. TD-DFT data are summarised in Table 6 along with observed absorption data. The predictions generally underestimate the absorption maxima energies which can be attributed to a number of factors, for example a mixture of many conformers exists in the solution state whereas only the static 'gas-phase' (most planar) conformer is computed. The trend of the absorption maxima, nevertheless, is in broad agreement with the observed maxima. The lowest energy bands observed are assigned as charge-transfer transitions from the carbazolyl donor unit to the acceptor ring unit directly linked to the oxadiazole ring. The considerable orbital contribution of the oxadiazole character in all the LUMOs suggests that the diaryloxadiazole unit is a more appropriate description of the acceptor in these molecules. The higher energy bands observed in 4, 5 and 7 are assigned to local  $\pi$ - $\pi$ \* transitions.

#### Electroluminescence properties of OLEDs

In a previous communication we reported that compound 1 could be successfully integrated into a simple and efficient, singleactive-layer device that emitted deep-blue electroluminescence.<sup>21</sup> The Commission Internationale de l'Eclairage (CIE) chromaticity diagram (x,y) co-ordinates were (0.16, 0.07), close to the National Television System Committee (NTSC) standard blue co-ordinates of (0.14, 0.08). The blue device possessed a high external quantum efficiency for a single-active-later device (EQE - over 4% in the case of OLEDs produced by thermal evaporation). Here, it was anticipated that the systematic modifications to the molecular structure of 1 would enable a degree of tuning on the OLED output colour, turn-on voltage and efficiency. The current versus voltage, I-V, and EL (measured by the photocurrent in the photodiode detector) versus voltage, L-V, characteristics of OLEDs based on 1-7 are contrasted in Fig. 5. The device architecture in all cases is: ITO/PEDOT:PSS/X/Ca/Al (X = 1-7). The corresponding EQEs and EL spectra are shown in Fig. 6 and 7, respectively, while the CIE co-ordinates of the various devices are depicted in Fig. 8. Important electro-optical characteristics of the various OLEDs are collated in Table 7.

The electrical data in Fig. 5 reveal similar I-V characteristics for **2** and **3** (*i.e.* within experimental error), but with currents significantly higher than measured for the OLED based on **1**. The predicted HOMO levels for these three compounds are approximately the same (Fig. 4 and Table 5) while the LUMO levels of **2** 



Fig. 5 (a) Current–voltage and (b) photocurrent–voltage characteristics of the devices incorporating the new materials. Device architecture: ITO/PEDOT:PSS/X/Ca/Al (X = 1-7).



**Fig. 6** External Quantum Efficiency of devices incorporating materials **1–7**.

and **3** are lowered with respect to that for **1**. This suggests that the increased currents measured for devices based on **2** and **3** are electron currents. However, only the device based on **3** reveals an



Fig. 7 Electroluminescence spectra of each device.



Fig. 8 CIE diagram indicating the colour emission of each device compared to standard white light.

enhanced EL output and a reduced turn-on voltage for EL (Fig. 5), although the overall device efficiencies for OLEDs based on **2** and **3** are both significantly lower than that measured for OLEDs based on **1**. Lowering the LUMO level of the active molecule in our OLED architectures resulted in the peak EL emission moving from the blue end of the spectrum (Fig. 7), so the output colour of the OLED was no longer confined to the deep-blue region of the CIE diagram (Fig. 8). This is consistent with the reduced LUMO–HOMO separations of **2** and **3** (Fig. 4).

Compound 4 has increased donor strength relative to compound 1 due to the methoxy groups to the 3,6-positions of the carbazole rings. The predicted LUMO levels of 1 and 4 are similar, but the HOMO level of 4 is significantly increased (Fig. 4). The OLED based on compound 4 exhibited a green rather than blue EL as expected from a reduced LUMO-HOMO separation, with an EQE of 1.4%. This device possessed the lowest turn-on voltage (2.8 V) of all the OLEDs studied. Compound 5 has a higher HOMO-LUMO gap compared to 4, and therefore 5 retains the blue emission. Moreover, the current and EL output are both increased for the OLEDs manufactured with 5 compared to 1 (Fig. 5), leading to an EQE of 1.9% – the second highest of all the compounds studied in this work.

Compounds 6 and 7 provided the means to study the influence of the fluorene group on the OLED behaviour. Fig. 7 shows that the additional fluorene group in 6 has no impact on the device colour as supported by DFT predictions. In contrast, 7, which does not contain fluorene, provides the deepest blue OLEDs of all the compounds synthesised for this study again supported by HOMO-LUMO predictions here. However, the EQE of OLEDs based on this compound is low (0.36%). The above results suggest that the fluorene group is not itself responsible for the deep blue emission in some of our compounds but it is necessary for high efficiency. The deep blue colour must therefore arise from the presence of the carbazole group. This is consistent with results obtained in a previous study of two compounds,<sup>21</sup> where a diarylamine donor was replaced with carbazole and the colour of emission moved from greenish-blue to deep-blue. Fig. 5 and 6 reveal that OLEDs based on 6 and 7 possess similar I-V and L-Vcharacteristics. The key difference is the much deeper blue EL from devices based on 7. Although the predicted greater LUMO-HOMO separation explains the deeper blue EL for 7, it cannot account for their electrical behaviour. It is possible that the more difficult charge carrier injection into 7 (raised LUMO and

Table 7 Electroluminescence data for OLEDs based on compounds 1-7

Compound	<b>1</b> <sup><i>a</i></sup>	2	3	4	5	6	7
Turn on $V^{b}(\mathbf{V})$	4.18	3.87	3.04	2.80	3.03	3.22	3.68
$EOE^{c}$ (%)	4.71	0.20	0.38	1.48	1.89	0.54	0.36
Wavelength of maximum emission <sup>d</sup> (nm)	431	453	484	455	453	452	428
FWHM (nm)	81	66	87	63	73	81	70
$CIE^{e} x$ at 1 mA	0.157	0.158	0.181	0.150	0.151	0.164	0.161
$CIE^{e}$ v at 1 mA	0.079	0.120	0.273	0.177	0.096	0.114	0.049
Brightness <sup><math>f</math></sup> (cd m <sup>-2</sup> )	72.25	1.739	35.81	7.511	99.60	7.767	6.312
Current efficiency $(cd A^{-1})$	1.419	0.034	0.703	0.147	1.956	0.153	0.124
Power efficiency $f(\operatorname{Im} W^{-1})$	0.665	0.014	0.409	0.125	0.960	0.084	0.075

<sup>*a*</sup> Data for 1 are taken from ref. 21. <sup>*b*</sup> Turn on voltage given at 1 nA of photocurrent. <sup>*c*</sup> EQE measured at  $100 \pm 30$  cd m<sup>-2</sup>. <sup>*d*</sup> Peak emission of 5 and 7 measured under an applied current of 10 mA and 2 mA, respectively. All other OLEDs measured at 20 mA ( $J \approx 10^3$  A m<sup>-2</sup>). <sup>*e*</sup> CIE coordinates measured at an applied current of 1 mA. <sup>*f*</sup> Brightness, current efficiency and power efficiency measured under an applied current of 1 mA.

lowered HOMO in relation to 1) is compensated by much higher carrier mobilities for thin films of 7.

The most significant correlation that has emerged from our studies of OLEDs based on this series of bipolar carbazoleoxadiazole molecules is that between the EL maxima and the bandgap  $E_{g} (= E_{LUMO} - E_{HOMO})$  predicted by molecular orbital calculations. Fig. 9 shows a plot of  $E_{g}$  versus the reciprocal of the CIE(y) co-ordinate. The OLEDs based on molecules with the largest LUMO-HOMO separations generally show the largest values of 1/CIE(y) for the deepest blue EL. Two exceptions are compounds 3 and 6. A possible explanation is that these compounds are the least bipolar based on solvatochromic and computed data. Fig. 7 shows that OLEDs using compound 3 possess the most red-shifted EL spectra of all the molecules studied. The peaks in the EL emissions from 3 and 4 are quite similar; however, the broad shoulder on the low energy side of the peak emission for 3 results in dissimilar CIE co-ordinates. A comparison of the PL emission maxima of the thin films and EL of devices in Tables 3 and 4 shows similar data in these molecules except for 3. Compound 3 with the thiophene unit is unusual in that its emission maxima vary considerably and do not follow trends of other compounds in the series.

Important design rules that have emerged from our study are: (i) the most balanced carrier transport in the OLEDs (*i.e.* similar electron and hole currents, providing a high device efficiency) is achieved with a 2,5-diphenyl-1,3,4-oxadiazole acceptor and a carbazole donor; (ii) the deep blue emission from the molecules



Fig. 9 Dependence of band gap,  $E_g$  (from Fig. 4), on 1/CIE(y) for OLEDs based on the different molecules.

originates from the carbazole group; (iii) the presence of a fluorene group adjacent to the carbazole donor, and separated from the oxadiazole moiety by a phenylene ring spacer, is required to achieve a high device efficiency (*i.e.* compounds 1, 4 and 5). The links between other electro-optical parameters measured for the OLEDs (*e.g.* device currents and EL turn-on voltages) and their predicted electronic band structures are less clear. This indicates that different factors, for example, electron and hole carrier mobilities are a major influence in controlling the electro-optical parameters of these single-active-layer OLEDs.

To place our work in a broader context it should be noted that the OLEDs from compounds **1** and **5** are competitive with the most efficient deep-blue OLEDs based on all-organic smallmolecule fluorophores. There are very few literature reports of OLEDs of this type with emission close to the NTSC standard blue co-ordinates of (0.14, 0.08) that achieve EQE values >1% or current efficiencies >1 cd  $A^{-1}$ .<sup>32</sup>

## Conclusions

The syntheses, solution absorption and emission properties, and cyclic voltammetric data of a new series of bipolar carbazole-2,5diaryl-1,3,4-oxadiazole hybrid molecules, 1-7, are reported. Density functional theory calculations establish that these molecules possess molecular orbitals which favour bipolar charge-transport. Single-active-layer organic light emitting devices have been fabricated by thermal evaporation using the bipolar compounds as the emitters in the architecture ITO/ PEDOT:PSS/X/Ca/Al (X = 1-7). The results reveal an excellent correlation between the emitted EL spectrum and the  $E_{LUMO^{-1}}$  $E_{\rm HOMO}$  separation predicted by the molecular orbital calculations. OLEDs based on 1, incorporating a 2,5-diphenyl-1,3, 4-oxadiazole acceptor group and a carbazole donor unit emitted deep-blue electroluminescence, with CIE (x,y) co-ordinates of (0.16, 0.08), close to the NTSC standard blue co-ordinates of (0.14, 0.08). Important design rules that have emerged from our study are that the deep blue emission from the molecules originates from the carbazole group and that the presence of a fluorene group adjacent to the carbazole donor, and separated from the oxadiazole acceptor by a phenylene ring (i.e. compounds 1, 4 and 5) is required to achieve a high device efficiency (EQE > 1%). These materials are very attractive for further development due to the combination of good



Fig. 10 OLED architecture.

processability of the molecules, their bipolar structure, colour tuneability and efficient performance of OLEDs using a simple non-doped device architecture.

# **Experimental section**

## Materials and measurements

All air-sensitive reactions were conducted under a blanket of argon which was dried by passage through a column of phosphorus pentoxide. All commercial chemicals were used without further purification unless otherwise stated. Solvents were dried and degassed following standard procedures. Column chromatography was carried out using 40–60  $\mu$ m mesh silica. Melting points were determined in open-ended S2 capillaries using a Stuart Scientific SMP3 melting point apparatus at a ramping rate of 5 °C min<sup>-1</sup>. NMR spectra were recorded on Bruker Avance 400 or Varian VNMRS 700 spectrometers. Chemical shifts are referenced to TMS at 0.00 ppm. Mass spectra were measured on a Waters Xevo OTofMS with an ASAP probe, a Thermoquest Trace or a Thermo-Finnigan DSQ. Elemental analyses were performed on a CE-400 Elemental Analyzer.

#### Device fabrication and measurement

Devices were fabricated as shown in Fig. 10. PEDOT:PSS was spin-coated onto glass, ready-coated in ITO. Onto this, the new materials 1–7 were each thermally evaporated to give the active layer, followed by a calcium cathode and aluminium contact.

All OLED devices were deposited on glass substrates readycoated with indium-tin oxide (ITO) purchased from Merck and VisionTek Systems, with a sheet resistance of 8  $\Omega$  sq<sup>-1</sup>and 7  $\Omega$  sq<sup>-1</sup>, respectively. This was used as the anode in all cases. The glass was cut to the required size and cleaned by sonication in propan-2-ol, acetone, 2% Decon 90 solution in water and finally deionised water, each for 15 min and dried with a nitrogen gun. PEDOT:PSS, purchased from H. C. Starck (Clevios PVP AI 4083), was used as the hole injection layer. It was filtered through a 0.2 µm PTFE syringe filter, spin-coated at 2500 rpm for 45 seconds and dried at 180 °C for 2 min to give a layer of 45–60 nm thickness. Compounds 1–7 were evaporated onto the PEDOT:PSS to give layers approximately 80 nm thick. Ca (15 nm) and Al (80 nm) electrodes with 2.5 mm radius were then thermally evaporated to complete the devices.

Electrical measurements were carried out under vacuum. A D.C. bias was applied and the current was measured by a Keithley 2400 Source Meter and the light emitted from the device was collected by a large area photodiode  $(1 \text{ cm}^2)$  connected to a Keithley 485 Picoammeter. For external quantum efficiency measurements, the light power was calculated using the photocurrent and the conversion factor (wavelength dependent) of the photodiode (ampere watt<sup>-1</sup>). Electroluminescence spectra

were measured using an Ocean Optics USB2000 Miniature Fibre Optic Spectrometer and CIE coordinates measured using a SpectraScan PR-655 Spectroradiometer.

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