Organic Light-Emitting Diodes from Symmetrical and Unsymmetrical π-Extended Tetraoxa[8]circulenes

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The understanding and development of molecular electronics depends on the discovery and exploitation of new π-extended organic materials.[1] One area of interest is the design of small molecules that are suitable as the fluorescent component in blue organic light-emitting diodes (OLEDs). OLEDs based on small organic molecules or conjugated polymers have been explored for applications in full-colour flat-panel displays, since the seminal work by the group at Kodak.[2] Some classes of low-mass blue-emitting materials have been exploited, such as spirobifluorenes,[3] oligofluorenes,[4] siloles[5] and distyrylarylenes,[6] but the introduction of completely new structural motifs remain scarce. To this end, we report the acid-mediated condensation of a 2,3-dialkyl-1,4-benzoquinone with 1,4-naphthoquinone to produce a series of highly soluble π-extended tetraoxa[8]circulenes (Figure 1) as well as the application of these materials in blue OLEDs.

Tetraoxa[8]circulene (**4B**) is a planar heteroaromatic compound formed in trace amounts by treating 1,4-benzoquinone with strong acids.[7] The structure of the tetraoxa[8]-circulene framework was deduced by means of mass spectrometry of the all-naphthalene tetraoxa[8]circulene (**4N**) by Erdtman and Högberg, and was later confirmed by single-crystal X-ray crystallography.[8–11] It became clear that when one side of the 1,4-benzoquinone was substituted, either by using 1,4-naphthoquinone or a 2,3-disubstituted-1,4-benzoquinone, the tetraoxa[8]circulene was a major
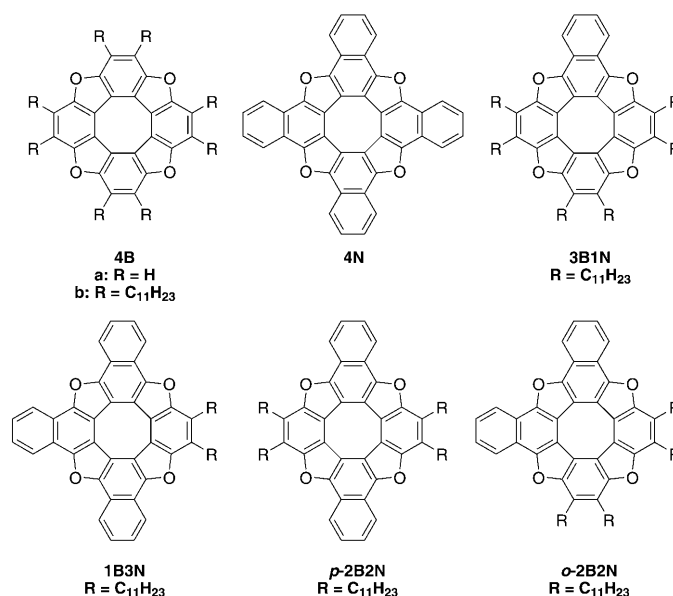

Figure 1. Structure of symmetrical and unsymmetrical π-extended tetraoxa[8]circulenes.

product upon acid treatment. More recently a series of liquid-crystalline tetraoxa[8]circulenes were synthesised by attachment of linear alkyl chains to the tetraoxa[8]circulene framework.[12] That work also introduced a relatively mild method for the cyclisation reaction: treatment of the quinone with $BF_3 \cdot OEt_2$ in boiling CH_2Cl_2. The tetraoxa[8]circulene has been suggested as an intercalator for DNA.[13] Rathore and co-workers used this synthetic protocol to prepare new stable radical cation salts based on tetraoxa[8]circulenes.[14]

From a synthetic and a materials point of view, the exploration of π-extended tetraoxa[8]circulenes is of interest. As the processing ability of large aromatic materials and polymers relies on solubility in organic solvents, the development of tetraoxa[8]circulenes based on 2,3-dialkyl-1,4-ben-

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zoquinones was a major development.[12] This methodology was key to the preparation of the alkane-soluble π-extended tetraoxa[8]circulenes described here (Scheme 1).
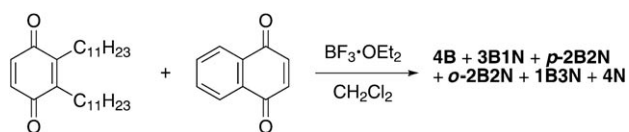
Scheme 1. Synthesis of symmetrical and unsymmetrical π-extended tetra-oxa[8]circulenes.

When treating a 1:1 mixture of naphthoquinone and 2,3-bisundecyl-1,4-benzoquinone with $BF_3 \cdot OEt_2$ the reaction mixture contains all the compounds illustrated in Figure 1. The all-naphthalene tetraoxa[8]circulene (**4N**) was removed by filtration, and the remaining tetraoxa[8]circulenes were separated by careful column chromatography on silica.

The UV/Vis and fluorescence spectra of the compounds **4B**, **3B1N**, **p-2B2N**, **o-2B2N** and **1B3N** are shown in Figure 2. The spectrum of **4B** shows two distinctive electronic transitions at approximately 375 and 260 nm, both exhibiting vibronic structures. The spectrum of **4B** is the simplest. The remaining compounds show multiple superimposed electronic transitions and vibrational fine structure, as exemplified by the spectrum of **p-2B2N**, which shows two
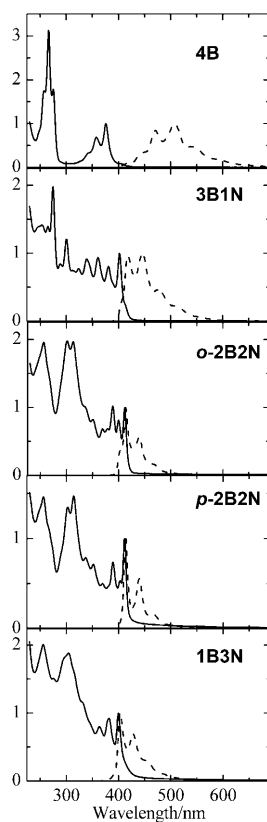

Figure 2. UV/Vis and fluorescence spectra (dotted line) of the series of tetraoxa[8]circulenes (**4B**, **3B1N**, **p-2B2N**, **o-2B2N** and **1B3N**) in CH_2Cl_2.

0–0 transitions at ≈415 and ≈380 nm and multiple other electronic transitions occurring at higher energy. Well-resolved vibronic structures were observed in the fluorescence spectra. The broad features observed in the fluorescence spectrum of **4B** probably originate from the decay of close lying excited electronic states.

Fluorescence lifetime measurements (Table 1) support this hypothesis; the decays observed could only be adequately modelled as a combination of two decays with dif-

Table 1. Quantum yields and fluorescence lifetimes. All measurements were done in degassed CH_2Cl_2.

Compound	Quantum yield	Fluorescence lifetime[a]			
4B	0.09	5.5	67	10.0	33
3B1N	0.55	7.2	100	–	–
p-2B2N	0.83	3.3	64	8.0	36
o-2B2N	0.51	3.3	78	5.7	22
1B3N	0.36	3.1	76	6.5	24

[a] Lifetimes are in ns and percentage contribution to the decay is indicated for each lifetime.

ferent lifetimes, the exception being the decay measured for **3B1N**. The fluorescence quantum yield for **4B** was low (0.09) in comparison to the rest of the compounds, the highest observed for **p-2B2N** with a quantum yield of 0.83. The large effect of regiochemistry on the physical properties was augmented by comparing **p-2B2N** and **o-2B2N**. The quantum yield for the regioisomers differs by ≈0.3. The difference in lifetimes was a bit more subtle for **p-2B2N** and **o-2B2N** and was seen in the long component, which is 8.0 ns for **p-2B2N** and 5.7 ns for **o-2B2N**. The measured single exponential decay for **3B1N** was significantly slower (lifetime of 7.2 ns) than the shortest component in the fluorescence decay for the other compounds (3.1–5.5 ns).

The fluorescence spectra shift hypsochromically as the number of naphthalene units is increased. This counterintuitive observation may be explained in terms of symmetry and consideration of which electronic transitions are allowed, bearing in mind that **4B** and **4N** have the highest symmetry.

To further investigate the electronic properties of the tetraoxa[8]circulenes square-wave voltammetry was performed (Table 2).

Orbital energies, at least relative values, can be inferred from the reduction and oxidation potentials; the order of reduction and oxidation potentials reflects the ordering of or-

Table 2. Oxidation and reduction potentials for the tetraoxa[8]circulenes using square-wave voltammetry. All potentials are reported with respect to the oxidation potential of ferrocene/ferrocenium in CH_2Cl_2 with Bu_4NPF_6 as the electrolyte.

Compound	Potential [V]					
4B	−2.81	−2.60	−2.39	1.10		
3B1N	−2.78	−2.55	−2.38	0.85	0.95	
p-2B2N	−2.75	−2.55	−2.39	0.76	0.94	1.20
o-2B2N	−2.74	−2.55	−2.39	0.72	0.97	
1B3N	−2.72	−2.55	−2.41	0.73	0.96	

bital energies. Keeping this in mind, it is interesting that the first and second reduction potentials are relatively unaffected by the nature of the tetraoxa[8]circulene, that is, the first and second reduction potentials for **3B1N** are −2.38 and −2.55 V, respectively, whereas values of −2.41 and −2.55 V are found for **1B3N**. For **4B** a slightly lower second reduction potential (−2.60 V) was observed.

Despite almost identical values for the highest reduction potential, the LUMOs are remarkably different, as illustrated by the orbital plots of the LUMOs and HOMOs of **4B** and **4N** in Figure 3. The lowest reduction potentials show
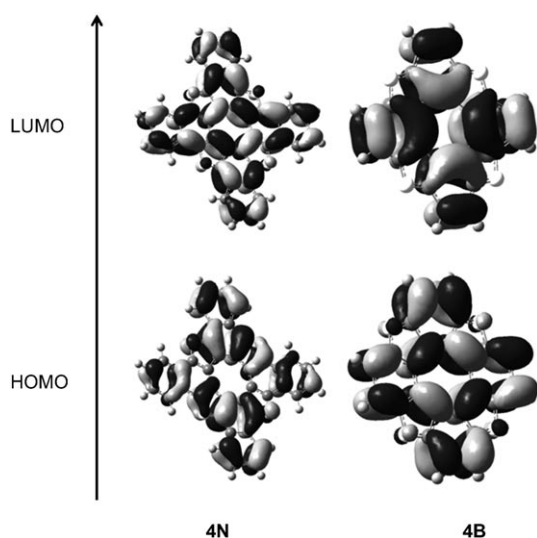

Figure 3. HOMO and LUMO of unsubstituted all-benzene tetraoxa[8]circulene (**4B**) and all-naphthalene tetraoxa[8]circulene (**4N**) obtained from B3LYP/6-31G(d) geometry optimisations and subsequent calculations of orbitals.[15]

dependence on the system; a linear correlation between the potentials and the number of naphthalene units was observed. The lowest oxidation potential shows an exponential dependence on the number of naphthalene units, indicating an exponential correlation of the HOMO–LUMO gap. Such behaviour is often observed in π-extended systems, in which the absorption energy exponentially reaches an asymptotic value with the number of aromatic or chromophoric units.[15] It is reassuring that this relationship can be identified from the reduction and oxidation potentials, as it is difficult to infer from the absorption spectra. This is due to overlapping tran-

sitions of several electronic states in the absorption spectra, which corroborates the conjugated nature of the entire system.

The electronic properties of the tetraoxa[8]circulene series, deduced from the electrochemical studies, suggested that an OLED made from **4B** should have a blue shifted electroluminescence (EL) spectrum as compared to OLEDs of the other tetraoxa[8]circulenes. This was confirmed by comparing the normalised EL spectra of devices made from **4B**, **3B1N**, *p*-**2B2N** and *o*-**2B2N** (Figure 4a).

The optoelectronic performance of the tetraoxa[8]circulenes were examined by fabricating devices on patterned indiumtinoxide (ITO) glass plates. A mixture of poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonate) (PEDOT:PSS) was initially deposited on the ITO plates followed by spin coating a layer of a mixture of the tetraoxa[8]circulene and (4,4′-*N*,*N*′-dicarbazole)biphenyl (CBP). A layer of 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TPBI) was then thermally evaporated onto the substrate followed by a layer of Ba and finally Al. The EL spectra are shown in Figure 4a, in which a peak at ≈380 nm was observed for **3B1N** and *p*-**2B2N**. This peak was ascribed to luminescence from the CBP host, which indicates that for these devices there is not a complete energy transfer. Characteristic properties for the optoelectronic devices are listed in Table 3.

The devices have moderate light intensities at the maximum operation voltage; in particular *p*-**2B2N** displays the largest intensity at an operation voltage of 12 V. In the interest of preparing a blue OLED, it is worth noting that **4B** has a significant light intensity of 276 cd m^{-2} at 10 V. The CIE coordinates for the devices are: 0.20, 0.22 (**4B**); 0.22, 0.41 (*o*-**2B2N**); 0.25, 0.38 (*p*-**2B2N**) and 0.29, 0.41 (**3B1N**). These are plotted in Figure 4c). In comparison to other non-polymeric OLEDs, the devices exhibit a somewhat high
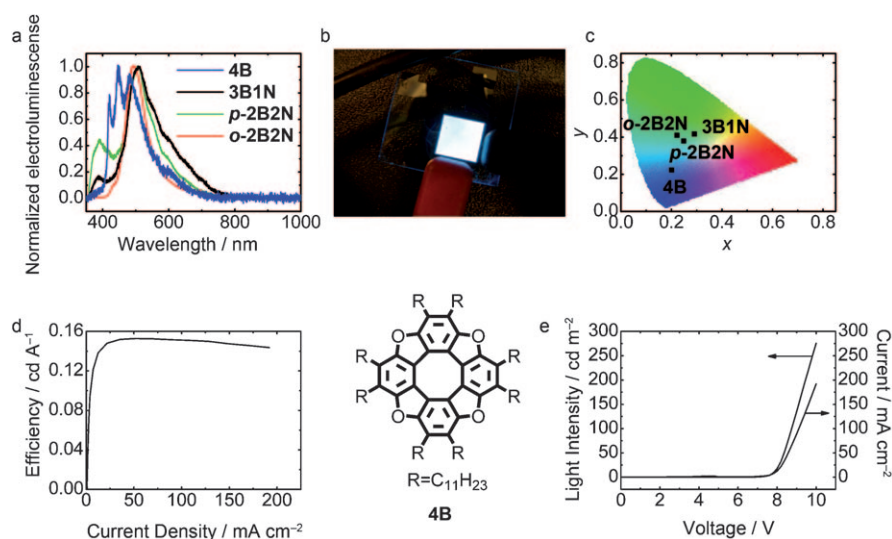

Figure 4. OLED data for the serie of the π-extended-tetraoxa[8]circulenes. a) EL spectra of the devices. b) Picture of a working OLED of **4B**. c) Plot of the CIE coordinates for the working OLED devices. d) and e) Diode characteristics for an OLED device made from **4B**.

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Table 3. Device properties.

Compound	Max. efficiency [cd A^{-1}][a]	Onset [V]	Intensity [cd m^2]	Current [mA cm^{-2}][b]
4B	0.15 (70)	7	276	192 (10)
o-2B2N	1.7 (0.44)	7	3.76	0.22 (10)
			14	13 (11.6)
p-2B2N	0.62 (79)	8	196	35 (10)
			817	135 (12)
3B1N	1.1 (12)	9	47	4.5 (10)
			386	44 (12)

[a] The numbers in parentheses are currents in mA cm^{-2} measured at maximum efficiency. [b] The numbers in parentheses are voltages in V measured for the tabulated currents.

onset voltage.[16] However, it is difficult to compare the devices to other non-polymeric OLEDs, as most of the reported OLED devices are made by thermally evaporating the organic layer onto the substrates, whereas the devices discussed above are made by spin-coating the organic layer.[17]

A schematic of an electroluminescent device with **4B** is shown in Figure 5a, in which the TPBI layer serves as a hole barrier, owing to its comparably low HOMO. It has been shown in previous work that efficiency increases considerably when electron–hole recombination does not occur directly at the cathode.[18] All the devices were fabricated with

CBP as the host material, doped with the tetraoxa[8]circulenes. CBP is known to harvest nearly all formed excitons, and luminescence occurs from the devices by charge transfer from the CBP host to the tetraoxa[8]circulene.[19] Both singlet and triplet excitons are formed in the CBP host, but since the tetraoxa[8]circulenes used are not likely to have a significant triplet quantum yield, the devices are expected to display only negligible electrophosphorescence.

To further investigate the performance of the OLEDs, the tunnelling of holes was investigated using the Fowler–Nordheim expression, valid at higher electrical field strengths. It is speculated that the Schottky barrier model applies at lower field strengths.[20] When plotting $\ln(I/U^2)$ (in which I is the current measured at the potential U) against the reciprocal potential, a linear region is identified for all the devices above the turn-on voltage.[15] At high potentials a fall-off was observed, which is interpreted to originate from local heating effects in the device. Assuming a square potential for the tunnel barrier, energies for the barrier height can be deduced if the thickness of the PEDOT:PSS and CBP/tetraoxa[8]circulene layers are known. A total layer thickness between 80 and 120 nm gives reasonable results for the barrier heights when comparing with the barrier heights for hole-injection deduced from the Fermi- and HOMO levels outlined in Table 3 and Figure 5.

In summary, we have prepared a series on π-extended tetraoxa[8]circulenes and have identified a promising platform for the development of blue OLEDs. The very high chemical stability and the intriguing optical and electrochemical properties of the tetraoxa[8]circulenes gives rise to optimism with regards to their use in optical devices.
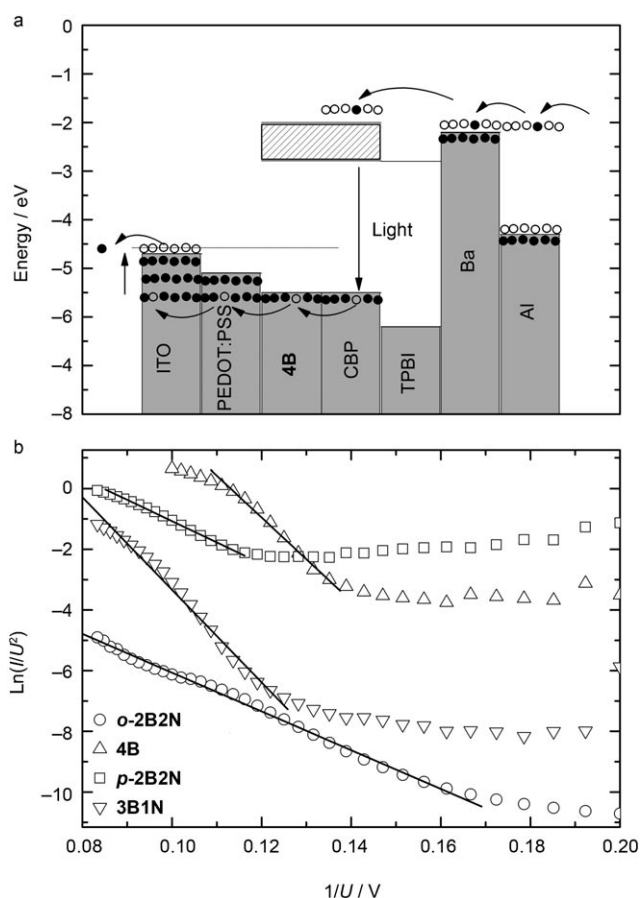

Figure 5. a) Schematic illustration of the OLED devices (e.g., **4B**). b) Fowler–Nordheim plots for the devices.

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