

Designing molecules to bypass the singlet-triplet bottleneck in the electroluminescence of organic light-emitting-diode materials.

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Electroluminescence in organic light emitting diode (OLED) materials occurs via the recombination of excitonic electrons-hole pairs. Only the singlet excitons of commonly used OLED materials, e.g., Aluminum trihydroxyquinoline (AlQ_3), decay radiatively, limiting the external quantum efficiency to a maximum 25%. Thus 75% of the energy is lost due to the triplet bottleneck for radiative recombination. We consider molecules derived from AlQ_3 which bypass the triplet bottleneck by designing structures which contain strong spin-orbit coupling. As a first stage of this work, we calculate the groundstate energies and vertical excitation energies of Al-arsenoquinolines and Al-boroarsenoquinolines. It is found that the substitution of N by As leads to very favourable results, while the boron substitution leads to no advantage.

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I. INTRODUCTION

Increased interest in the use of organic materials[1] for a variety of optical and electronic applications, including the fabrication of electroluminescent devices, field-effect transistors, lasers etc., has followed the successful demonstration of devices with useful lifetimes and performance.[2, 3, 4, 5, 6] The new advances depend on a better choice of organic materials, and on new technologies borrowed from recent developments in semiconductor technology, thin films, surface science and materials preparation. The luminescence of organic light emitting diodes (OLED) proceeds by the injection of electrons and holes which form excitons and then decay radiatively to the ground state.[7] Although better design of the diode structure can improve the quantum efficiency of the device considerably, selection rules for optical transitions in these organic materials limit the radiative channel to singlet excitons. Hence the three-times more abundant triplet excitons decay by *nonradiative* channels and are wasted. This raises the possibility of an enormous gain in efficiency if the triplet excitons could also be harvested for light emission. Baldo et al. attempted to tap the triplet excitons by energy transfer from the host organic to a porphine-platinum fluorescent dye.[8]

The objective of this work is to design the *host material itself* so that the singlet-triplet selection rules become irrelevant. This is done using heavy atoms where spin-orbit interactions ($L-S$ coupling) become important, so that S^z is no longer a good quantum number. We note in passing that the spin selection rules cannot be circumvented by applying magnetic fields, or incorporating local magnetic impurities since the spin remains a good

quantum number even in the presence of such fields. It is necessary to bring the electrons into atomic sites where the spin-orbit coupling intervenes to break the spin selection rules. Since metal chelates (e.g., Al, In, Sc) of 8-hydroxyquinoline have provided some of the most successful OLED materials, we will consider molecules based on modifications of these standard materials.

II. NEW MOLECULES

Since AlQ_3 , i.e., $\text{Al}(\text{8-hydroxyquinoline})_3$, has been a very successful host material (fig. 1) in OLEDs, we consider two structures derived from AlQ_3 where the quinoline part is modified. These are shown in Figs. 2 and 3, and are obtained by first replacing the N atom by an As atom (an arsenoquinoline, denoted by $\text{Al}(\text{AsQ})_3$), and then replacing the carbon atom *para* to the As atom by a boron atom, cf., fig. 3, to give $\text{Al}(\text{AsBQ})_3$. We proceed to investigate if such molecules are stable, and what luminescence properties could be expected from them, using sophisticated state of the art quantum chemical calculations. These molecules were chosen for this investigation following detailed studies of AlQ_3 itself. For example, on examining the electron densities of the ground state and the excitonic states of AlQ_3 , it is found that the Al ion itself does not play a strong role in determining the exciton density. That is, replacing the Al by a heavy chelating atom where the $L-S$ coupling is strong would not help the luminescence. This is also experimentally known to be true, e.g., in the Scandium complex. On the other hand, the N atom in the quinoline ring participates decisively in the relevant excitonic states. Thus replacing the N atom by As is appealing. Of course, the spin-orbit interaction is even stronger in Sb, but replacing N by Sb would be too strong a chemical modification and the synthesis of

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the corresponding molecule may be even more difficult. hence here we examine the case of replacing N by As. Preliminary calculations showed that the N→As substitution had the effect of shifting the luminescence to the red, while the shorter wavelength of the AlQ₃ is more attractive for device applications. It was envisaged that replacing the *p*-C atom, i.e, the C atom in the *para*-position to the N-atom, by boron would shift the spectrum back to the shorter wavelength regime. In this communication we examine these questions using sophisticated quantum calculations. We find that the N→As leads to a strong improvement in the spectrum, without too much of an adverse red shift, while the further substitution of the *p*-C atom by B is not useful.

III. RESULTS

The ground states of the metal chelates were calculated using the Gaussian-98 code at the B3LYP/3-21G* level.[9, 10]. Both Al(AsQ)₃ and Al(AsBQ)₃ were found to be stable. Hence it should be possible to achieve a synthesis of these materials. The vertical excitation spectra were calculated at the TDB3LYP/3-21G* level.[11]. At this point we have *not* included spin-orbit coupling as yet. This is because the chelate structures, containing three 8-hydroxyquinoline groups, are too large for a direct implementation of relativistic effects. This would be undertaken as the next stage of this investigation. In anticipation of those results we have simply replaced the triplet oscillator strengths which are zero by an analogous singlet oscillator strength and plotted the excitation spectra (see also table I). Some justification for the assumption that the singlet → groundstate oscillator strength and that for the triplet → ground become very similar in the presence of the spin-orbit interaction in As is given in the appendix. The resulting enhanced triplet+singlet spectra as well as the standard (singlet only) spectra are shown in Fig. 4

The excitations marked with an asterisk in Table I, for AlQ₃ and Al(AsQ)₃ are transitions which involve the H (i.e., HOMO) and L (i.e, LUMO) orbitals in a major way. Thus in AlQ₃, the first singlet, i.e., S1, is approximately 0.98H → L + other configurations. while the T4 is approximately 0.96H → L + other configurations. In the As substituted form Al(AsQ)₃ we have T4 being 0.9H → L + other configurations, while the S1 is higher in energy and is an admixture with 0.94H → L + other configurations. Hence these transitions may be identified with the HOMO-LUMO gaps used in simplified theoretical schemes. Such simplified schemes are of course modified when CI is included, where in various excited states (based on the ground state determinant) get included. The deficiencies of the simpler schemes become quite evident when we go to the boron substituted form Al(AsBQ)₃. Here it is not possible to identify a transition where the initial state is mostly HOMO (i.e.,

> 90%). In fact, T5, at 2.105 eV has 0.9H but the final orbital is L+4 admixed with other configurations. The H → L transitions are at T8 with 0.76H in the initial orbital, and S4 with 0.79H in the initial orbital. This shows that the B substitution effectively introduces transitions in the nominal H → L gap of simplified theories. Four additional transitions of Al(AsBQ)₃, which might be labeled T10, S7, S8, and S9 in the notation of Table I are at 2.908, 2.913, 3.057, and 3.103 eV and complete the same energy window as in the other two compounds.

Comparison of the calculate Al(Q)₃ spectra with experiment is not shown here, since such a comparison was carried out in a previous publication.[7] Such comparison require taking due account of solvent effects, or aggregation effects etc, and as well as considerations of non-radiative pathways, since the experimental spectral intensities are affected by many such factors. The objective of this study is to examine the Al(Q)₃, Al(AsQ)₃, and Al(AsBQ)₃ spectra calculated under the *same* conditions, and in the same energy window.

These results show the Al(AsQ)₃ spectrum in the same energy window as Al(Q)₃; however, its spectral features are more intense. The main intensity is red shifted by 0.3 eV, confirming the conclusions based on more elementary considerations. However, there are now transitions in the blue as well. The substitution of the *p*-carbon by boron, i.e, Al(AsBQ)₃, shows that the stronger absorption lines are somewhat blue shifted. The center of gravity of the spectral intensity is slightly blue shifted, although many peaks in the middle of the energy range are red shifted. The substitution of a nominally trivalent boron atom for a nominally *sp*² C site leads to some distortion of the original ring structure. The improvement of the spectrum is questionable. Hence, it is clear that we need to look for a better choice than boron. In fact, Fig. 4 suggests that the Al(AsQ)₃ provides an excellent improvement over the more usual AlQ₃ while its synthesis would not be as difficult as the boron substituted form.

IV. CONCLUSION

We show that the spectra of metal chelated 8-hydroxyquinolines can be manipulated and improved to obtain much better luminescence properties. We have shown how the spectrum can be shifted and that the intensity would increase if the triplet excitations could be harvested. The replacement of the N in AlQ₃ by an As atom provides a definite improvement, while the further substitution of the *p*-Carbon by B is not seen to provide a useful improvement. This is a preliminary study which anticipates a more detailed calculation where the *L* – *S* coupling would be explicitly included.

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APPENDIX A: SOME CONSIDERATIONS OF THE SPIN-ORBIT INTERACTION

The relativistic effects for heavy atoms can be included up to α^2 , where α is the fine structure constant, in first principles pseudopotentials. The result splits into two terms of the form:

$$V_{rel}(r) = \sum_l |l > [V_l(r) + V_l^{so}(r)\mathbf{L}\cdot\mathbf{S}] < l| \quad (\text{A1})$$

where the l -sum is a sum over angular momentum states. The first term is the scalar part, and is not significant for the problem of the singlet-triplet bottleneck. The second term in the above equation, $V_2 = \sum_l |l > V_l^{so}(r)\mathbf{L}\cdot\mathbf{S} < l|$ introduces mixing between orbital and spin angular momentum states, leading to the break down of the usual spin selection rules. However, the full inclusion of the spin-orbit term in first-principles CI calculations of the type discussed in this paper is numerically quite prohibitive, given the large number of electrons which need to be handled in typical LED materials. Leave aside CI calculations, the numerical evaluation even with a pseudopotential scheme is extremely demanding.[13]

The spin-orbit operator is highly local in the sense that it is mostly sensitive to changes in electron density close to the nucleus, where relativistic effects dominate. Thus we may look at calculations for systems containing As as

a guide. In order to get at least a simple “grosso modo” estimate, we may compare the homo-lumo gap (bandgap) of As obtained from a non-relativistic (i.e, standard) calculation with a calculation where some effort is put into an evaluation of the relativistic effects.[14] Thus Gonze et al. have carried out calculations which can be used for a simple estimate of the effect of the spin-orbit effect in As. The s-levels in As are about 9 eV lower than the p-levels. The p-levels suffer a splitting of about 0.36 eV in As, and is a measure of the strength of the spin-orbit term in As. Since we are concerned with singlet and triplet excitons, we should compare this spin-orbit splitting with the gap between hole energies and the Fermi energy, and electron energies and the Fermi energy in As. Numerical values for these, for As have been given by J.-P. Issi,[15], and by Priestly et al.,[16]. Issi gives 0.154 eV and 0.202 eV for electrons and holes, while Priestly et al give 0.177 and 0.190 eV. Hence the total effect for an electron-hole pair is of the order of 0.35 eV by one estimate, and 0.36 eV by the second estimate. These numbers are in fact very similar to the spin-orbit energy (~ 0.36 eV). These considerations suggest that when estimating the oscillator strengths for the processes $< eh(\uparrow, \uparrow)|\vec{r}|\text{groundstate}>$ and $< eh(\uparrow, \downarrow)|\vec{r}|\text{groundstate}>$, we may, as a *grosso modo* estimate take the oscillator strengths to be of the same magnitude.

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Fig.1 Structure of the light emitter AlQ₃. See ref.[12] for bond lengths, angles etc.

Fig.2 N atoms of the quinolines have been replaced by As in Al(AsQ)₃

Fig.3 The C atom in the *para*-position to N has been replaced by B in Al(AsBQ)₃. The Kekule-type structure is only schematic.

Fig.4 Calculated spectra of the three compounds. Solid curves: only the singlet is available for light emission; dashed curves: the triplet exciton is also harvested (using a f_{os} comparable to the nearest singlet (see appendix). Note that the intensity axis is logarithmic. The calculation is for isolated molecules, and hence a broadening of 0.025 eV has been included.

TABLE I: Transition Energies E in eV, Oscillator Strengths (a.u.), f_{os} , for AlQ_3 , Al(AsQ)_3 , and Al(AsBQ)_3 . Transition type is labeled S or T to indicate singlet or triplet character for no L-S coupling (thus, e.g., T7 is the 7th triplet). The oscillator strength f_o for triplets are not given. The transitions marked with an asterisk are the ones which are most closely identifiable with a HOMO \rightarrow LUMO transition. This identification is not very satisfactory in the Al(AsBQ)_3 molecule (see the text)

Transition	AlQ_3		Transition	Al(AsQ)_3		Transition	Al(AsBQ)_3	
type	E	f_{os}	type	E	f_{os}	type	E	f_{os}
T1	2.152		T1	1.847		T1	1.870	
T2	2.190		T2	1.854		T2	1.932	
T3	2.228		T3	1.867		T3	1.945	
S1*	2.718	0.0047	T4*	2.613		T4	2.102	
T4*	2.741		S1*	2.631	0.0129	T5	2.105	
S2	2.909	0.0590	T5	2.744		T6	2.181	
S3	2.924	0.0180	S2	2.769	0.0060	S1	2.333	0.0008
T5	2.925		S3	2.897	0.1066	S2	2.337	0.0015
S4	3.000	0.0423	S4	2.998	0.0265	S3	2.409	0.0011
S5	3.029	0.0027	T6	3.002		T7	2.595	
T6	3.056		T7	3.054		*T8	2.609	
S6	3.187	0.0173	S5	3.116	0.0242	*S4	2.614	0.0169
T7	3.228		S6	3.195	0.0244	S5	2.643	0.0138
T8	3.255		T8	3.232		T9	2.753	
S7	3.273	0.0049	S7	3.324	0.0741	S6	2.756	0.0004

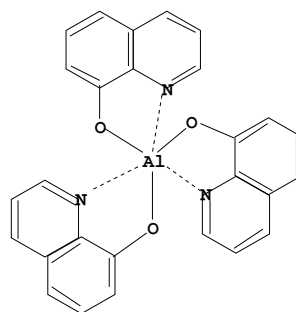


Fig.1 Dharma

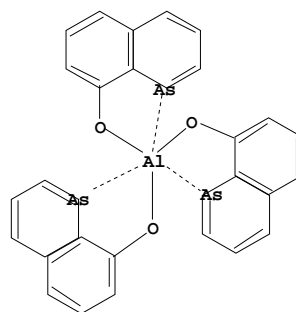


Fig.2 Dharma

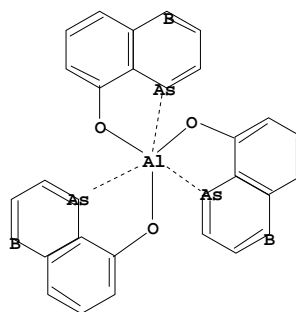


Fig.3 Dharma

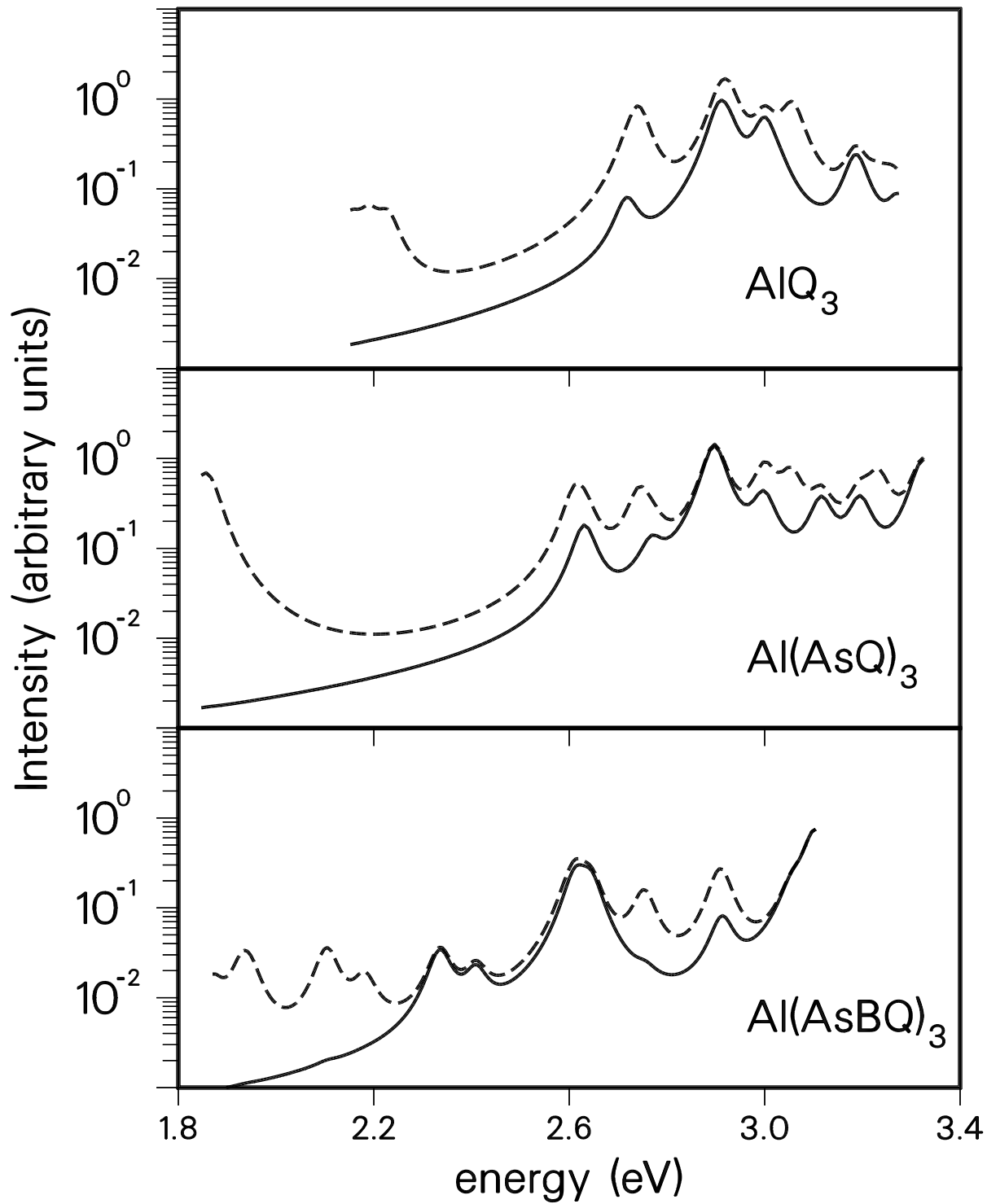


Fig.4 Dharma