

# Molecular Building Blocks for Efficient Solid State Lighting

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## ABSTRACT

General illumination consumes 22% of the electricity generated in the U.S. This huge proportion is partly due to the ubiquity of artificial lighting but also the inefficiency of converting electrical energy to light. Incandescent lightbulbs convert a mere 5% of the supplied power into light (most of the rest emerging as heat) whereas the more efficient fluorescent bulbs achieve about 20% efficiency. Improving the efficiency of these light sources is difficult since in all cases the emission of light is essentially a by-product of an energetic excitation process. In contrast, solid state lighting utilizes materials which directly convert electrical energy to light with little production of heat and therefore have the potential for far higher efficiency, with over 70% demonstrated in the infrared. New materials based on direct bandgap semiconductors and organic light emitters may permit this level of efficiency for general lighting. In both cases, however, understanding the nanoscale structure of the material is critical to achieving high efficiency. This is particularly evident in the case of organic molecular compounds, where weak inter-molecular interactions can permit the photophysical properties of a solid to be tuned by changing the chemical structure of the molecular building block.

**Keywords:** lighting, molecular, organic, solid state

## 1 INTRODUCTION

Organic light emitting device (OLED) technology has improved in efficiency over the last decade due to the development of new molecular materials.<sup>1</sup> As a result, commercially available products (e.g., small color displays for cellular telephones) based on this technology have become available in the marketplace.<sup>2</sup> A further outcome of this progress is that the efficiency of OLEDs has increased to the point where they are worth considering for solid state lighting applications.<sup>3</sup> OLEDs have unique advantages for lighting applications in that they are large area emitters (as opposed to point sources) which can therefore be used without a diffuser or luminaire, potentially increasing the overall lighting system efficiency.

Realizing this potential has created new challenges to overcome. For example, a white OLED-based lighting solution reaching the efficiencies in excess of 150 lm/W will require devices, which operate at close to 100% internal quantum efficiency (IQE) and close to the

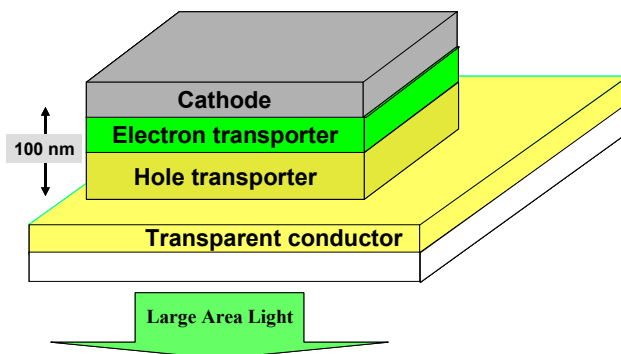


Figure 1: Simplified schematic cross-section of an organic light emitting devices (OLED)

minimum achievable operating voltage. An IQE in excess of 80% has already been demonstrated and various schemes exist<sup>4,5</sup> to improve the optical out coupling at least to 50%. In all cases, however, the most efficient materials on the basis of IQE are guest-host composites consisting of up to 20% of an organometallic phosphor in a charge transporting host material. Electroluminescence (EL) from the dopant results either from energy transfer from the host, direct trapping of charge on the phosphor or a combination of the two processes.<sup>6,7</sup> The best phosphors are based on a chelated heavy metal ion (typically Ir and Pt). Operating voltages of small molecule composites, however, remain high (typically ~ 10 V at the high brightness relevant to lighting) compared to polymer-based OLEDs unless ionic or small molecule dopants are added.<sup>8</sup> Blue electrophosphorescence, which is a necessary component of white light, has been a particular challenge because the triplet excited state of the host material must be higher than that of the dopant in order to prevent quenching of the dopant emission. This requires a host material with even higher triplet energy than the blue phosphor dopant and this is difficult to achieve in a molecule which also forms morphologically stable thin films.

The host material for a blue OLED must have a triplet energy ( $E_t$ ) > 2.8 eV which requires an extremely short conjugation length. There is a tradeoff, however, between decreasing the extent of the  $\pi$ -aromatic system to increase the singlet and triplet exciton energies and adversely affecting charge transport. Deep blue phosphors have been demonstrated using insulating, wide bandgap host materials based on tetra aryl silanes with charge transport occurring via hopping between adjacent dopant molecules, but at increased operating voltage, and therefore less power

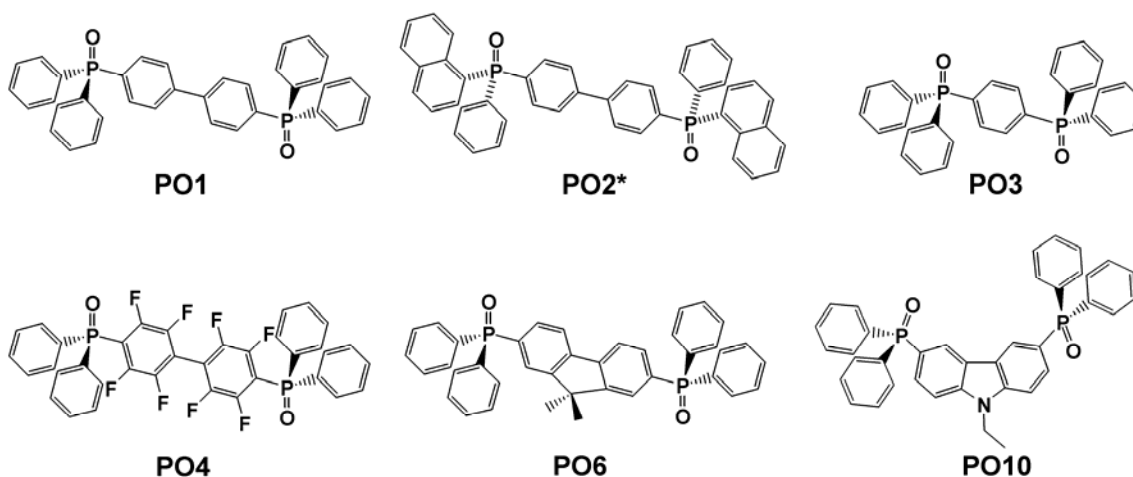
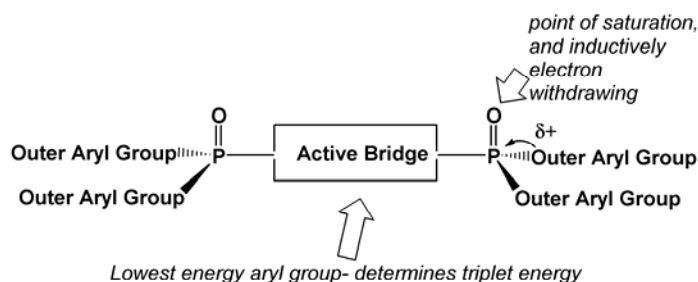


Fig. 2. General design concept for achieving organic charge transporting host materials with high triplet energies and the chemical structures of specific examples are shown. Note that the “active” aryl group in PO2 is the naphthyl ring, rather than the biphenyl bridge. \*PO2 is a mixture of optical isomers and no stereochemistry is specified.

efficient devices. In this paper, we present a design strategy for developing organic host materials for blue electrophosphorescence which have the targeted high triplet energies without sacrificing the corresponding charge transport properties required for power efficient OLEDs. This is accomplished by using saturated linkers to connect molecular building blocks with high triplet exciton energy to build larger, tractable molecules in a bottom-up design scheme.

We recently reported that organic phosphine oxides function as wide band gap and charge transporting host materials for the sky blue phosphorescent dopant, iridium(III)bis(4,6-(di-fluorophenyl)-pyridinato-*N,C2'*)picolinate (FIrpic) in OLEDs with peak quantum efficiencies of  $\sim 8\%$  and low drive voltages.<sup>9,10</sup> The phosphine oxide (P=O) moieties act as a point of saturation (i.e., breaks  $\pi$ -electron conjugation) between the “active” chromophore bridge (biphenyl and 9,9-dimethylfluorene in PO1 and PO6, respectively) and outer phenyl groups, resulting in materials with triplet energies characteristic of the lowest energy aryl group in the molecule (i.e. the active bridge) but with physical properties suitable for device fabrication by thermal sublimation. Here, we describe a general design concept for high triplet energy host materials (Fig. 2) by extending the work to other high triplet energy chromophores including naphthalene, phenyl,

octafluorobiphenyl, and N-ethylcarbazole. Device results using some of these hosts doped with FIrpic are discussed.

## 2 MOLECULAR BUILDING BLOCKS

The PO compounds were designed to have photophysical properties (e.g. high triplet exciton energy) characteristic of the lowest energy aryl group with the thermal and charge transport properties of a larger molecule. To demonstrate the effectiveness of the design, absorption and emission spectra of PO1, PO2, PO4, and PO10 in  $\text{CH}_2\text{Cl}_2$  solution are shown in Fig. 3 compared to the absorption and emission properties of the relevant aryl group.

The absorption maximum of PO1 was red shifted from biphenyl by  $\sim 20$  nm (corresponding to an energy shift of 0.4 eV) and was closer to the absorption spectrum of the dibromo derivative (see Fig. 3a). This result is similar to previously reported work using the 9,9-dimethylfluorene bridged PO derivative, PO6. The energy shifts for both PO1 and PO6 are similar to the brominated aryl bridges because both  $\text{Ph}_2\text{P}=\text{O}$  and Br substitution impart an inductive electron withdrawing effect along the long axis of the respective bridge. Similar trends were observed for PO4, shown in Fig. 3c. In the case of PO2, which is the only material in this study containing two extended chromophores (the biphenyl bridge and the outer naphthyl

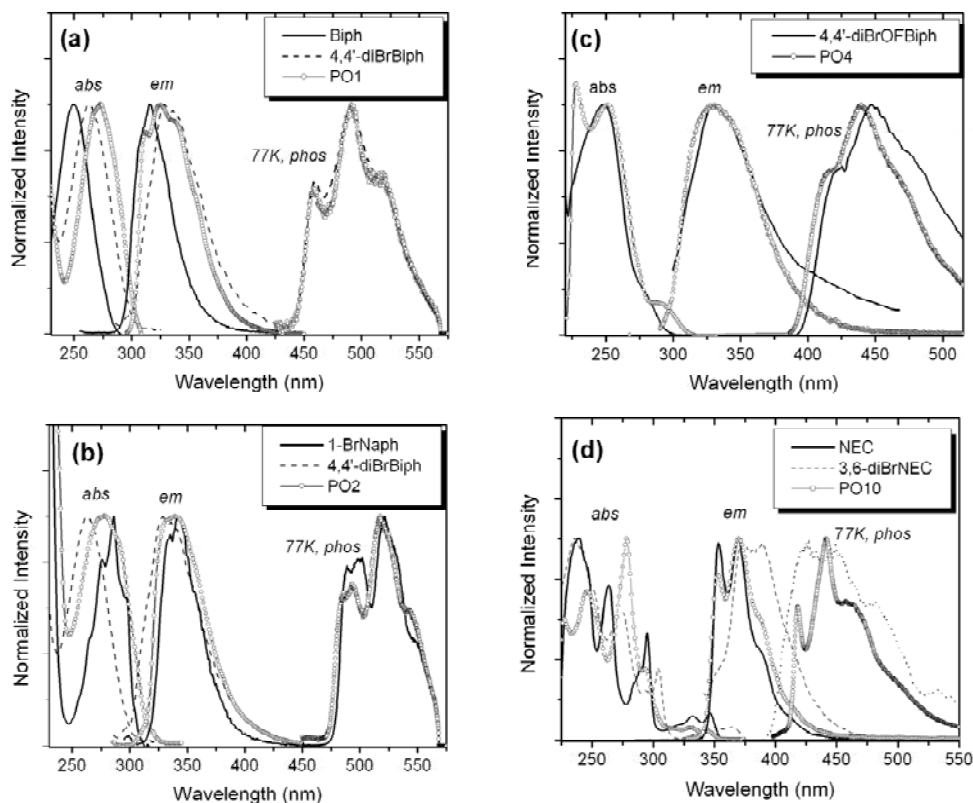


Fig. 3. Absorption and emission spectra (room temperature,  $\text{CH}_2\text{Cl}_2$ ) and phosphorescence spectra (77K,  $\text{CH}_2\text{Cl}_2$ ) shown for (a) PO1, (b) PO2, (c) PO4 and (d) PO10 compared to their component aryl groups [biphenyl (Biph), 4,4'-dibromobiphenyl (4,4'-diBrBiph), 1-bromonaphthalene (1-BrNaph), 4,4'-dibromooctofluorobiphenyl (4,4'-diBrOFBiph), 3,6-dibromo-N-ethylcarbazole (3,6-diBrNEC) and N-ethylcarbazole (NEC)].

groups), the absorption spectrum showed contributions from both aryl groups (see Fig. 3b). The lowest energy absorption band originates from the naphthyl ring, which is also the lowest energy aryl group in the molecule. The absorption spectrum of the carbazole bridged compound, PO10, shown in Fig. 3d, was closer to N-ethylcarbazole (NEC) than the dibrominated derivative (3,6-diBrNEC) because substitution of the NEC chromophore is along the *short* axis of the molecule (as discussed previously by Marsal, et al. for different brominated derivatives of carbazole).<sup>9</sup> Photophysical spectra for PO3 are shown in Fig. 4. This wide band gap phenyl bridged PO compound exhibited an absorption spectrum similar to triphenyl phosphine oxide (TPPO),<sup>10</sup> but with a weak red shifted absorption band likely from the bridging phenyl ring.

### 3. LIGHT EMITTING DEVICES

To evaluate the usefulness of the PO compounds as electron transporting host materials for blue electrophosphorescence, OLEDs were fabricated using the shortest wavelength commercially available phosphorescent dopant, FIrpic, doped at 5%, 10% and 20% by mass via co-evaporation into a PO (PO1, PO3, PO6 and PO10) host

layer. The device structure was grown on ITO glass ( $< 15\Omega/\square$ ) by thermal evaporation as described previously<sup>11,12</sup> and was composed of, in sequence, 200 Å CuPc / 200 Å  $\alpha$ -NPD / 60 Å TCTA / 200 Å 5, 10 or 20% FIrpic in PO / 200 Å PO / 6 Å LiF / 1000 Å Al. The PO compounds served both as electron transporting host in the emissive layer and as an exciton and hole blocking layer in this device configuration. It is assumed that holes are transported in the doped light emitting layer by hopping conduction between FIrpic molecules. Device results are reported in Table 1 and compared to previous results reported for PO1 and PO6.

All PO materials were effective as hosts for FIrpic giving maximum external quantum and luminance efficiencies of  $\sim 8\%$  and  $\sim 21$  cd/A, respectively. Furthermore, light emission was observed at very low applied voltage of  $< 3.9$  V at maximum quantum efficiency (at which point the brightness was typically  $\sim 10$  cd/m<sup>2</sup>) giving luminous power efficiencies ranging from  $\sim 17$  to 25 lm/W. The high brightness results (800 cd/m<sup>2</sup>) were obtained at 4.8 – 6.3V as compared with  $> 9$ V typically reported using carbazole-based host layers.<sup>13</sup> Only FIrpic emission was observed from devices with a 20% FIrpic doping concentration. At 10% doping, a small contribution from TCTA fluorescence

is observable. This becomes more significant at the lowest doping concentration of 5%. This is consistent with electron leakage from the light emitting layer into the TCTA and poor hole injection from the TCTA into the light emitting layer at low FIrpic concentrations (because holes are injected directly into FIrpic states due to the low-lying HOMO of the PO molecules), suggesting that the efficiency data could be further improved by incorporation of an electron blocking layer and use of higher work function anode materials or additional hole injection layers.

Table 1. Device properties for OLEDs using PO hosts doped with FIrpic

	Property / Host : % FIrpic	PO1 : 20%	PO3 : 10%	PO6 : 10%	PO10 : 20%
Results at maximum quantum efficiency	$\eta_{\text{ex,max}}(\%) [J (\text{mA}/\text{cm}^2)]$	7.8 (0.09)	8.1 (0.23)	8.1 (0.002)	8.3 (0.03)
	$\eta_{\text{c,max}}(\text{cd}/\text{A})$	20.8	21.5	21.5	22.2
	$V_{\text{@max QE}}$	3.9	3.6	3.0	3.7
	$\eta_{\text{p,max}}(\text{lm}/\text{W})$	16.7	18.8	25.1	18.8
Results at "lighting brightness" taken to be 800 cd/m <sup>2</sup>	$\eta_{\text{ex}}(\%)$	6.7	7.2	4.4	5.7
	$J (\text{mA}/\text{cm}^2)$	4.2	4.1	7.6	5.6
	$\eta_{\text{c}}(\text{cd}/\text{A})$	18.0	19.3	11.8	15.0
	$V_{\text{opt}}$	5.6	4.8	5.6	6.3
	$\eta_{\text{p}}(\text{lm}/\text{W})$	10.1	12.7	6.7	7.7

<sup>a</sup> $\eta_{\text{ex,max}}$ , maximum external quantum efficiency;  $\eta_{\text{c,max}}$ , maximum luminance efficiency;  $\eta_{\text{p,max}}$ , maximum luminance power efficiency; and  $V_{\text{opt}}$ , operating voltage at a specified current. \*Reported at lighting brightness (800 cd/m<sup>2</sup>).

#### 4. CONCLUSIONS

The phosphine oxide moiety has been successfully used as a point of saturation in order to build sublimable, electron transporting host materials starting from small, wide bandgap molecular building blocks. The presence of the P=O group is expected to lead to a lowering of the LUMO and HOMO states, which is consistent with the photophysical data presented. This design principle leads to a range of new materials suitable as host materials for blue organic phosphors which generate bright light at a lower voltage than previously published material systems. The low operating voltage is ascribed to a combination of facile electron injection into the PO layer and hole transport by hopping conduction between phosphorescent dopant molecules. All the materials tested give similar external

quantum efficiencies although the current density and phosphor loading at peak efficiency and the operating voltage show some variation. These variations do not appear to be correlated with the band gap or frontier orbital energies of the particular host material. We note, however, that the P=O moiety also has a strong order-directing influence on the material and some evidence of molecular-scale aggregation has been previously obtained for PO6. The bridge unit also influences the preferred intermolecular interaction geometry via hydrogen bonding and edge-to-face interactions.<sup>14</sup> These properties are expected to strongly influence electron transport within the layer, which has a concomitant effect on the charge balance in the light emitting layer, and therefore on the device efficiency as a function of injected current. Further study of the nanoscale structure of these materials is therefore necessary to fully understand how to maximize the efficiency and minimize the voltage of devices based on these materials.

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