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Acridinone/Amine(carbazole)-Based Bipolar Molecules: Efficient Hosts for Fluorescent and Phosphorescent Emitters

Dileep A. K. Vezzu,[†] Joseph C. Deaton,[‡] Mohammad Shayeghi,[†] Yumin Li,[†] and Shouquan Huo*,[†]

Department of Chemistry, East Carolina University, Greenville, North Carolina 27858, and Research Laboratories, Eastman Kodak Company, 1999 Lake Avenue, Rochester, New York 14650

huos@ecu.edu

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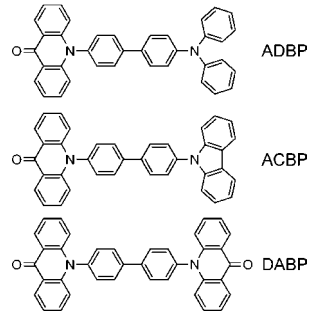
ABSTRACT



Three acridinone-based molecules ADBP, ACBP, and DABP were synthesized, and their application to the OLED devices was investigated. When used as the host for either the deep blue singlet or the green triplet emitter in OLED devices, the bipolar molecules ADBP and ACBP demonstrated superior performance compared to either DABP or commonly used host CBP, remarkably lowering the drive voltage and improving efficiencies.

Since the ground-breaking demonstration of organic light-emitting diodes (OLEDs) by Tang and VanSlyke,[1] there has been increasing interest in developing highly efficient OLED devices because of their great potential in display, solid-state lighting, and other applications.[2] The OLEDs are current-driven devices; therefore, power efficiency is one of the major issues associated with OLED technology, which has attracted much research interest, particularly under the current environment of an energy crisis. There are two ways of improving power efficiency; one is to increase the quantum efficiency and the other is to reduce the drive voltage. Quantum efficiency can be maximized by using a phosphorescent emitter doped into the emissive layer of an OLED device since both singlet and triplet excited states

[†] East Carolina University.
[‡] Eastman Kodak Company.

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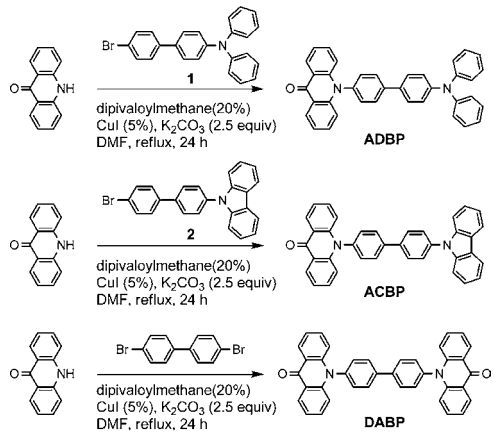
generated by the charge recombination (electroexcitation) can be harnessed with the use of a phosphorescent dopant (triplet dopant).[3] However, in principle, phosphorescent OLEDs require higher drive voltage because the host used in the emissive layer needs to have a larger band gap than that of a host used in a fluorescent device that emits the same color of light. Therefore, reduction in drive voltage becomes critical to the development of highly efficient phosphorescent devices in terms of energy consumption.

Several approaches can be employed to reduce drive voltage and improve the performance of OLED devices, which include doping transporting layers,[4] designing better transporting materials,[5] and using mixed host materials[6] in the emissive layer. Instead of the mixed host, bipolar molecules capable of transporting both charges offer clear advantage because of the simplification of the device fabrication. Several bipolar molecules have been reported,[7] such as borane/amine-,[7a] quinoxaline/fluorene-,[7b] triazole/amine-,[7c] bathophenanthroline/amine-,[7d] benzimidazole/amine-,[7e] and oxadiazole/carbazole-based[7f] compounds. They have been used either as the host for phosphorescent emitters or used in single-layer fluorescence OLEDs. Herein reported are novel bipolar molecules ACBP and ADBP (Scheme 1)

Scheme 1. Synthesis of ADBP, ACBP, and DABP



designed by incorporating an acridinone moiety and a triarylamine or carbazole moiety into one molecule, which can be used as the host for both fluorescent and phosphorescent OLEDs with remarkable reduction in drive voltage and improvement in efficiencies.

The design of ACBP and ADBP is based on the following considerations. First, triarylamines are well-known hole-transporting materials. Second, compared to CBP (4,4′-di(9*H*-carbazol-9-yl)biphenyl) that is considered to be bipolar and has been widely used as the host in phosphorescent OLEDs, acridinone should possess better electron injecting/transporting ability because of the presence of the electron-withdrawing carbonyl group. Third, steric hindrance would lead to a twisted geometry in these molecules and make extension of conjugation between the acridinone moiety and the biphenyl moiety unlikely; therefore, the required energy gap is maintained while both electron-transporting and hole-transporting properties are being introduced into one molecule.

The synthesis of ADBP and ACBP is shown in Scheme 1. A procedure reported by Buchwald et al.[8] was used for the C−N cross coupling of the intermediate 4′-bromo-*N*,*N*-diphenylbiphenyl-4-amine (**1**) and 9-(4′-bromobiphenyl-4-yl)-9*H*-carbazole (**2**) with acridinone to give ADBP and ACBP, respectively. The coupling reaction proceeded in refluxing DMF to produce the desired compounds in high yields. The diketone ligand is critical to the success of the reaction. When replacing the diketone ligand with a diamine ligand such as *trans*-*N*,*N*′-dimethylcyclohexanediamine, only a small amount of the desired product (<5%) was detected under otherwise the same reaction conditions. No reaction was detected without using a ligand in the reaction. The choice of the solvent was also important. For example, although the use of DMA gave similar results, the reaction did not proceed when dioxane or toluene was used as the solvent under refluxing conditions. DABP[9] was also synthesized similarly by cross coupling of 4,4′-dibromobiphenyl with acridinone.

Photophysical properties of the compounds were investigated, and the results are summarized in Table 1. The

Table 1. Physical and Chemical Properties of ADBP, ACBP, and DABP

	ADBP	ACBP	DABP
λ_{abs}[a] (nm)	375, 394	375, 394	376, 394
λ_{em}[nm]/Φ_f[b](%)	408/1.8	404/28	405/31
E_{ox}[c] (eV)	1.07	1.37	1.56
E_{red}[c] (eV)	−1.84	−1.82	−1.82
HOMO/LUMO[d](eV)	−5.41/−1.66	−5.76/−1.75	−5.92/−1.93
ΔE[e] (eV)	3.75	4.00	3.99
E_T[f] (eV)	2.65 (2.73)	2.66 (2.74)	2.67 (2.74)

[a] Lowest absorptions in dichloromethane. [b] Emission maximum in dichloromethane. Quantum yields were measured using quinine sulfate monohydrate in 0.1 M aqueous sulfuric acid solution as reference. [c] Determined vs SCE in toluene−acetonitrile (v/v 1:1). [d] Estimated from the DFT calculations. [e] HOMO−LUMO gap. [f] Triplet energy estimated from the phosphorescent spectra. Calculated values are shown in parentheses.

comparison of the absorption spectra of ADBP, ACBP, and DABP with those of intermediates **1**, **2**, and acridinone suggests that the conjugation is essentially interrupted between acridinone and biphenyl moieties, since the lowest

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energy absorptions for all three compounds are almost the same and very similar in both shape and energy to those of acridinone (371, 389 nm). The lowest energy absorption can be assigned as $\pi \rightarrow \pi^*$ transition.[10] All three compounds emitted in the deep blue region with the emission maximum between 404 and 408 nm in dichloromethane. The quantum yield measured in solution for ADBP is significantly lower than those of the other two compounds. Triplet energies were estimated to be 2.65−2.67 eV from the phosphorescent spectra of the compounds measured in a frozen matrix in toluene at 77 K, which indicate that all three compounds can be used to sensitize triplet green emitters or even blue green emitters. The oxidation and reduction potentials were measured from their cyclic voltammograms. All three compounds exhibited similar reduction potentials ranging from 1.82 to 1.84 eV (vs SCE), indicating that they are potentially electron-transporting materials. The oxidation potential increases in the order of ADBP, ACBP, and DABP, indicating the decreasing hole injection/transporting ability of the molecules.

Further examination of the electronic properties by DFT calculations was carried out on ADBP, ACBP, and DABP. Optimized ground-state geometries revealed twisted structures for these molecules. The acridinone moiety and its *N*-phenyl ring are nearly perpendicular to each other with the torsional angle between 89.8° and 90.8° for the three compounds. For ACBP, the torsional angle between the carbazole and its *N*-phenyl ring is 57.1°. The two phenyl rings of the biphenyl unit are twisted by 38.2°, 38.3°, and 41.0° in ADBP, ACBP, and DABP, respectively. These structural features offer further explanation for the disruption of the conjugation in the molecules. Calculated HOMO and LUMO energies and triplet energies of the compounds are listed in Table 1. The HOMO and LUMO characters are shown in Figure 1. ADBP has clearly localized frontier

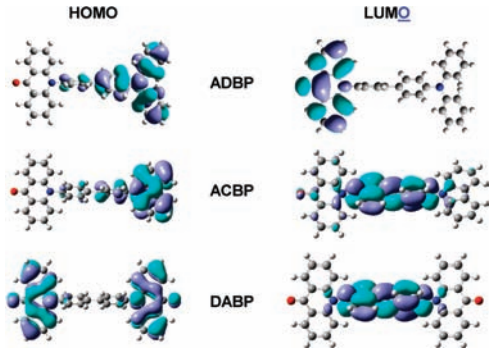

Figure 1. HOMO and LUMO surfaces from DFT calculations.

orbitals with HOMO localized in triphenylamine moiety and LUMO in acridinone moiety. The HOMO and LUMO in ACBP are less localized with HOMO predominately in carbazolyl and the LUMO in the biphenyl moiety. Interestingly, the HOMO in DABP are localized in the acridinone moiety and the LUMO is localized in the biphenyl moiety. This might be explained by considering the 9-oxoacridin-10(9*H*)-yl group as an electron-withdrawing group, since the nitrogen would provide its lone pair to form an extended conjugation within the acridinone moiety. Therefore, the biphenyl in DABP becomes more electron-deficient. The same argument is also applied to ACBP.

To evaluate new compounds as a host for triplet emitters in phosphorescent OLED devices, we have chosen the commonly used triplet green emitter $Ir(ppy)_3$ for our device fabrications. The OLED devices were fabricated by multilayer vapor deposition with the structure of indium tin oxide(ITO)/NPB(75 nm)/TCTA(10 nm)/host + $Ir(ppy)_3$ (6%) (20 nm)/Bphen (50 nm)/LiF/Al. TCTA is used as the exciton-blocking layer to prevent excitons generated by electroexcitation from diffusing into the hole-transporting NPB layer. LiF is used as the electron injection layer and Bphen (4,7-diphenyl-1,10-phenanthroline) as the electron-transporting layer. The performance of the devices at 1 and 5 mA/cm^2 is summarized in Table 2 with the data obtained at 5 mA/cm^2 listed on the right-hand column. All four devices emit essentially the same color of green light that is from the triplet dopant $Ir(ppy)_3$. Several points are noteworthy by comparing the performance of these devcies, for example, at 1 mA/cm^2. First, the drive voltage for devices with new bipolar host ADBP (2.79 V) or ACBP (3.29 V) is substantially lower than that for the device with CBP (4.16 V) or DABP (3.99 V) as the host. Second, the efficiencies achieved with new bipolar hosts ADBP (49.1 cd/A; 14.0% EQE) and ACBP (58.9 cd/A; 16.9% EQE) are higher than those obtained with CBP (40.5 cd/A; 11.6% EQE) or DABP (47 cd/A; 13.4% EQE) as the host. Third, as can be seen from Table 2, the combination of both the improvement in quantum efficiency and the reduction in the drive voltage results in remarkably higher power efficiency. Both ADBP (55.3 lm/W) and ACBP (56.2 lm/W) demonstrated around 80% and 50% increases in power efficiency when compared to CBP and DABP, respectively. The performance at 5 mA/cm^2 shows the same trend but with a slight decrease in efficiencies for all hosts.

The use of the bipolar materials as the host for singlet emitters in OLED devices was also explored. By using recently developed deep blue dopant, difluoro[6-mesityl-*N*-(2(1*H*)-quinolinylidene-κN)-(6-mesityl-2-quinolinaminato-$\kappa N1$)]boron (BFD),[11] the devices were fabricated with the structure of ITO/NPB(75 nm)/TCTA(10 nm)/host + BFD (1%) (20 nm)/Bphen (40 nm)/LiF/Al. The performances of the devices with different hosts are shown in Table 2. The

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Table 2. Performance of OLED Devices at Different Current Densities (1 mA/cm^2 and 5 mA/cm^2)[a]

host	dopant	V^b (V)		L^c (cd/m^2)		$\eta_c{}^d$ (cd/A)		$\eta_p{}^e$ (lm/W)		EQE^f (%)		$\lambda_{max}{}^g$ (nm)		CIE (x,y)^h	
ADBP	$Ir(ppy)_3$	2.79	3.38	491	2361	49.1	47.2	55.3	44.0	14.0	13.5	513	513	0.29, 0.63	0.29,0.63
ACBP	$Ir(ppy)_3$	3.29	3.94	589	2793	58.9	55.9	56.2	44.5	16.9	16.1	514	514	0.29, 0.63	0.29,0.63
DABP	$Ir(ppy)_3$	3.99	4.83	472	2290	47.0	45.8	37.1	29.8	13.4	13.0	519	518	0.32, 0.62	0.31,0.62
CBP	$Ir(ppy)_3$	4.16	5.05	405	1849	40.5	37.0	30.6	23.0	11.6	10.6	515	514	0.29, 0.63	0.29,0.63
ADBP	BFD	2.91	3.50	57	278	5.7	5.6	6.1	5.0	4.1	4.1	453	453	0.15, 0.17	0.15, 0.17
ACBP	BFD	3.43	4.06	56	266	5.6	5.3	5.1	4.1	5.3	5.1	454	454	0.14. 0.13	0.14, 0.13
DABP	BFD	3.87	4.52	26	150	2.6	3.0	2.1	2.1	2.1	2.5	456	456	0.15, 0.16	0.15,0.15
CBP	BFD	4.10	5.29	9	62	1.0	1.3	0.7	0.7	1.0	1.3	453	453	0.14, 0.11	0.14, 0.11

[a] The values at 5 mA/cm^2 are listed on the right-hand column. [b] Drive voltage. [c] Luminance. [d] Current efficiency. [e] Power efficiency. [f] External quantum efficiency. [g] Electroluminescent emission maximum. [h] Commission Internationale de I'Eclairage chromaticity coordinates.

same trends as those observed in the performance of the triplet devices were also found for the corresponding singlet devices. For example, ADBP demonstrated 190% and 770% increase in power efficiency compared to DABP and CBP, respectively. The lowest drive voltage (2.91 V) was observed for the devices with ADBP as the host while the highest quantum efficicency (5.3% EQE) was obtained when ACBP was used as the host.

In summary, new bipolar molecules capable of transporting both electrons and holes have been constructed by incorporating both acridinone and triarylamine/carbazolyl moieties into the molecule while maintaining a desired energy gap for using as the host for both singlet and triplet emitters. The photophysical properties of the compounds have been investigated. DFT calculations were performed to further elucidate the electronic structures and geometries of the molecules. Bipolar ADBP and ACBP have demonstrated superior performance as the host for the deep blue fluorescent dopant and the green phosphorescent dopant in the OLED devices, showing significant reductions in drive voltage and improvements in efficiencies. The new host materials capable of sensitizing both deep blue fluorescent and green phosphorescent dopants may have potential for use as the host material in hybrid white OLED devices where the quantum efficiency of the devices could be maximized.[12]

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Supporting Information Available: Synthesis information, experimental details; ^{1}H and ^{13}C NMR chemical shifts; photophysical spectra of ADBP, ACBP, and DABP. This material is available free of charge via the Internet at http://pubs.acs.org.

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