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A High Efficiency Pure Organic Room Temperature Phosphorescence Polymer PPV Derivative for OLED

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ABSTRACT: For the purpose of improving device efficiency and reducing cost, it is necessary to develop pure organic molecules with room temperature phosphorescence (RTP). A high efficiency pure organic RTP polymer, poly-p-phenylene vinylene (PPV) derivative (Br-PPV-CHO), was designed and synthesized, which possesses a blue emission at 496 nm, an emission lifetime of 14.1 µs, and a photoluminescence quantum yield of 12.2 %, and the HOMO and LUMO of -5.35 eV and -2.75 eV, respectively, showing a great potential application in the emitting layer of OLED. A device fabricated with the PPV derivative as the emitting material layer shows a max luminance of 194 cd/m² when the Br-PPV-CHO content was 0.5 wt %, demonstrating the best RTP performance. The good properties of Br-PPV-CHO come from the substituent groups of bromine and aromatic aldehyde, and the molecular structure design strategy in the PPV derivative supplies a useful guidance for the design and syntheses of organic RTP materials.

Keywords: Optoelectronic Materials, Room temperature phosphorescence, PPV derivative, Heavy atom effect, Pure organic molecule

1. Introduction

The internal quantum efficiency (IQE) of emitting materials has received much concern because it is essential to improve the device external quantum efficiency (EQE). According to the quantum spin theory statistics, the excitons generated from electrical excitation can be divided into singlet excitons and triplet excitons, with a ratio of 1:3. By this theory, the highest IQE is limited to 25 %, so devices based on the traditional

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fluorescence materials which produce light from the radiative transition of singlet excitons are hard to use widely. However, the phosphorescence materials may harvest the energy of both singlet and triplet excitons, and reach a 100 % IQE [1,2]. To accomplish this quantum efficiency, the traditional phosphorescence materials are mostly designed to have metal complex [3], where the strong spin-orbit coupling of transition metal promotes the spin deflection of triplet excitons, and thus contributes to the radiating transition of triplet excitons [4,5].Due to the high cost and limited resources, the further developments and practical applications of devices based on heavy metals are subjected to limitations. So it is extremely attractive about the design and development of pure organic RTP materials.

However, without heavy atoms, the long lifetime triplet excitons cannot achieve radiative transition successfully due to the molecular rotation vibration and oxygen quenching. For this reason, all organic phosphorescence emission only can generally be observed in the inert and low-temperature environment, such as at 77 K and nitrogen environment. Recently, some materials that can successfully achieve pure organic RTP have been reported. Shi et al [6] reported that a series of dibromobenzene derivatives can be observed efficient phosphorescence emission from their crystals, in which the highest phosphorescence quantum efficiency can reach 21.9 %. These structures prove the importance of bromine atoms to the generation of phosphorescence. Adachi et al [7] reported a host-guest structure, with hydroxysteroid as the host, which provides a rigid environment for the guest through a strong intermolecular interaction, to suppress the molecular rotation vibration. The deposited film with this host-guest structure achieved a quantum efficiency of 39.7 %, and the OLED device fabricated by that deposited film, with a highest EQE of 1 %, could be observed a continuous green emission after power off. Kwon and others [8] obtained a cross-linked phosphor-doped polymer system by Diels-Alder reaction, achieving a phosphorescence quantum efficiency of 28 %. Lee and co-workers [9] introduced pure organic phosphors, 2,5dihexyloxy-4-bromobenzaldehyde (Br6A), into polymethylmethacrylate (PMMA), and achieved a quantum efficiency of 7.5 %. All this showed that in the organic molecules containing both bromine and aromatic carbonyl, the RTP can be achieved successfully

[10,11].

In this work, we designed and synthesized pure organic RTP polymer, poly-pphenylene vinylene (PPV) derivative (Br-PPV-CHO), with bromine atoms to enhance the phosphorescence efficiency via heavy-atom interaction. Based on the photophysical properties and electrochemical properties of those organics, we have fabricated OLED devices with different configurations and demonstrated the potential application in the emitting layer of OLED.

2. Experiment

By a series of chemical reactions, 2,5-dibromo-1,4-bis(octyloxy)benzene (M1) and 1,4-dibromo-2,5-divinylbenzene (M2), were synthesized. Through the halogen-metal exchange reaction of M1 and M2, a high efficiency pure organic RTP polymer, PPV derivative (Br-PPV-CHO), was synthesized. All the synthesized polymers were characterized by a Bruker 500 MHz spectrometer. The electrochemical property of the PPV derivative was measured through a three-electrode system in an anhydrous acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆). The photoluminescence performance was characterized by using Fluoromax-4, FLS900, and FLS920 equipped with integrating sphere.

3. Results and discussion

The synthesis of the pure organic RTP material was performed following the outline in Fig. 1. In this synthetic scheme, 2,5-dibromo-1,4-bis(octyloxy)benzene (M1) and 1,4-dibromo-2,5-divinylbenzene (M2) were synthesized separately and the polymer precursor (Br-PPV-Br) was obtained by the heck reaction of M1 and M2. Subsequently, through the halogen-metal exchange reaction, PPV derivative (Br-PPV-CHO) was synthesized.





Fig. 1. The synthetic scheme for the Br-PPV-CHO

The photoluminescence spectrum, emission lifetime and luminous efficiency were measured to judge whether the polymer could meet the requirements for device preparation. The photoluminescence spectra are showed in Fig. 2. At room temperature and 77 K, the PPV derivative emits efficient blue-green light with major emission peaks at 496 nm and 510 nm, respectively; obviously, the emission at 77 K shifts red slightly. This emission difference between RT and 77 K indicated that under the low temperature environment, the molecular were bounded, and some molecular aggregation may enhance the conjugate area, resulting in an emission red shift.



Fig. 2. PL spectra of Br-PPV-CHO in CHCl₃ solution. Insert: a photo of the solution emission

The luminous life is an important characteristic which could determine whether the material belongs to fluorescence or phosphorescence materials. For fluorescence materials, the lifetime of emission is usually $10^{-12} \sim 10^{-9}$ s, i.e., -ns, while phosphorescence materials possess a μ s - ms lifetime.

The lifetime of emission of this derivative was measured at room temperature and 77 K as shown in Fig. 3. Obviously, at RT or 77 K, the derivative has almost the same lifetime of emission, i.e., 14.1 μ s and 13.9 μ s, which differs from the traditional organic electroluminescent materials. The latter usually possess an ms-s lifetime due to the triplet excitons generated from $\pi \rightarrow \pi *$. The lifetime value of the derivative at RT and 77 K may induce that the luminescence mechanism is dependent on the aldehyde group and bromine atom. The aldehyde group reduces the energy gaps between singlet and

triplet, and thus the singlet excitons could successfully convert into triplet excitons by ISC; meanwhile under the action of bromine atom, a strong spin-orbit coupling promotes the triplet excitons transit to the ground state and produce light. So the prepared pure organic polymer material can emit efficient phosphorescence.



Fig. 3. Photoluminescence decays of Br-PPV-CHO at RT and 77 K

It is recognized that the IQE of fluorescence materials is essential to the device efficiency, so excitation line and emission spectra of Br-PPV-CHO were measured by integrating sphere, as shown in Fig. 4. By simple calculation, it can be obtained that the photoluminescence quantum yield is 12.2 %.



Fig. 4. Excitation line and emission spectra of Br-PPV-CHO collected by using an integrating sphere. The inset figure shows the magnification of excitation line and emission spectra

Table 1 lists some performance of different electroluminescent polymers. By comparison to fluorescence polymer materials, i.e., PspiroF, Me-LPyP and PDHFMPPV, Br-PPV-CHO showed a longer lifetime, which could achieve phosphorescence emission. Comparing with phosphorescence materials, i.e, Compound 1, Br-PPV-CHO showed higher photoluminescence quantum yield. All this data demonstrated that Br-PPV-CHO had a good luminous performance.

 Table 1. Photophysical properties of polymer emitting materials

polymer $\lambda_{\rm em} = \Phi(\%) = \tau(s)$ Ref.

	(nm)			
Br-PPV-	496	12.2	14.1×10 ⁶	
СНО				
PspiroF	423	17.18±0.07	1.69×109	[12]
Me-LPyP	440	-	4.3×109	[13]
PDHFMPPV	475	-	0.476×10	[14]
			9	
PFA-OXD	449	0.72	-	[15]
Compound 1	550	5.4	1.3×10 ⁶	[16]
a • •	1	.	· 11	1.0

 λ_{em} = the emission peak, Φ = quantum yield, τ = lifetime

As an OLED emitting layer, the materials need not only good photophysical properties but also a match of the energy level with other functional layers. During the electron injection process, it requires electron across energy barriers to achieve an effective injection. For this consideration, the electrochemical properties of the prepared derivative were investigated by cyclic voltammetry. As shown in Fig. 5, the oxidation potential of Br-PPV-CHO in CH₃CN solution is 0.946 V, and the reduction potential is -1.655 V. The energy of HOMO and LUMO as well as the energy gap can be obtained by equations (1) to (3):

$$HOME = -(E_{onset}^{OX} + E_{ref} + 4.80)eV$$
(1)

$$LUMO = -\left(E_{onset}^{red} + E_{ref} + 4.80\right)eV$$
 (2)

$$E_{\rm g} = {\rm LUMO} - {\rm HOMO} = E_{\rm onset}^{\rm OX} - E_{\rm onset}^{\rm red}$$
 (3)

where E_{onset}^{OX} , E_{onset}^{red} are oxidation potential and reduction potential measured by cyclic voltammetry, respectively; herein the ferrocene/ferrocenium couple potential is determined to be -0.40 V vs Pt.

According to the equations, the highest occupied molecular orbital (HOMO) is -5.35 eV, the lowest unoccupied molecular orbital (LUMO) is -2.75 eV, and the energy gap $E_g = 2.60 \text{ eV}.$



The photoluminescence performance and electrochemical properties showed that Br-PPV-CHO could be applied to the OLED devices. Based on those results, we have fabricated different devices with several guest materials to demonstrate the application. The device configurations are denoted as Device I, Device II and Device III, as follows, and, as an example, the energy-level diagram of the device I is showed in Fig. 6.

Device I: ITO / PEDOT:PSS / PVK:PBD:Br-PPV-CHO / TmPyPB / Liq / Al

Device II: ITO / PEDOT:PSS / PVK:NPB:Br-PPV-CHO / TmPyPB / Al

Device III: ITO / PEDOT:PSS / TAPC / PEI / TAPC:Br-PPV-CHO / TmPyPB / Liq / Al



Fig. 6. Energy-level diagrams of the Device I: ITO / PEDOT:PSS / PVK:PBD:Br-PPV-CHO / TmPyPB / Liq / Al

Among these three devices, the Device I showed a best performance. The EL spectrum (Fig. 7) shows two major emission peaks at 464 nm and 504 nm. According to the PL spectra (Fig. 2), the emission peak at 504 nm belongs to Br-PPV-CHO, indicating that electroluminescence originated from the RTP material, while the emission peak at 464 nm may come from PVK:PBD, which is characteristic of an incomplete energy transfer from host PVK:PBD to Br-PPV-CHO.



Fig. 7. EL spectra of the (a) PVK: PBD and (b) PVK: PBD: Br-PPV-CHO based devices. Insert: A digital photograph of working pixel of device based on PVK: PBD: Br-PPV-CHO

Device II based on NPB did not occur efficient emission from Br-PPV-CHO, showing that NPB is not appropriate to be a host for Br-PPV-CHO. This phenomenon comes from that the triplet energy level of NPB is as low as 2.2 eV, by which the energy cannot transfer to Br-PPV-CHO effectively. In Device III, TAPC was selected as the base material due to its high triplet energy level (2.75 eV). This device was prepared by solution process, and water-soluble conducting polymer polyethylenimine (PEI) was utilized between hole-transporting layer (HTL) and light-emitting layer (EML) to avoid the mutually soluble between HTL and EML in spin coating. Obviously, the Device III showed a poor performance, such as high driven voltage (20 V) and fast luminance decay. This luminous behavior is probably due to the electron transporting of PEI, especially in the case that PET was placed on the hole-transporting materials.

Based on the luminance-doping concentration curve shown in Fig. 8, device I with the best performance has been fabricated. The max luminance achieved is 194 cd/m² when the Br-PPV-CHO content is 0.5 wt %. Obviously, the luminance of device I reduced with the increase of Br-PPV-CHO, indicating that Br-PPV-CHO has a clear concentration quenching effect. This phenomenon may be explained as with the increase of the Br-PPV-CHO, as a phosphorescence guest, the number of triplet excitons formed after excitation also increases, and the probability of collision between triplet excitons increases significantly, leading to annihilation. In this case, those triplet excitons do not emit light but result in the loss of energy, and therefore, the brightness of the device reduces obviously with increasing doping concentration in the light-emitting layer.



Fig. 8. Current density–voltage–luminance of the Br-PPV-CHO based device when the Br-PPV-CHO content was 0.5 wt %. The inset figure shows the luminance variation with different doping concentrations

4. Conclusions

In summary, we have prepared the pure organic room temperature phosphorescence material PPV derivate Br-PPV-CHO, and applied it to OLED devices. Br-PPV-CHO showed a room temperature phosphorescence emission at 496 nm, an emission lifetime of 14.1 µs, and the photoluminescence quantum yield of 12.2 %. The max luminance of the devices based on Br-PPV-CHO could reach 194 cd/m², while the devices still need to be optimized to enhance the performance of luminance and device efficiency. The good properties of Br-PPV-CHO originate from the substituent groups of bromine and aromatic aldehyde. The molecular structure design strategy in PPV derivate Br-PPV-CHO supplies a useful guidance for the design and syntheses of all organic RTP materials for OLED.

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References

- C. Adachi, M.A. Baldo, M.E. Thompson, S.R. Forrest, Nearly 100% internal phosphorescence efficiency in an organic light-emitting device, J. Applied Physics 90 (2001) 5048-5051.
- [2] C. Adachi, Third-generation organic electroluminescence materials, Japanese Journal of Applied Physics 53 (2014) 060101
- [3] M.A. Baldo, S.R. Forrest, Transient analysis of organic electrophosphorescence: I. Transient analysis of triplet energy transfer, Physical Review B 62 (2000) 10958-10966.
- [4] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.E. Lee, C. Adachi, P.E. Burrows, S.R. Forrest, M.E. Thompson, Highly phosphorescent bis-cyclometalated iridium complexes: Synthesis, photophysical characterization, and use in organic light emitting diodes, J. American Chemical Society 123 (2001) 4304-4312.

- [5] Y.H. Niu, Y.L. Tung, Y. Chi, C.F. Shu, J.H. Kim, B.Q. Chen, J.D. Luo, A.J. Carty, A.K.Y. Jen, Highly efficient electrophosphorescent devices with saturated red emission from a neutral osmium complex, Chemistry of Materials 17 (2005) 3532-3536.
- [6] H.F. Shi, Z.F. An, P.Z. Li, J. Yin, G.C. Xing, T.C. He, H.Z. Chen, J.G. Wang, H.D. Sun, W. Huang, Enhancing organic phosphorescence by manipulating heavy-atom interaction, Crystal Growth & Design 16 (2016) 808-813.
- [7] R. Kabe, N. Notsuka, K. Yoshida, C. Adachi, Afterglow Organic Light-Emitting Diode, Adv Mater 28 (2016) 655-660.
- [8] M.S. Kwon, Y. Yu, C. Coburn, A.W. Phillips, K. Chung, A. Shanker, J. Jung, G. Kim, K. Pipe, S.R. Forrest, J.H. Youk, J. Gierschner, J. Kim, Suppressing molecular motions for enhanced roomtemperature phosphorescence of metal-free organic materials, Nat Commun. 6 (2015) 8947
- [9] D. Lee, O. Bolton, B.C. Kim, J.H. Youk, S. Takayama, J. Kim, Room temperature phosphorescence of metal-free organic materials in amorphous polymer matrices, J Am Chem Soc. 135 (2013) 6325-6329.
- [10] R.C. Evans, P. Douglas, C.J. Winscom, Coordination complexes exhibiting room-temperature phosphorescence: Evaluation of their suitability as triplet emitters in organic light emitting diodes, Coordination Chemistry Reviews 250 (2006) 2093-2126.
- [11] O. Bolton, K. Lee, H.J. Kim, K.Y. Lin, J. Kim, Activating efficient phosphorescence from purely organic materials by crystal design, Nature Chemistry 3 (2011) 205-210.
- [12] V.H.K. Fell, A. Mikosch, A.K. Steppert, W. Ogieglo, E. Senol, D. Canneson, M. Bayer, F. Schoenebeck, A. Greilich, J.C. Kuehne, Synthesis and optical characterization of hybrid organic-inorganic heterofluorene polymers, Macromolecules 50 (2017) 2338-2343.
- [13] A. Rudnick, K.J. Kass, E. Preis, U. Scherf, H. Bassler, A. Kohler, Interplay of localized pyrene chromophores and pi-conjugation in novel poly(2,7-pyrene) ladder polymers, J Chem Phys. 146 (2017) 174903
- [14] H.N. Cho, J.K. Kim, D.Y. Kim, C.Y. Kim, N.W. Song, D. Kim, Statistical copolymers for bluelight-emitting diodes, Macromolecules 32 (1999) 1476-1481.
- [15] F.I. Wu, P.I. Shih, C.F. Shu, Y.L. Tung, Y. Chi, Highly efficient light-emitting diodes based on fluorene copolymer consisting of triarylamine units in the main chain and oxadiazole pendent groups, Macromolecules 38 (2005) 9028-9036.
- [16] H.W. Wu, Y.Y. Zhou, L.Y. Yin, C. Hang, X. Li, H. Agren, T. Yi, Q. Zhang, L.L. Zhu, Helical Selfassembly-induced singlet-triplet emissive switching in a mechanically sensitive system, J Am Chem Soc. 39 (2017) 785-791

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Highlights:

• High efficiency and low cost pure organic polymer with room temperature phosphorescence,

PPV derivate Br-PPV-CHO, was designed and synthesized.

• The luminescence control mechanism of the new pure organic polymer material is dependent

on the aldehyde group and bromine atom.

• The performance of the organic RTP material is suitable to be the emitting layer of OLED.

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