

Effect of donor and acceptor position on light emitting performances of thermally activated delayed fluorescent emitters with two bicarbazole donors and two cyano acceptors



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ABSTRACT

Positional effect of donors and acceptors in the thermally activated delayed fluorescent (TADF) emitters was examined using TADF emitters with two donors and two acceptors. The position of the donors and acceptors at the phenyl linker was regulated as ortho-, meta- and para- to study the positional effect of the donors and acceptors. The comparison of the three TADF emitters with the different substitution positions suggested that ortho- or meta- substitution of each donor or acceptor is a useful way of improving light-emitting performances of the TADF emitters. The TADF emitter with the two donors at meta- position achieved high quantum efficiency of 18.0% compared with 15.1% and 3.8% of other emitters. High photoluminescence quantum yield, high fluorescence rate constant, and high reverse intersystem crossing rate constant were the main factors for the high quantum efficiency of the meta-substituted emitter.

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1. Introduction

Thermally activated delayed fluorescent (TADF) emitters are generally designed based on a framework of donor-acceptor structure to meet the key parameter of small singlet-triplet energy gap (ΔE_{ST}) for full utilization of generated excitons for light emission [1–5]. There are a few ways of building the donor-acceptor framework, but the most common and effective way is to make the TADF emitter to have a molecular structure with the donor and acceptor interlinked via an aromatic linker [6]. Several TADF emitters designed based on this concept were successful as the high efficiency TADF emitters [7–11].

Within the molecular framework of donor-linker-acceptor structure, the donor and acceptor moieties can be substituted to the linker in various ways. For example, in the case of TADF emitters with one donor, one acceptor, and one phenyl linker, the donor and the acceptor can be substituted to a phenyl linker via ortho-, meta- or para- positions [12]. When the TADF emitters have two donors and two acceptors, the donors and acceptors can be positioned in more complicated ways [1,11,13,14]. However, no systematic investigation of the positional effect of the donor and

acceptor moieties on the photophysical properties such as photoluminescence (PL) emission characteristics, and device characteristics has not been conducted in spite of the importance of the molecular structure of the organic emitters. This information is very important because the correlation of the molecular structure with the photophysical and device properties may guide how to design highly efficient TADF emitters.

Here, we present a guideline to build the framework of TADF emitters having two donor moieties and two acceptor moieties through systematic study of the positional effect of the donors and acceptors on the light-emitting characteristics of the TADF emitters. Three TADF emitters with two 3,3'-bicarbazole donors and two CN acceptors at different positions of the phenyl unit were prepared, identified, characterized and evaluated as emitters in the TADF organic light-emitting diodes (OLEDs). It was concluded that ortho- or meta- substitution is better than para- substitution of the donors or acceptors in terms of external quantum efficiency (EQE) of the TADF devices.

2. Experimental

2.1. General information

1,2-Dibromo-4,5-difluorobenzene, 1-bromo-2,4-difluorobenzene and 1,4-dibromo-2,5-difluorobenzene supplied from

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Fluorochem Ltd. were used after purification by column chromatography. Iron powder purchased from Sigma Aldrich Co. was used without purification. 3-Bromo-9H-carbazole, (9-phenyl-9H-carbazol-3-yl)boronic acid and tetrakis(triphenylphosphine) palladium(0) from PH,9'H-3,3'-bicarbazole, 1,5-dibromo-2,4-difluorobenzene, 4,5-difluorophthalonitrile, 4,6-difluorophthalonitrile and 2,5-difluorophthalonitrile were synthesized according to literature [1,14–17]. Characterization of the materials was carried out according to the general method described in other papers [18–20].

2.2. Synthesis

2.2.1. 4,5-Bis(9'-phenyl-9H,9'H-[3,3'-bicarbazol]-9-yl)phthalonitrile (o-BCzDCN)

Sodium hydride (60% in oil, 0.12 g, 1.0 mmol) was washed three times with n-hexane in round-bottomed flask and a solution of 9-phenyl-9H,9'H-3,3'-bicarbazole (0.94 g, 2.3 mmol) in dry tetrahydrofuran (15 ml) was added under a nitrogen atmosphere at room temperature. After stirring for 10 min, a solution of 4,5-difluorophthalonitrile (0.16 g, 3.0 mmol) in dry tetrahydrofuran (5 ml) was added slowly and the reaction mixture was stirred for 30 min and quenched with distilled water for 1 h. The product dissolved in methylene chloride was dehydrated with MgSO₄, evaporated and dried under a vacuum condition. The crude product was purified by column chromatography (methylene chloride: n-Hexane = 4: 1) to obtain a yellow powder (0.73 g, 78%). ¹H NMR (500 MHz, DMSO-*d*₆): δ 8.92(d, 2H, *J* = 6.5 Hz), 8.59(s, 1H), 8.54(s, 1H), 8.42(s, 1H), 8.38(s, 1H), 8.33(d, 1H, 8.0 Hz), 8.22(d, 1H, *J* = 7.5 Hz), 8.10–8.06(m, 2H), 7.76–7.50(m, 16H), 7.45–7.37(m, 8H), 7.30(t, 1H, *J* = 7.5 Hz), 7.19–7.14(m, 5H). ¹³C NMR (125 MHz, DMSO-*d*₆): δ 140.6, 140.5, 139.3, 139.3, 139.1, 138.1, 138.0, 137.9, 137.8, 136.9, 136.8, 136.4, 134.1, 132.7, 132.6, 130.2, 130.2, 127.7, 127.6, 126.6, 126.5, 126.4, 126.3, 126.1, 126.0, 125.3, 125.0, 124.9, 124.2, 124.1, 123.6, 123.4, 123.0, 122.9, 121.1, 120.8, 120.7, 120.5, 120.1, 120.0, 118.5, 118.3, 118.2, 115.4, 115.1, 115.0,

110.4, 110.3, 110.4, 110.0, 109.9, 109.7, 109.6. LC/MS (*m/z*): found, 941.1 ([M + H]⁺); Calcd. for C₆₈H₄₀N₆, 941.1.

2.2.2. 4,6-Bis(9'-phenyl-9H,9'H-[3,3'-bicarbazol]-9-yl)isophthalonitrile (m-BCzDCN)

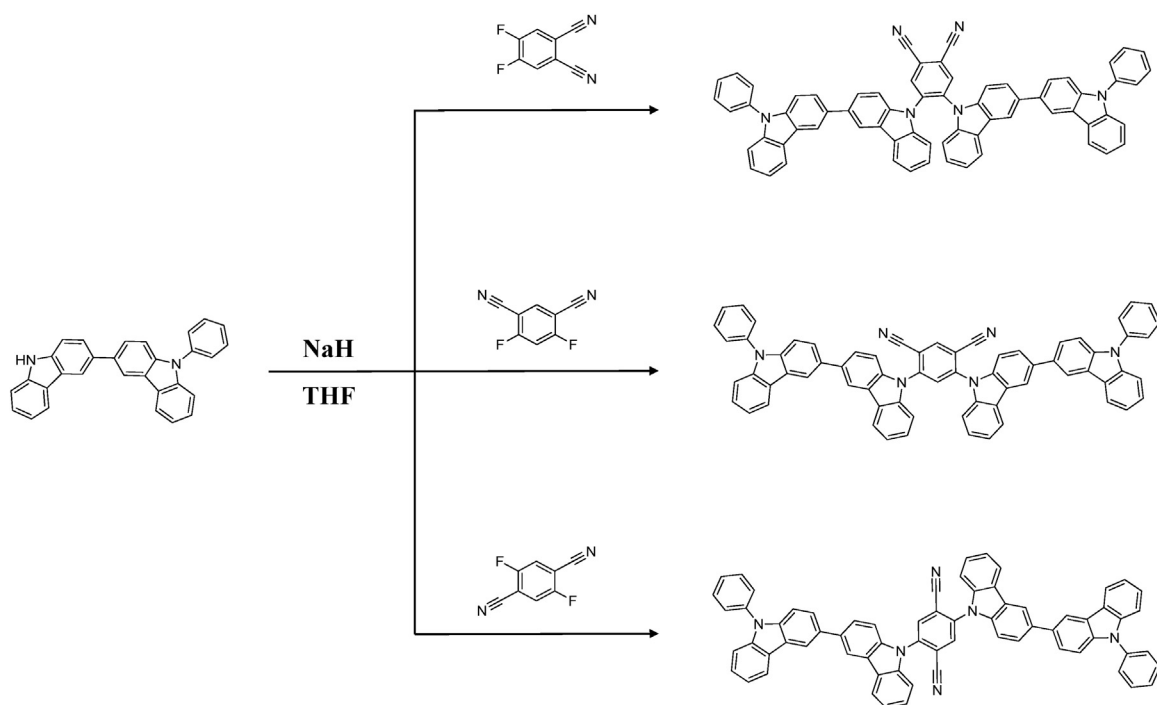
4,6-Bis(9'-phenyl-9H,9'H-[3,3'-bicarbazol]-9-yl)isophthalonitrile (m-BCzDCN) was synthesized according to the synthesis procedure of 4,5-bis(9'-phenyl-9H,9'H-[3,3'-bicarbazol]-9-yl)phthalonitrile (o-BCzDCN) except for use of 4,6-difluorophthalonitrile instead of 4,5-difluorophthalonitrile.

Yield 82% (0.77 g). ¹H NMR (500 MHz, DMSO-*d*₆): δ 9.27(s, 1H), 8.72(s, 4H), 8.44(s, 1H), 8.42(d, 2H, *J* = 7.5 Hz), 8.40–8.38(m, 2H), 7.98(t, 2H, *J* = 7.5 Hz), 7.90(d, 2H, *J* = 8.5 Hz), 7.75–7.61(m, 12H), 7.75–7.51(m, 4H), 7.50–7.40(m, 8H), 7.35–7.31(m, 2H). ¹³C NMR (125 MHz, DMSO-*d*₆): δ 145.1, 142.0, 140.6, 140.3, 140.3, 139.4, 139.0, 138.9, 136.9, 134.7, 132.9, 130.5, 130.2, 127.7, 126.8, 126.6, 126.4, 125.8, 125.6, 124.3, 123.8, 123.5, 123.0, 121.5, 121.0, 120.8, 120.1, 118.7, 115.0, 111.5, 111.4, 110.9, 110.6, 110.0, 109.7. LC/MS (*m/z*): found, 941.1 ([M + H]⁺); Calcd. for C₆₈H₄₀N₆, 941.1.

2.2.3. 2,5-Bis(9'-phenyl-9H,9'H-[3,3'-bicarbazol]-9-yl)terephthalonitrile (p-BCzDCN)

2,5-bis(9'-phenyl-9H,9'H-[3,3'-bicarbazol]-9-yl)terephthalonitrile (p-BCzDCN) was synthesized according to the synthesis procedure of 4,5-bis(9'-phenyl-9H,9'H-[3,3'-bicarbazol]-9-yl)phthalonitrile (o-BCzDCN) except for use of 2,5-difluorophthalonitrile instead of 4,5-difluorophthalonitrile.

Yield 86% (0.81 g). ¹H NMR (500 MHz, DMSO-*d*₆): δ 8.86(s, 2H), 8.77–8.75(m, 4H), 8.47(d, 2H, *J* = 8.0 Hz), 8.43(d, 2H, 7.5 Hz), 8.00–7.97(m, 2H), 8.95(d, 2H, *J* = 8.0 Hz), 7.81–7.79(m, 2H), 7.75–7.70(m, 10H), 7.60–7.57(m, 4H), 7.54(d, 2H, 8.5 Hz), 7.50–7.43(m, 6H), 7.35(t, 2H, *J* = 7.5 Hz). ¹³C NMR (125 MHz, DMSO-*d*₆): δ 140.8, 140.6, 139.5, 139.4, 139.3, 136.9, 136.5, 134.5, 133.1, 130.2, 127.7, 126.7, 126.5, 125.7, 124.0, 123.5, 123.0, 121.3, 121.0, 120.9, 120.2, 118.8, 117.9, 114.8, 111.0, 110.7, 110.1, 109.7. LC/MS (*m/z*): found, 941.1 ([M + H]⁺); Calcd. for C₆₈H₄₀N₆, 941.1.



Scheme 1. Synthetic scheme of o-BCzDCN, m-BCzDCN and p-BCzDCN.

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