**Table S1**. Crystal parameters for DTPF-ν-DABNA and DTP-ν-DABNA.

|  |  |  |
| --- | --- | --- |
| Identification code | DTPF-ν-DABNA | DTP-ν-DABNA |
| Empirical formula | C90H56B2F4N4 | C90H60B2N4 |
| Formula weight | 1291 | 1219.04 |
| Temperature/K | 170 | 100 |
| Crystal system | monoclinic | triclinic |
| Space group | P21/c | P-1 |
| a/Å | 17.1615(8) | 13.8558(11) |
| b/Å | 14.0010(6) | 16.8935(15) |
| c/Å | 33.9349(16) | 21.1023(18) |
| α/° | 90 | 102.224(3) |
| β/° | 101.338(2) | 104.161(2) |
| γ/° | 90 | 108.425(2) |
| Volume/Å3 | 7994.7(6) | 4313.7(6) |
| Z | 4 | 2 |
| ρcalcg/cm3 | 1.073 | 0.939 |
| μ/mm‑1 | 0.068 | 0.054 |
| F(000) | 2680 | 1276 |
| Crystal size/mm3 | 0.15 × 0.08 × 0.05 | 0.12 × 0.07 × 0.04 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.828 to 51.422 | 3.884 to 52.884 |
| Index ranges | -20 ≤ h ≤ 20, -17 ≤ k ≤ 16, -39 ≤ l ≤ 41 | -15 ≤ h ≤ 17, -21 ≤ k ≤ 20, -26 ≤ l ≤ 26 |
| Reflections collected | 51828 | 45482 |
| Independent reflections | 14904 [Rint = 0.0801, Rsigma = 0.0827] | 17247 [Rint = 0.0683, Rsigma = 0.0938] |
| Data/restraints/parameters | 14904/0/901 | 17247/0/865 |
| Goodness-of-fit on F2 | 1.039 | 1.048 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0553, wR2 = 0.1294 | R1 = 0.0958, wR2 = 0.2628 |
| Final R indexes [all data] | R1 = 0.1013, wR2 = 0.1487 | R1 = 0.1521, wR2 = 0.2974 |
| Largest diff. peak/hole / e Å-3 | 0.21/-0.22 | 0.66/-0.39 |

**Table S2.** Photophysical properties of DTP-ν-DABNA and DTPF-ν-DABNA.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Solvent** | **DTPF-ν-DABNA** |  | **DTP-ν-DABNA** | |
| **λPL** | **FWHM** | **λPL** | **FWHM** |
| **nm** | **nm** | **nm** | **nm** |
| n-Hexane | 466 | 18 | 474 | 18 |
| Toluene | 474 | 16 | 484 | 17 |
| 1,4-Dioxane | 473 | 17 | 482 | 18 |
| Tetrahydrofuran | 477 | 20 | 487 | 17 |
| Trichloromethane | 478 | 20 | 490 | 17 |
| Dichloromethane | 480 | 22 | 491 | 20 |
| N,N-Dimethylformamide | 481 | 20 | 490 | 21 |

**Table S3.** Photophysical properties DTP-ν-DABNA and DTPF-ν-DABNA in doped PPF films (2 wt%)

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Compound** | **ФPF/ФDF**  **%/%** | **τPF/τDF**  **ns/μs** | ***k*PF**  **×108 s-1** | ***k*DF**  **×104 s-1** | ***k*rS**  **×108 s-1** | ***k*ISC**  **×107 s-1** | ***k*RISC**  **×105 s-1** | ***k*nrS**  **×106 s-1** |
| DTPF-ν-DABNA | 67.4/31.8 | 3.40/11.66 | 2.94 | 8.58 | 1.98 | 9.41 | 1.26 | 1.60 |
| DTP-ν-DABNA | 53.4/42.1 | 2.98/13.15 | 3.36 | 7.60 | 1.79 | 14.8 | 1.36 | 8.44 |
| In this work, the doped films of DTP-ν-DABNA and DTPF-ν-DABNA do not exhibit phosphorescence emission at 300 K. In other words, the efficiency of phosphorescence is zero (ФPhos = 0). Thus, the quantum efficiency of delayed emission (ФDE) is equal to the efficiency of delayed fluorescence (ФDF). Thus, the quantum efficiencies of prompt (ФPF) and delayed emission (ФDF) are evaluated by the corrected estimation method and the rate constants were calculated according to the reported method[42].  where *k*PF and *k*DF are the radiative decay rate for prompt and delayed fluorescence, respectively, Фall is the total photoluminescence quantum efficiency, *K*rS and *k*nrS are the radiative and nonradiative decay rate constants from a singlet excited state, respectively, *k*ISC and *k*RISC are the intersystem crossing and reverse intersystem crossing rate constants, respectively, *k*nrT is the nonradiative decay rate constant from a triplet excited state. | | | | | | | | |

**Table S4.** Summary of OLED device performance utilizing **ν-DABNA**, DTPF-ν-DABNA and DTP-ν-DABNA

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Dopant** | **x**  **(wt%)** | **CEmax/10/100/1000**  **(cd A-1)** | **PE max/10/100/1000**  **(lm W-1)** | **EQE max/10/100/1000**  **(%)** |
| **ν-DABNA** | 1 | 31.0/-/29.5/23.2 | 25.6/-/20.8/11.7 | 34.4/-/32.8/26.0 |
| **DTPF-ν-DABNA** | 2 | 40.0/33.7/22.8/7.8 | 40.5/33.1/19.3/4.4 | 36.0/28.9/18.5/6.3 |
| 5 | 40.0/33.7/21.3/6.6 | 40.4/32.8/17.8/3.4 | 34.2/27.3/18.2/5.7 |
| 10 | 30.0/27.3/18.6/5.9 | 30.4/26.5/15.6/3.0 | 24.6/21.2/14.6/4.6 |
| **DTP-ν-DABNA** | 2 | 50.0/44.7/34.8/16.2 | 50.0/43.2/28.8/9.9 | 31.5/27.0/20.9/9.1 |
| 5 | 44.9/44.2/33.7/14.5 | 43.7/42.9/28.2/8.5 | 25.6/25.1/19.1/8.7 |
| 10 | 40.0/34.6/28.6/13.5 | 40.8/33.8/24.1/8.0 | 22.7/18.8/15.4/7.4 |

Values of current efficiency (CE), power efficiency (PE), and external quantum efficiency (EQE) at the maximum, 10/100/1000 cd m-2

**Table S5** Summary of reported diboron blue MR-TADF emitters with high efficiency (EQEmax > 30%).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Emitters** | **λEL**  **(nm)** | **FWHM (nm)** | **EQEmax**  **(%)** | **CIE**  **(x, y)** | **Ref.** |
| DTPF-ν-DABNA | 480 | 21 | 36.0 | (0.09, 0.22) | This work |
| DTP-ν-DABNA | 492 | 22 | 31.5 | (0.07, 0.38) |
| CFDBCz | 488 | 22 | 32.4 | (0.12, 0.43) | Adv. Opt. Mater. 2024, 12(15):2302987. |
| ν-DABNA | 469 | 18 | 34.4 | (0.12, 0.11) | Nat. Photon. 2019, 13(10):678-682. |
| NO-DBMR | 469 | 26 | 33.7% | (0.12, 0.12) | Angewandte Chemie International Edition. 2023, 62(32):e202306768. |
| Π-CzBN | 494 | 21 | 37.4 | (0.08, 0.45) | Angewandte Chemie International Edition. 2023, 62(32):e202306413. |
| DTBA-B2N3 | 475 | 28 | 30.9 | (0.11,0.18) | Nat. Photon. 2023, 17(3):280-285. |
| *o*-Tol-ν-DABNA-Me | 472 | 18 | 33.1 | (0.11, 0.12) | Sci. Adv. 2023, 9(22):eadf1388. |
| m-ν-DABNA | 471 | 18 | 36.2 | (0.12, 0.12) | Chem. Eng. J. 2022, 432:134381. |
| 4F-ν-DABNA | 464 | 18 | 35.8 | (0.13, 0.08) |
| 4F-mν-DABNA | 461 | 18 | 33.7 | (0.13, 0.06) |
| m[B-N]N1 | 478 | 30 | 30.4 | (0.13, 0.27) | Angewandte Chemie International Edition. 2022, 61(40):e202207293. |