



Tuning the Optical and Photophysical Properties of Boron Aza-Dipyridylmethene dyes for Optoelectronics Applications

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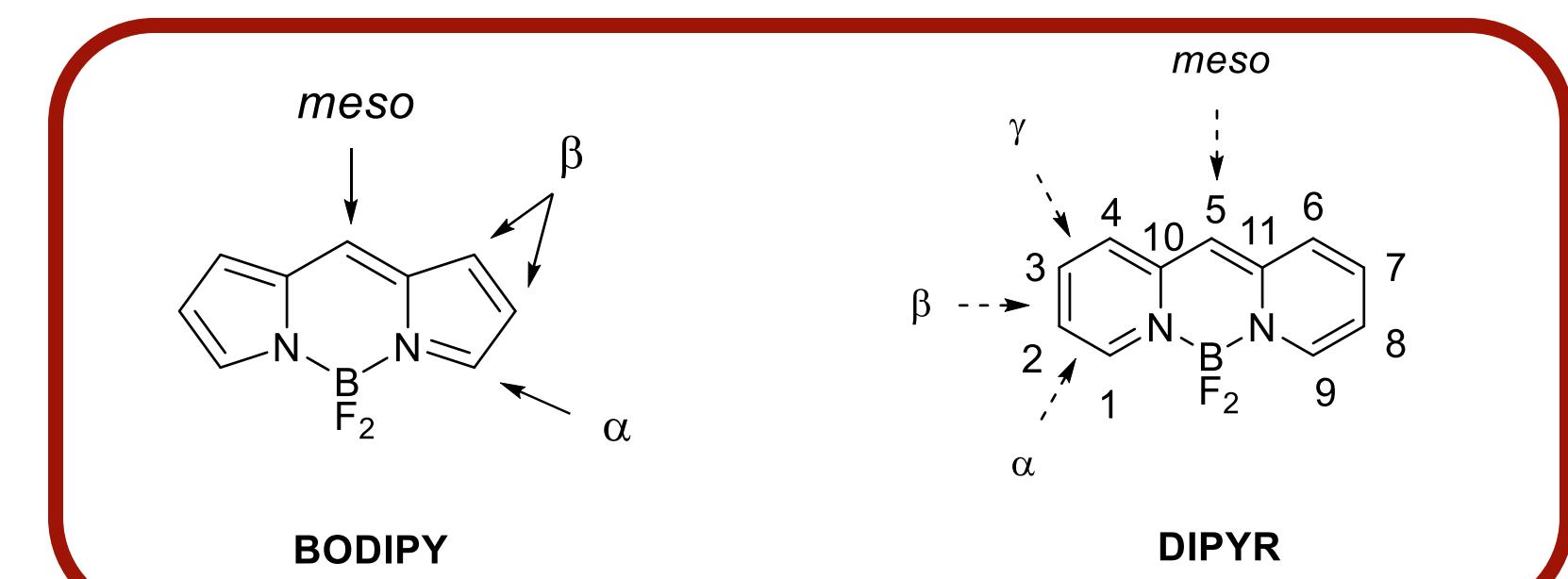


Abstract

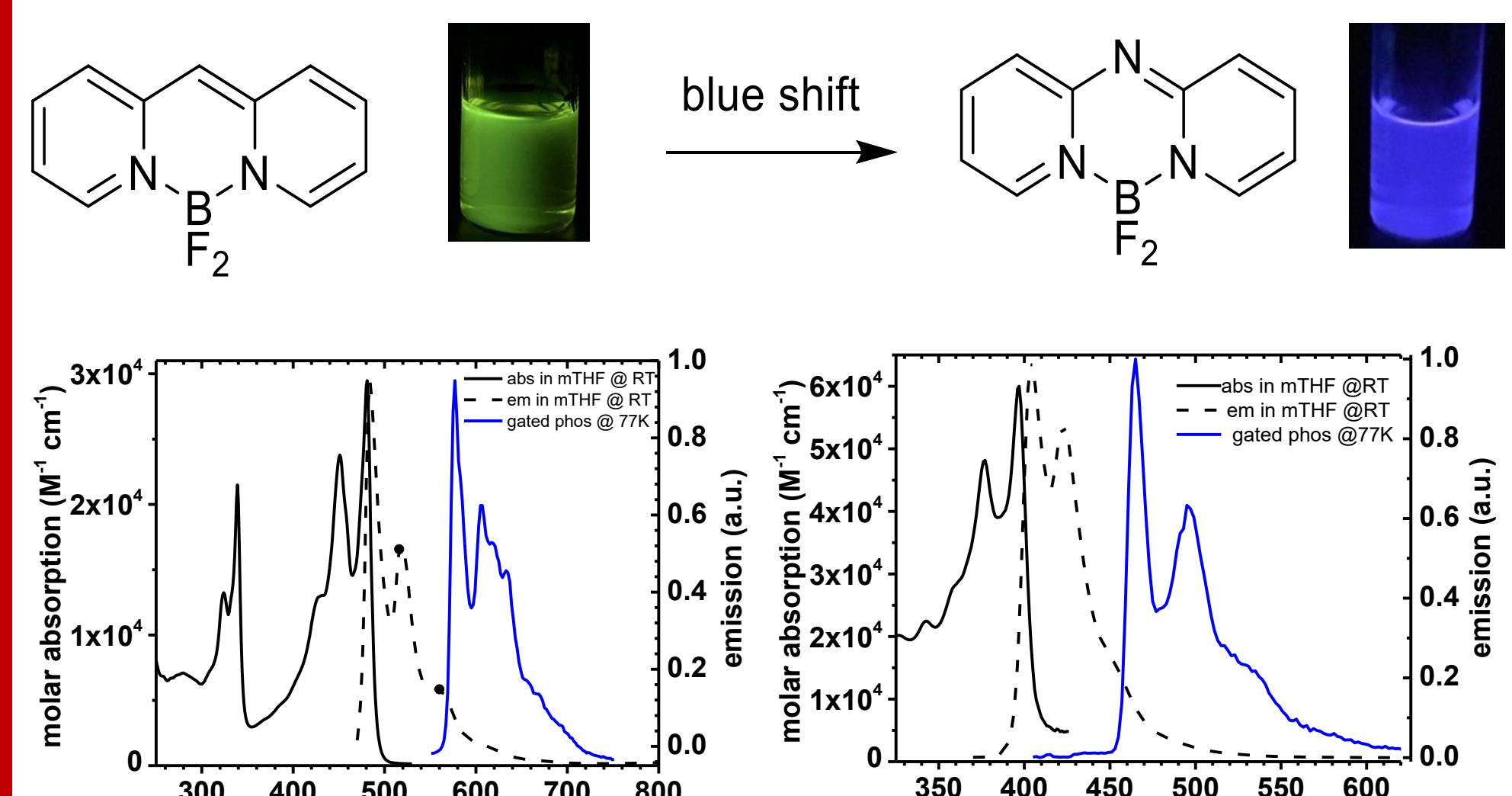
A series of substituted boron aza-dipyridylmethene (aD) compounds are explored for their attractive photophysical and electrochemical properties as fluorescent emitters for blue OLEDs. Previous work in our lab have demonstrated the synthetic ease of dipyridylmethene monomers¹ and their interesting photophysical properties as homoleptic meso-linked dimers². Using Density Functional Theory (DFT) modeling, we combine our theoretical and experimental efforts to synthesize a library of aD compounds by replacing the meso carbon with nitrogen to destabilize the HOMO energy. The synthesized aD derivatives emit blue light with λ_{max} between 400-460 nm and internal quantum efficiencies above 85 %. From TD-DFT calculations, estimation of the singlet and triplet energies that are deduced from fluorescence and phosphorescence emission, respectively, closely matches the experimental data of $\Delta E_{\text{ST}} \leq 0.4$ eV. Aza-dipyridylmethenes show promise as blue emitting fluorophores in OLEDs with EQE_{max} = 4.5 %, approaching the maximum theoretical limit of fluorescent (f) OLED of 5.5 %. Boron aza-dipyridylmethane are synthetically tunable compounds which show interesting photophysical properties for applications in organic electronics.

Background & Rationale

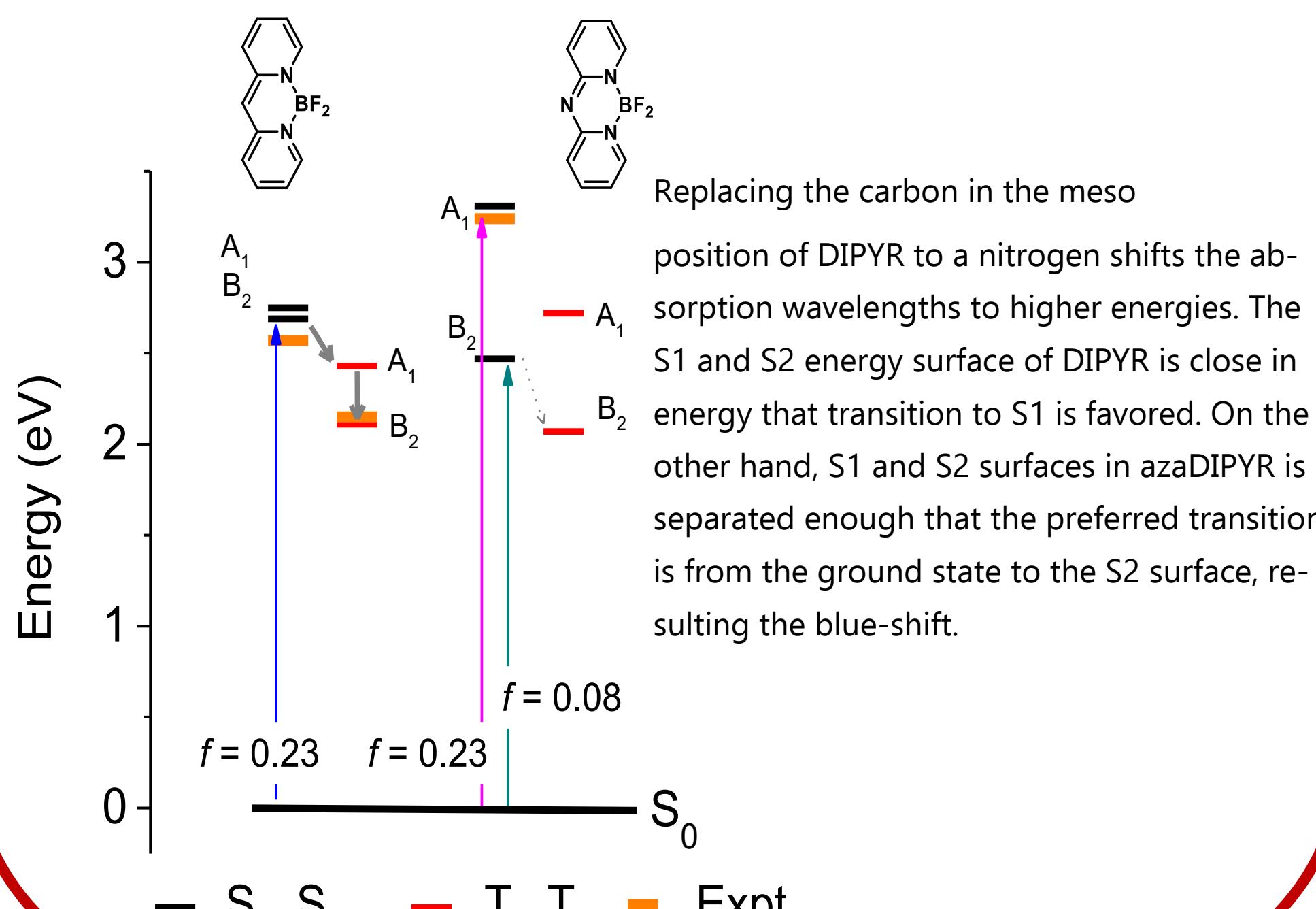
The DIPYR system is particularly interesting because of its orbital pattern where nodes bisect every other carbon atom in the HOMO and LUMO orbitals, a feature common for cyanine chromophores, leading to intense and narrow absorption. The synthesis of cyanine-like dyes, systems such as boron dipyromethene (BODIPY), is commonly used for application in organic electronics. However, synthetic modification is not easily achieved due to polymerization and porphyrin formation. The parent DIPYR molecule has shown to be a straightforward synthesis with desirable and tunable photophysical properties, leading to libraries of interesting fluorophores which can be used for systems such as, but not limited to, organic photovoltaic and organic light-emitting diode.



meso-CH vs. meso-N

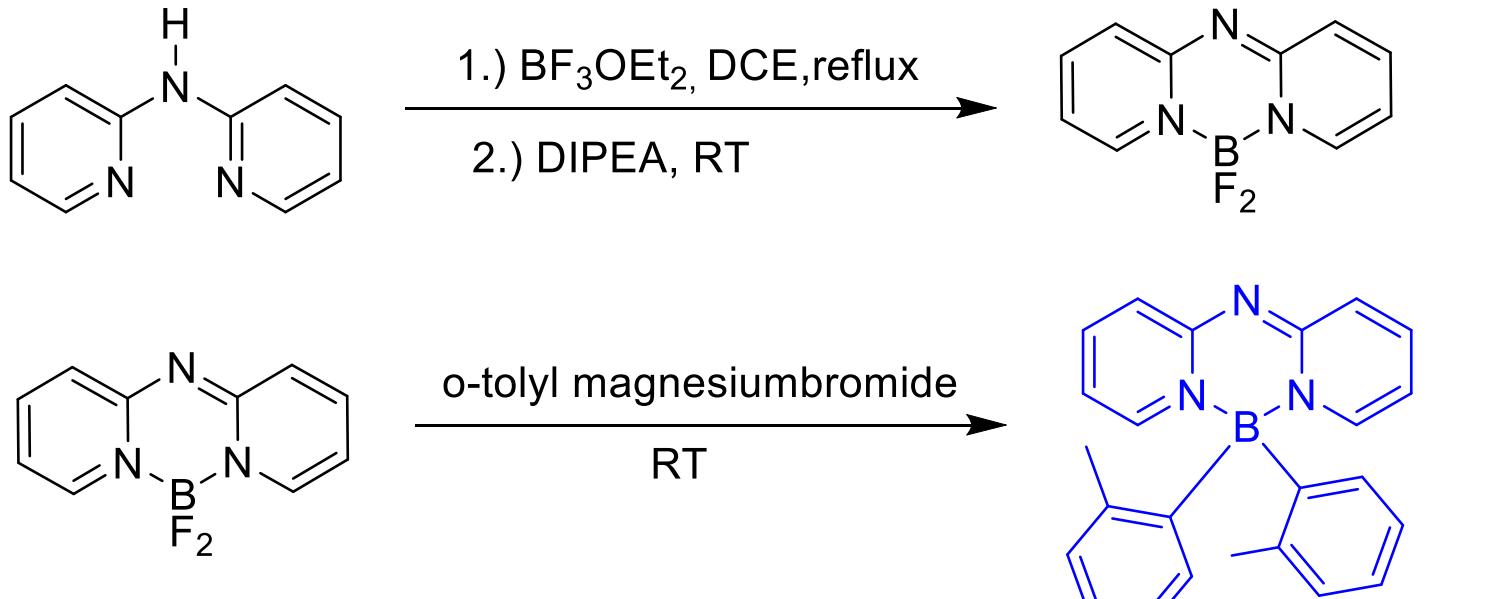


	Abs. λ_{max} (nm)	ϵ at λ_{max} ($\text{M}^{-1} \text{cm}^{-1}$)	Φ_{PL}	τ (ns)	k_r (10^8 s^{-1})	k_{nr} (10^8 s^{-1})
DIPYR	481	2.9×10^4	0.17	1.9	0.91	4.5
azaDIPYR	398	5.7×10^4	0.42	2.11	2.00	2.7

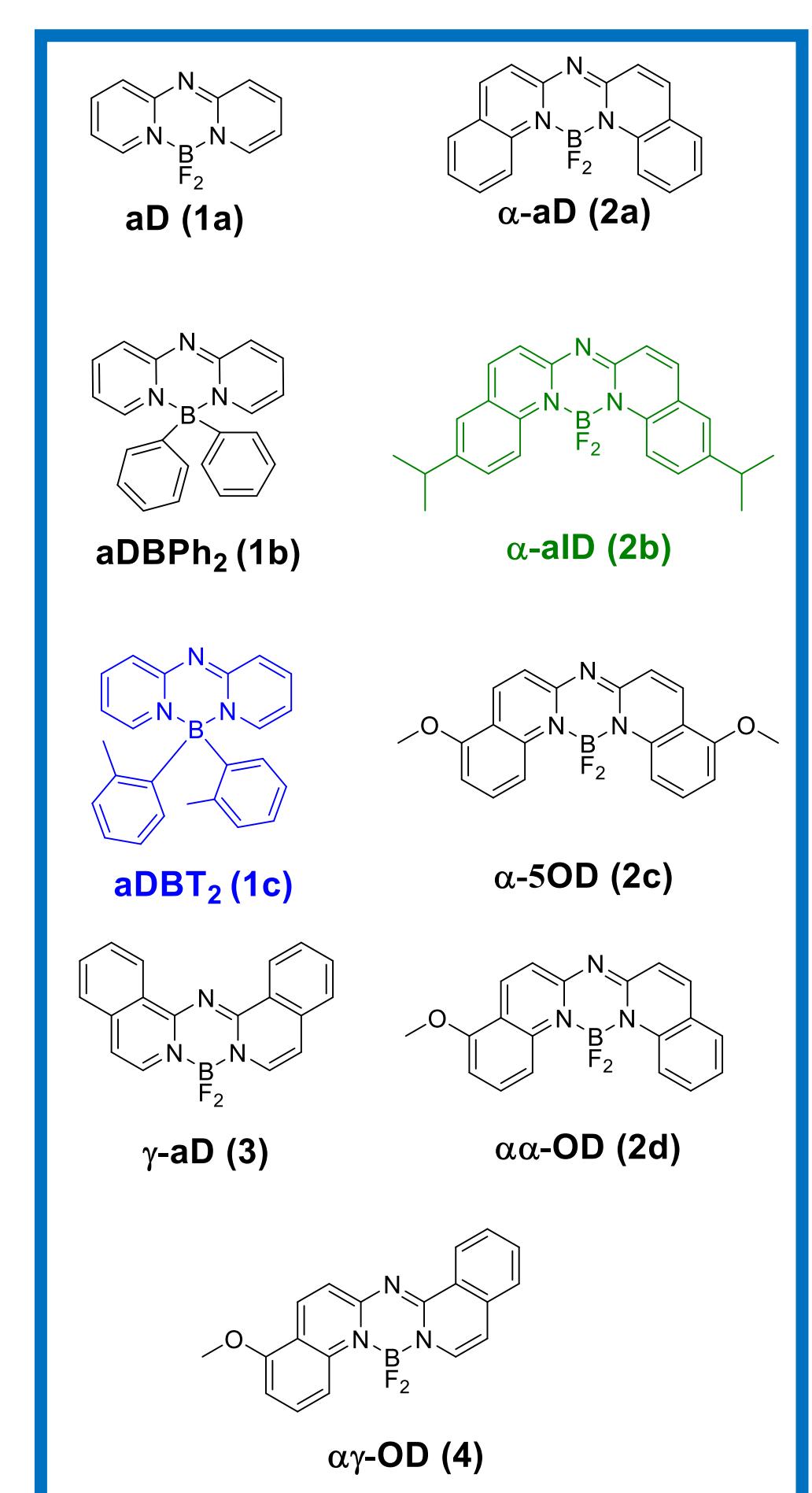
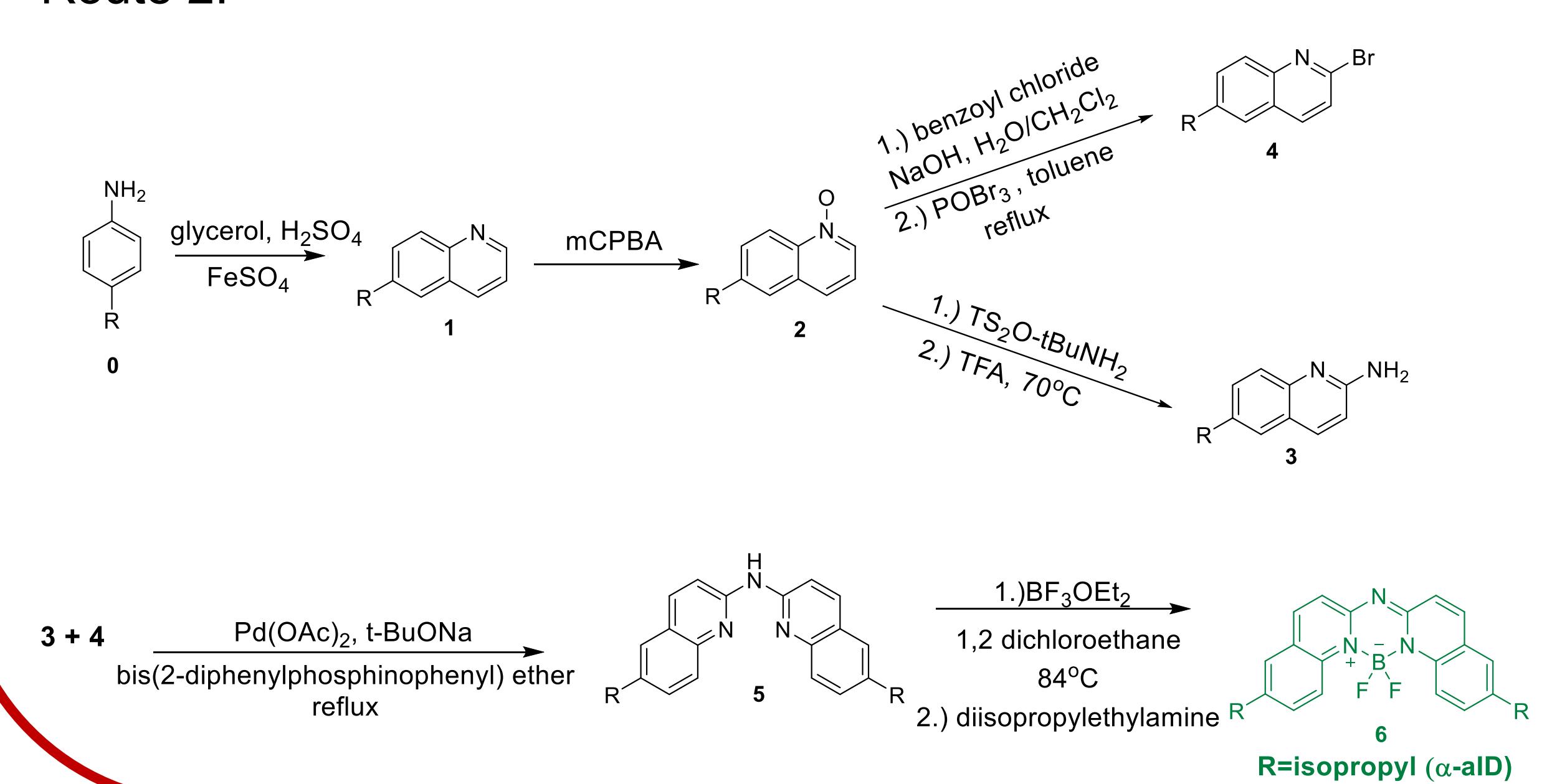


Synthesis

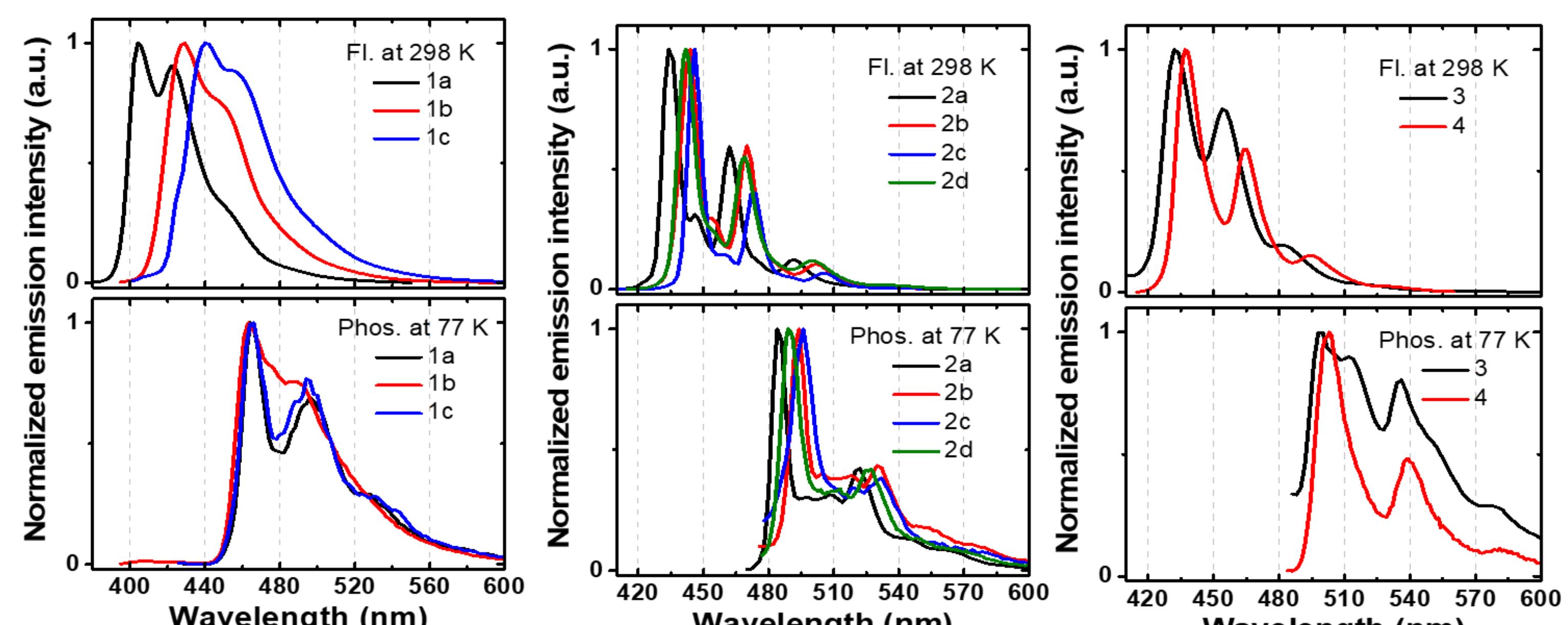
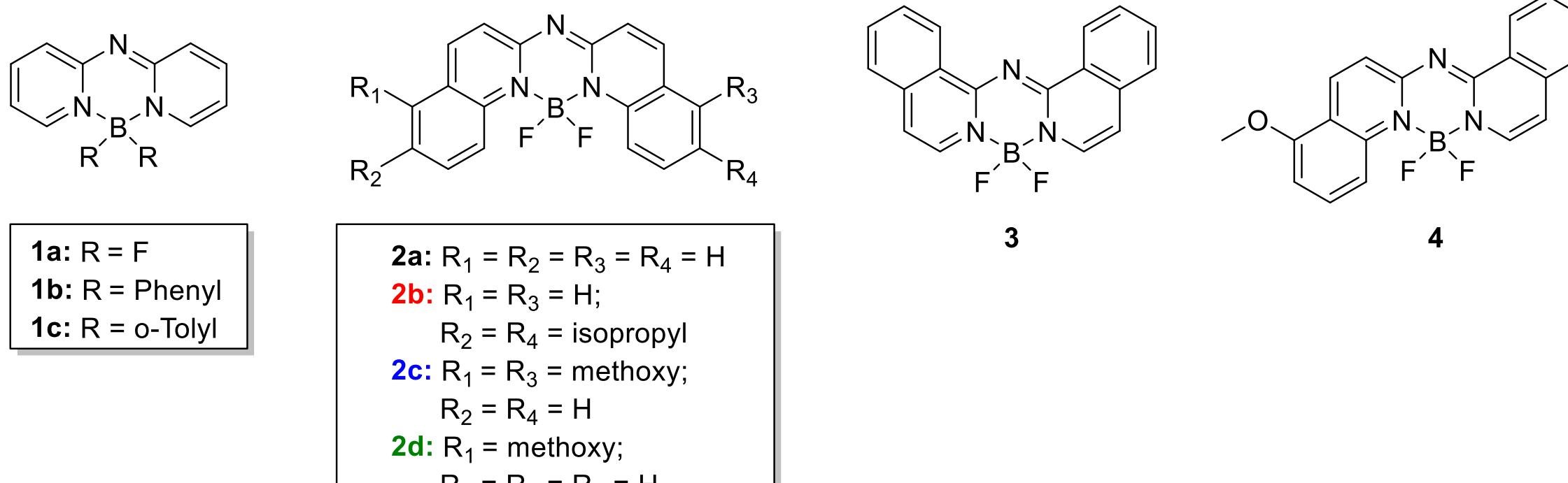
Route 1:



Route 2:



Characterization of α-aD Core Modifica-



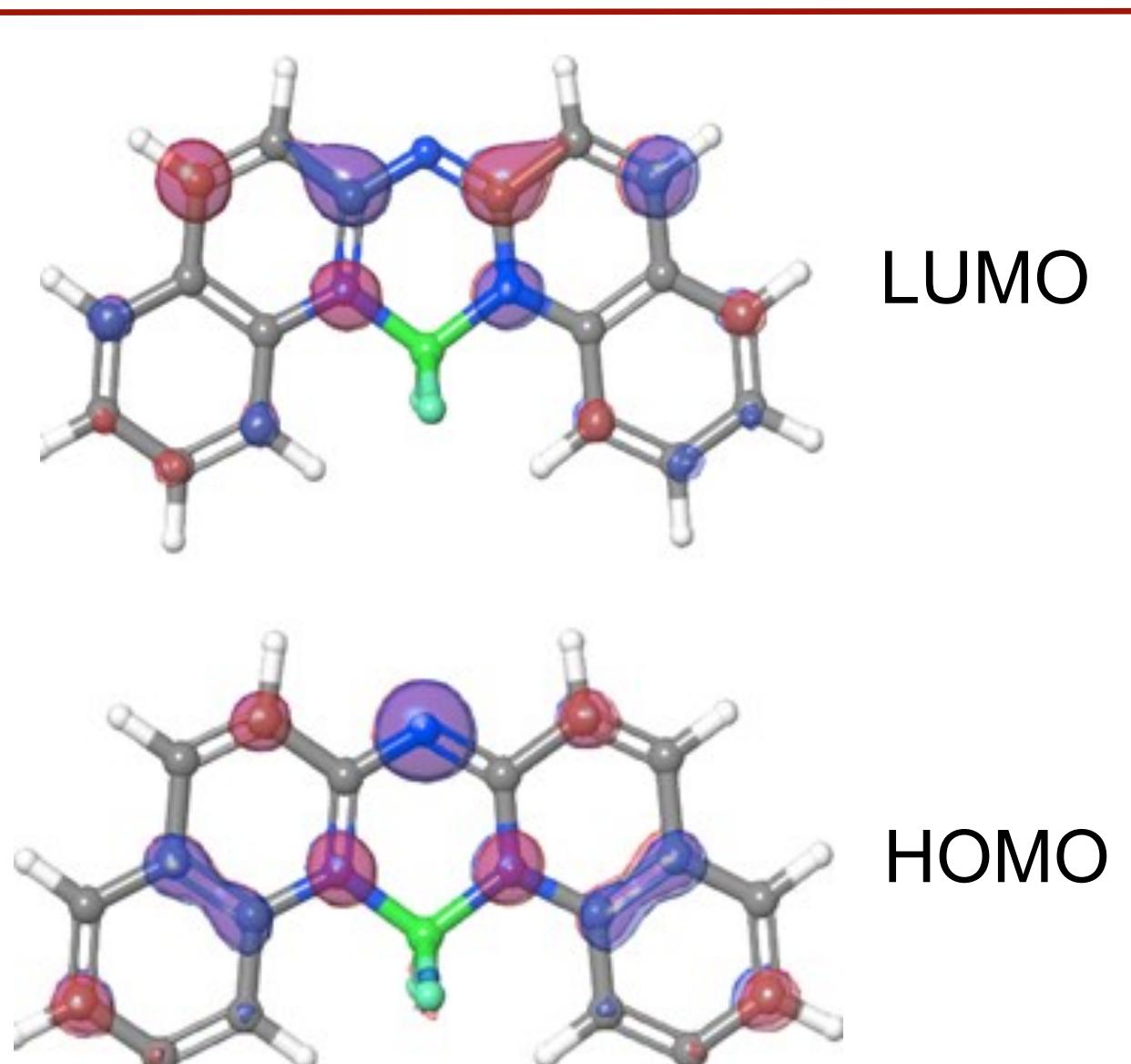
	2a	2b	2c	2d
Φ_{fl}	0.86	0.87	0.84	0.84
τ_{fl} (ns)	3.25	3.82	3.48	3.28
k_r (10^8 s^{-1})	2.65	2.27	2.41	2.56
k_{nr} (10^8 s^{-1})	0.43	0.34	0.46	0.49
S_1 (eV/nm)	2.86 / 434	2.79/444	2.77/447	2.81/442
T_1 (eV/nm)	2.56/484	2.51/494	2.51/494	2.53/490
$\Delta E(S_1-T_1)$	0.30	0.28	0.26	0.28
HOMO (eV)	-6.21	-6.10	-5.92	-6.13
LUMO (eV)	-2.52	-2.44	-2.38	-2.33

Φ_{fl} : Quantum Yield

τ : excited state lifetime

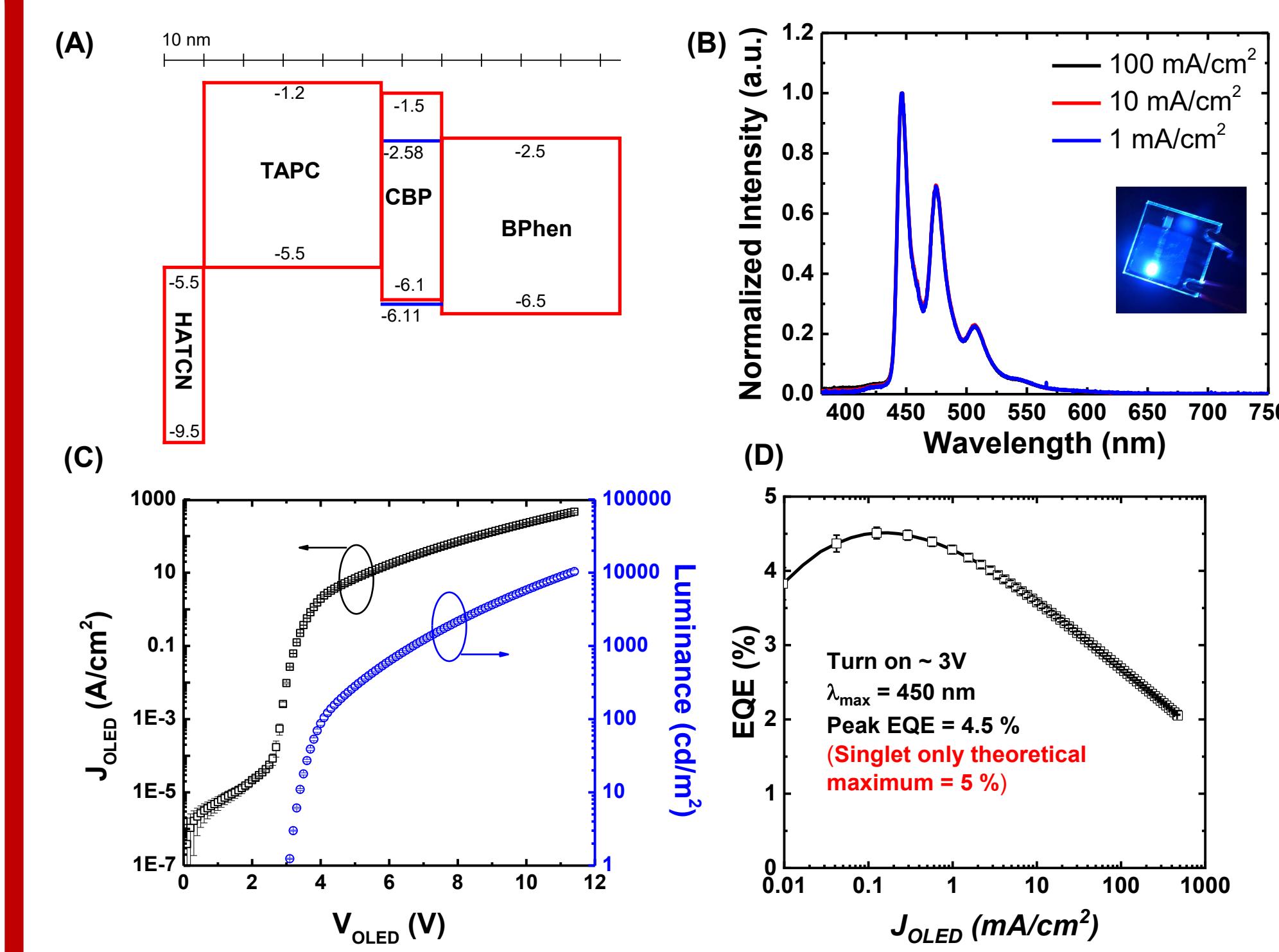
k_r : radiative decay

k_{nr} : nonradiative decay

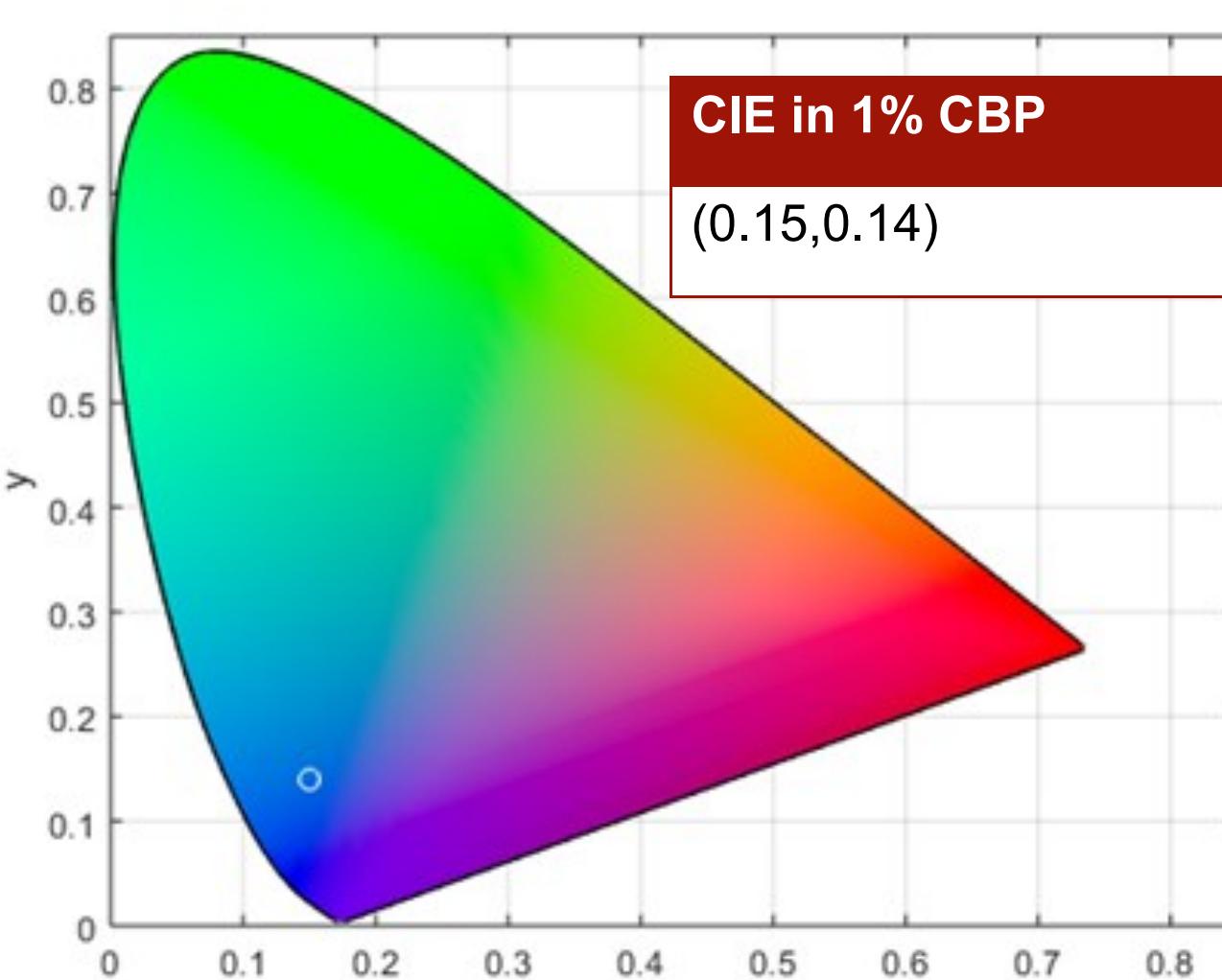


Our synthetic efforts were focused on the benzannulated derivatives because benzannulation of DIPYR has shown improvement in minimizing non-radiative decay pathways by eliminating the symmetry allowed transition through intersystem crossing to the low-lying T₂ state in DIPYR. (J.H. Golden et al., J.Org. Chem. 2017, 82, 7215-7222).

Blue OLED: α-aD doped at 1 % in CBP



-Solvatochromic shift in organic solid (434nm to 454nm)
-Reabsorption of first peak at higher concentration
-PLQY in 1% CBP: 71%



Conclusion

Substituted boron aza-dipyridylmethenes are an interesting structure which have been explored as fluorescent blue materials in OLEDs. These materials are easy to modify with a range of substituents to change their energetics, while maintaining a high quantum efficiency, small S₁-T₂ gap and small stoke shift. Substituted aza-boron-dipyridylamine (aD) complexes were explored for their attractive photophysical and electrochemical properties, giving intense blue fluorescence ($\lambda_{\text{em}} = 400 - 500$ nm) with quantum efficiency above 85 %. When S₁ is below the T₂ state, the fluorescence quantum yield is high. When T₂ is below the S₁, the quantum yield is low due to the fast rate of intersystem crossing. Minimum overlap between the HOMO and LUMO has narrowed the singlet-triplet energy gap ($\Delta E_{\text{ST}} \leq 0.4$ eV). Blue emitting fluorophores in OLEDs with turn on voltage of 3V and EQE_{max} = 4.5 %, approaching the maximum theoretical limit of fluorescent (f) OLED of 5.0 %. The high triplet energy for these materials offers promising energy transfer to other dopant or emitters that can also be engineered in a white emissive OLED, combining fluorescence and phosphorescence in the same device architecture.

Acknowledgments

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