BODIPY-based far-red/NIR chromophores with Aggregation-Induced Emission

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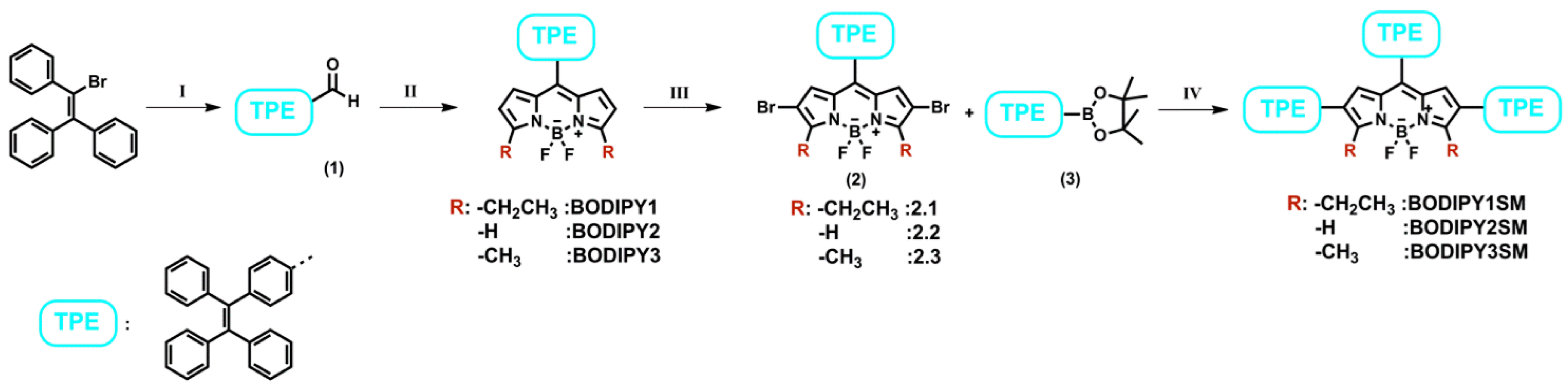
I. Abstract

BODIPY (boron dipyrromethene) dyes gained a lot of attention during the last years due to outstanding structural/optoelectronic properties such as an easily modifiable molecular backbone[1], a large molar absorption coefficient[2], a high fluorescence quantum yield[3], and excellent chemical and photochemical stability[4]. However, loss of fluorescence intensity in the solid state is limiting its application to organic electronic devices. A promising approach to improve the photo-physical properties of BODIPY is to leverage Aggregation-Induced Emission (AIE) behavior. With this in mind, far-red/NIR emitting BODIPY-tetraphenylethylene hybrids have been synthesized. The effect of varying substituents in different positions of the BODIPY core has been investigated as well as the EL performance of these hybrids in Organic Light-Emitting Diodes (OLEDs). Tri-TPE-substituted BODIPYs reach outstanding PL efficiencies of ≈ 100 % in the solid state. Incorporation of tri-TPE-substituted BODIPYs as dopant of F8BT in the active layer of PLEDs accomplished external electroluminescence quantum efficiencies (EQEs) up to 1.4% at 660 nm. The achieved external quantum efficiency (EQE) is one of the highest values reported so far for small molecule/F8BT blend in metal-free PLEDs at 660nm.

II. Synthetic Pathway



Scheme 1. Synthesis route for TPE-substituted BODIPYs (I: (4-formylphenyl)boronic acid, TBAB, $Pd(Ph_3)_4$, toluene. II: corresponding pyrrole, TFA, DDQ, Et_3N, $BF_3.OEt_2$, DCM. III: NBS, DCM:DMF(50:50). IV: K_2CO_3, $Pd(Ph_3)_4$, THF:water(80:20))

III. Optical Properties

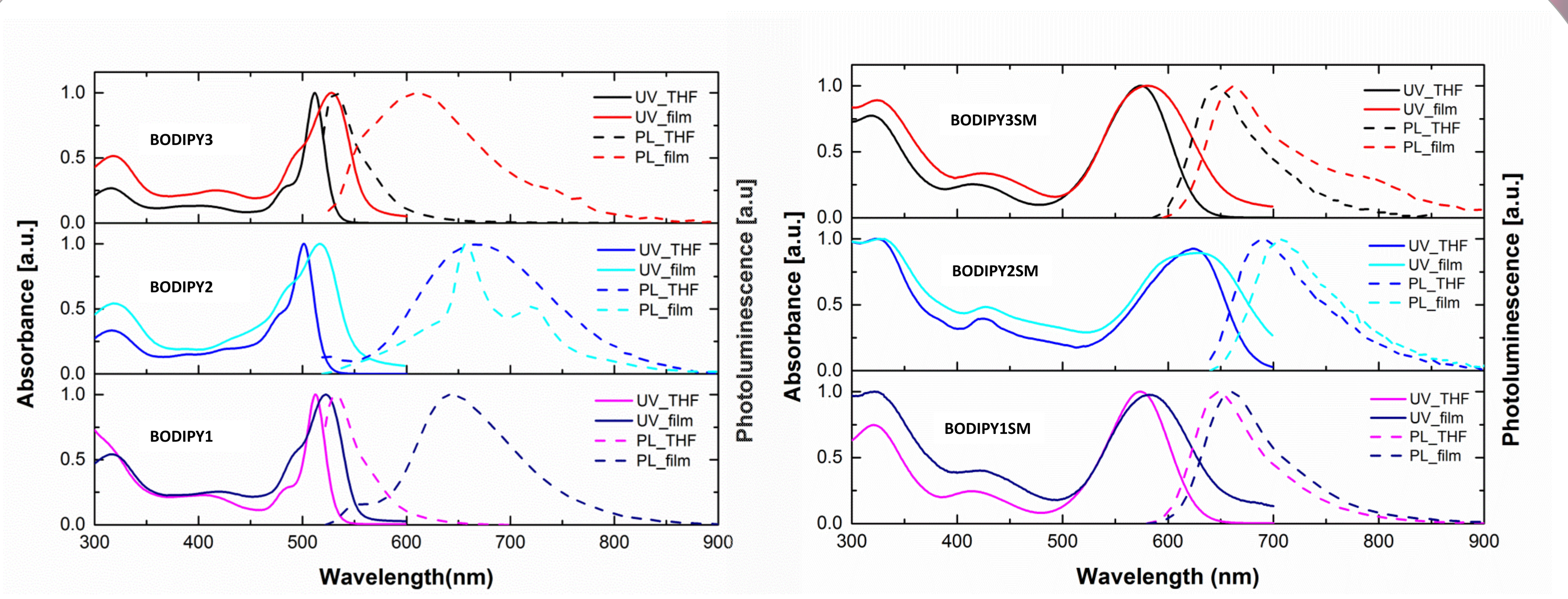


Figure 1. Absorption and emission of small molecules in THF and in solid-state thin films

Table 1. Summary of optical properties of small molecules

Compound	λ_{abs}(nm) in THF	λ_{PL}(nm) in THF	λ_{abs}(nm) in film	λ_{PL}(nm) in film	Φ (%) in THF	Φ (%) in film (Ex: 445/520nm)	Eg (eV)	HOMO(eV)	LUMO (eV)
BODIPY1	512	532	523	644	4	8/5	2.23	-5.82	-3.59
BODIPY2	502	666	516	658-723	8	8/6	2.24	-5.63	-3.39
BODIPY3	512	532	528	609	4	6/4	2.20	-5.84	-3.64
BODIPY1SM	575	532	583	662	44	98/68	1.87	-5.65	-3.78
BODIPY2SM	623	689	628	709	47	*	1.73	-5.69	-3.96
BODIPY3SM	574	646	580	663	29	68/100	1.87	-5.69	-3.82

* will be measured

λ_{abs} = absorption maximum of monomer in THF solution, λ_{PL} = emission maximum of monomer in THF solution, λ_{abs} in film = absorption maximum of monomer in film, λ_{PL} = emission maximum of monomer in film, Φ_{PL} (%) in THF (100%)= fluorescence quantum yield in 100% THF solution, Φ_{PL} (%) in film = fluorescence quantum yield of film, Eg (eV) = Optical band gap of monomer, HOMO= Highest occupied molecular orbital determined by atmospheric pressure photo-electron spectroscopy (AC-2) , LUMO= Lowest unoccupied molecular orbital calculated as LUMO= Eg(opt)-HOMO(AC-2). Concentration: 10^{-4} M, Excitation wavelength: 445 and 520 nm.

IV. AIE Properties

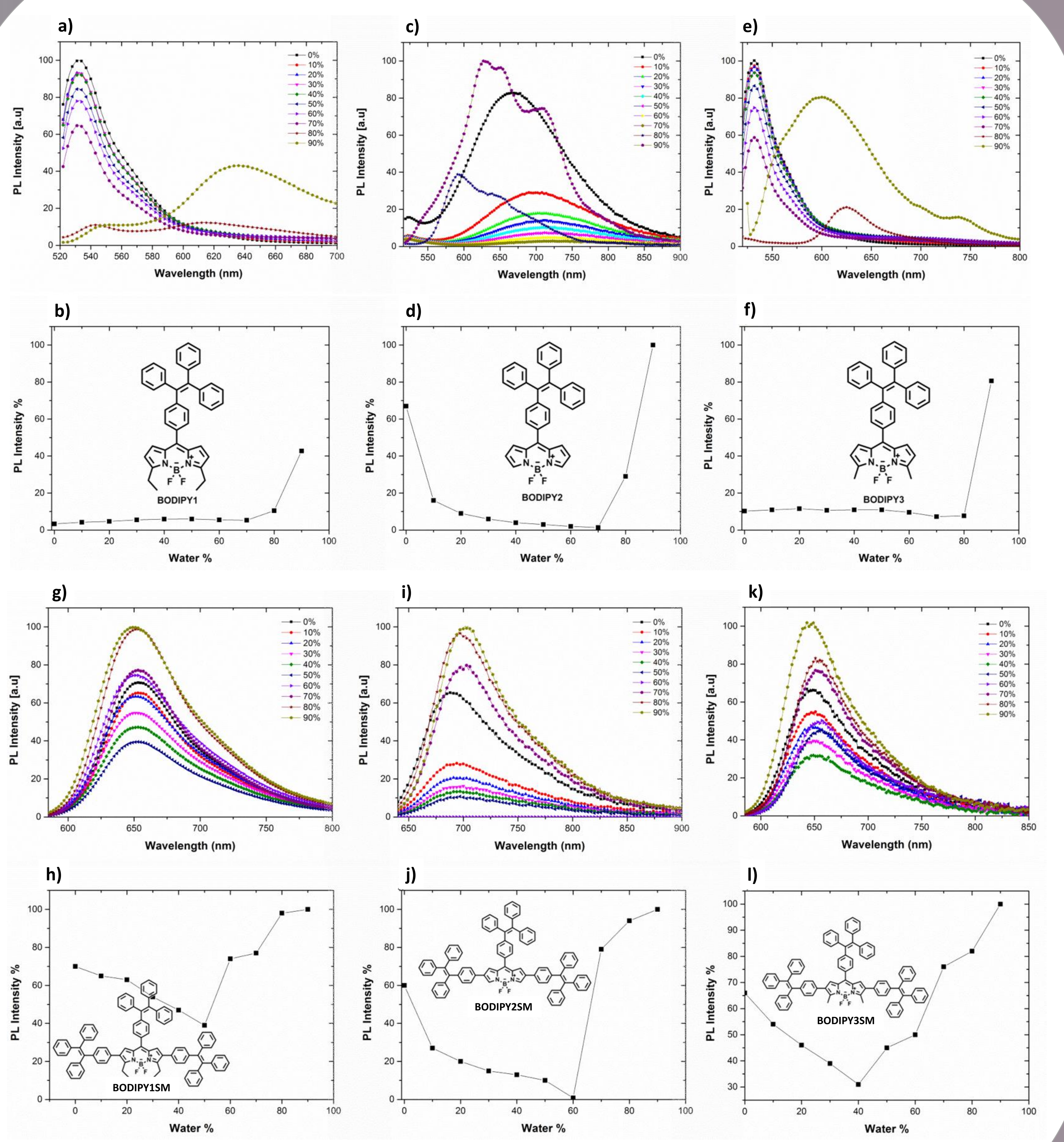
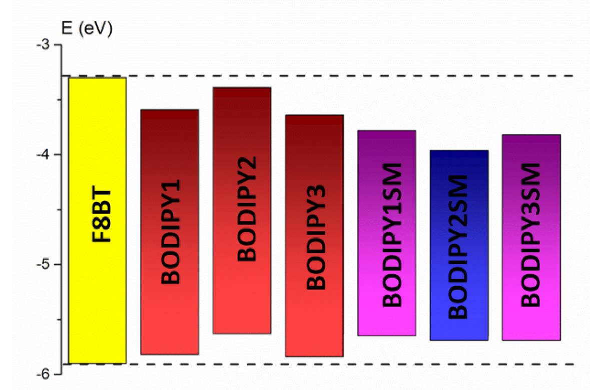


Figure 2. PL measurements in the presence of different water percentages **a-b)** BODIPY1, **c-d)** BODIPY2, **e-f)** BODIPY3 **g-h)** BODIPY1SM, **i-j)** BODIPY2SM, **k-l)** BODIPY3SM

V. OLEDs Measurements



- ✓ Efficient energy transfer (ET) from F8BT to SMs for the BODIPY1-3SM series
- ✓ Exciplex PL in F8BT/BODIPY blends for the BODIPY1-3 series

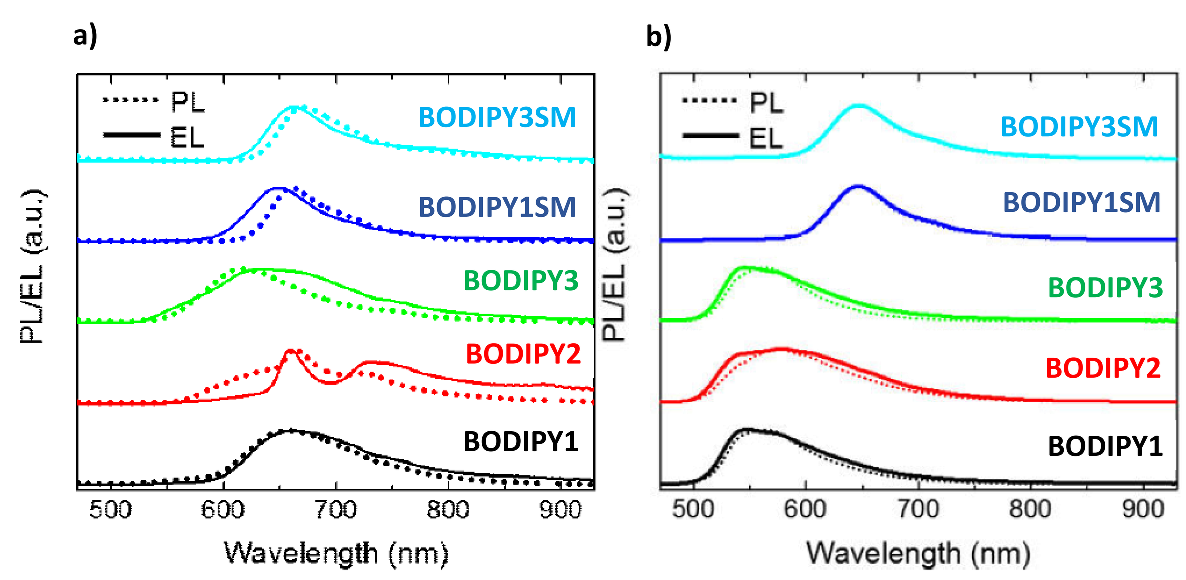


Figure 3. a) EL and PL spectra of TPE-BODIPY oligomers **b)** EL and PL spectra of F8BT:TPE-BODIPY blends with 1% w/w oligomer loading

Table 2. PLQY of bare BODIPY oligomer films and F8BT/oligomer blends with 1% w/w oligomer loading

	QY%	
w/w	bare	1% in F8BT
BODIPY1	8	38
BODIPY2	8	23
BODIPY3	6	41
BODIPY1SM	98	79
BODIPY3SM	68	67

PLQY $_{F8BT}$ =47%

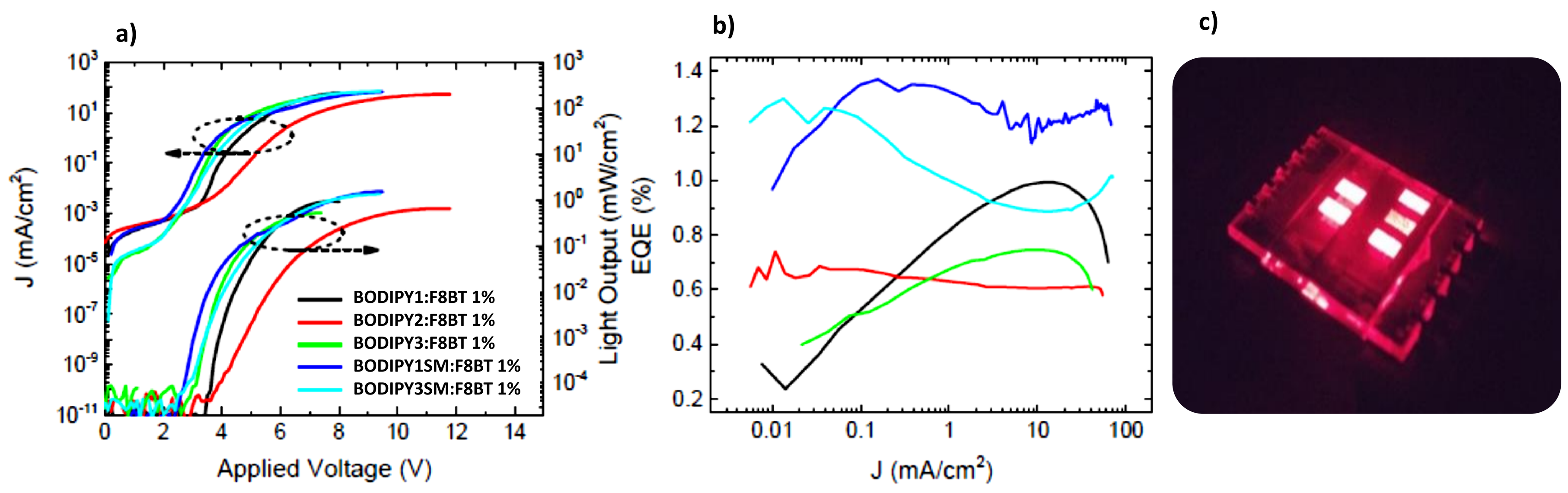


Figure 4. a) JVL plots of electroluminescent PLEDs having F8BT:TPE-BODIPY blends with 1% w/w oligomer loading as active layer **b)** EQE versus current density plot of F8BT-PLEDs with 1% w/w oligomer loading **c)** Photo of a F8BT:BODIPY1SM-based OLED device.

Results:
- ✓EQE > 1% for BODIPY1-3SM oligomers
- ✓Output > 1mW/cm^2
- ✓V_{on} ~3V (like F8BT)

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VII. References

[1] A. Loudet, K. Burgess Chem. Rev. 2007,107,4891-4932
[2] T.Rousseau, A. Cravino, T. Bura, G. Ulrich, Z. Ziessel, J.Roncali J. Chem. Commun. 2009, 19,2298
[3] J. Karolin, L.B.-A. Johansson, L.Strandberg, T. Ny J. Am. Chem. Soc. 1994, 116, 7801-7806
[4] G. Ulrich, R. Ziessel, A.Harriman Angew. Chem. Int. Ed. 2008, 47, 1184-1201