Designing Panchromic Dyes Based on Iridium

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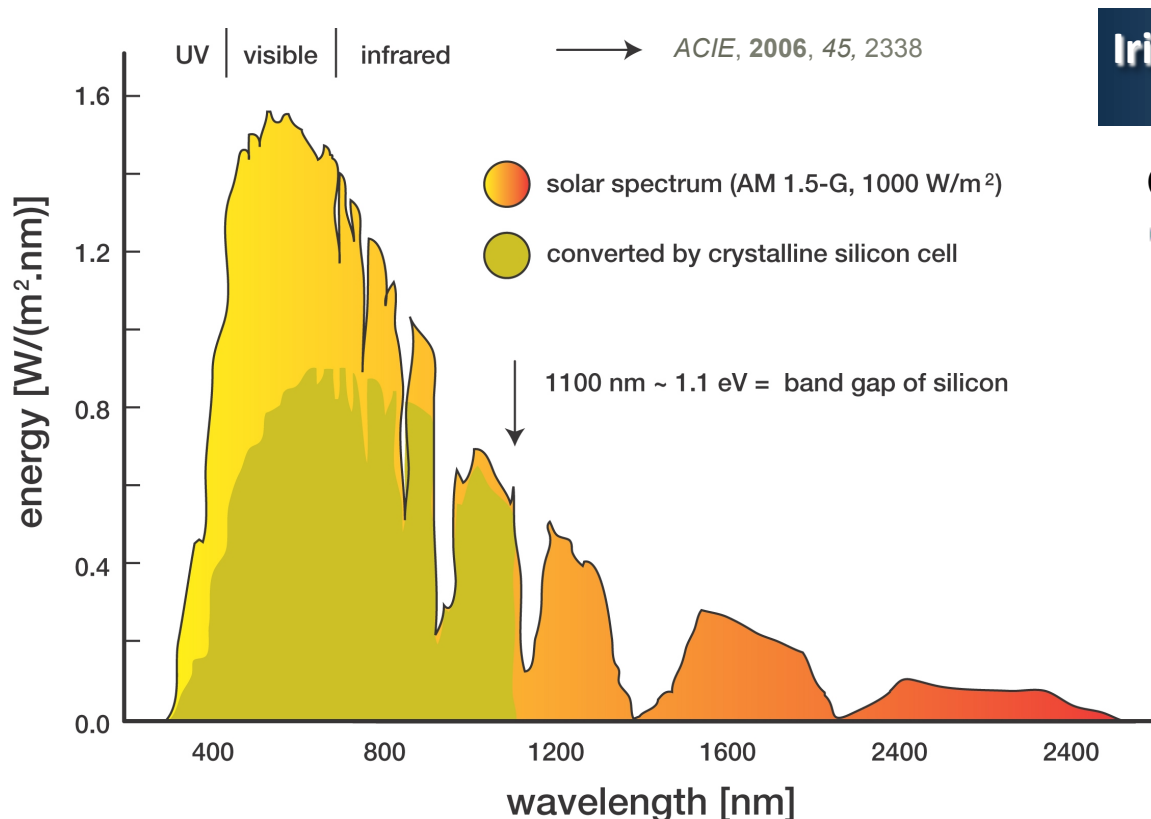
University of St Andrews

Introduction

Solar cells require highly absorptive panchromic materials to instigate efficient light-to-electricity conversion. Though a primary metric of a high performance solar cell is its efficiency, the stability of the cell, and by consequence its molecular components, is also important.
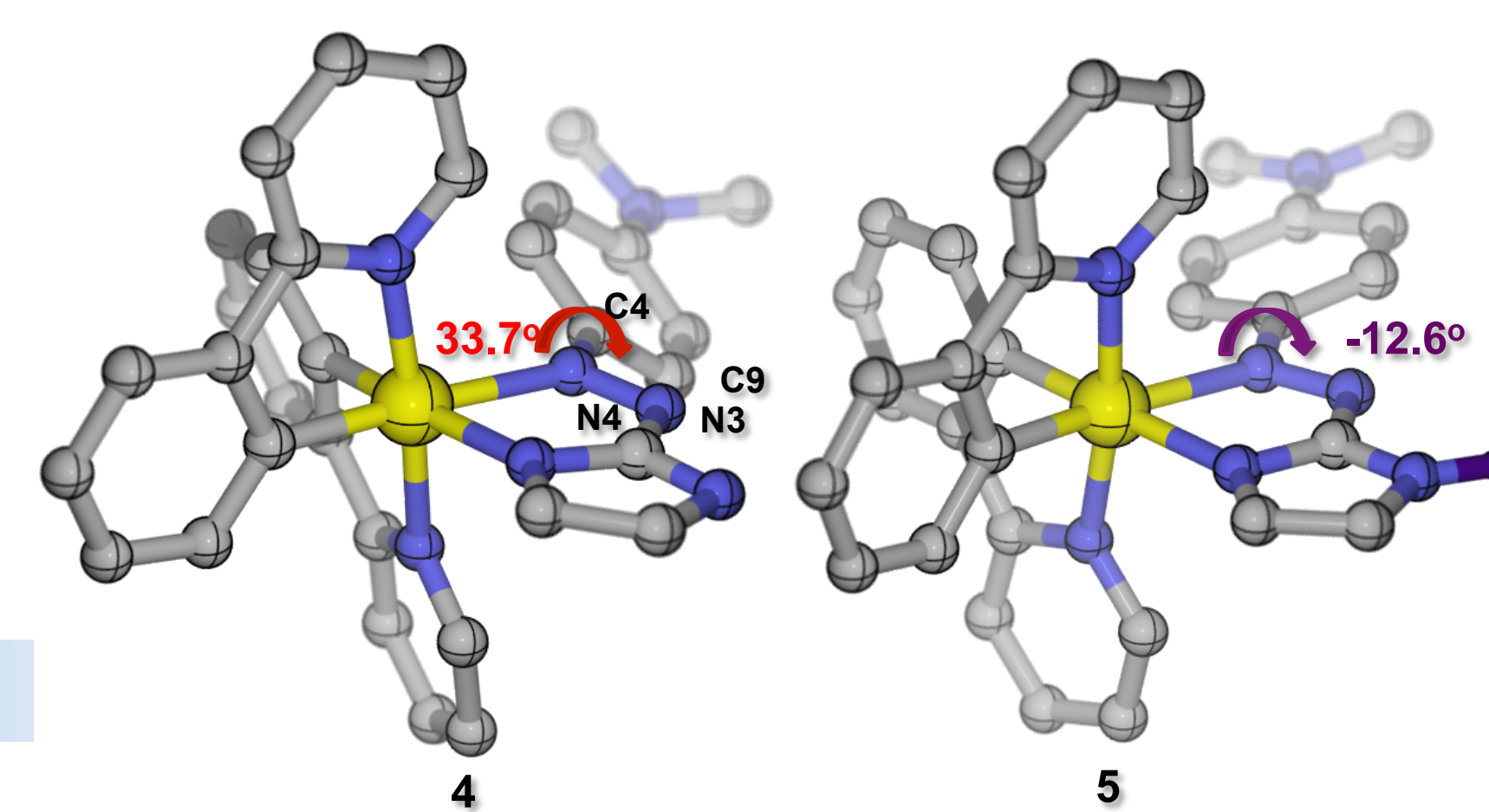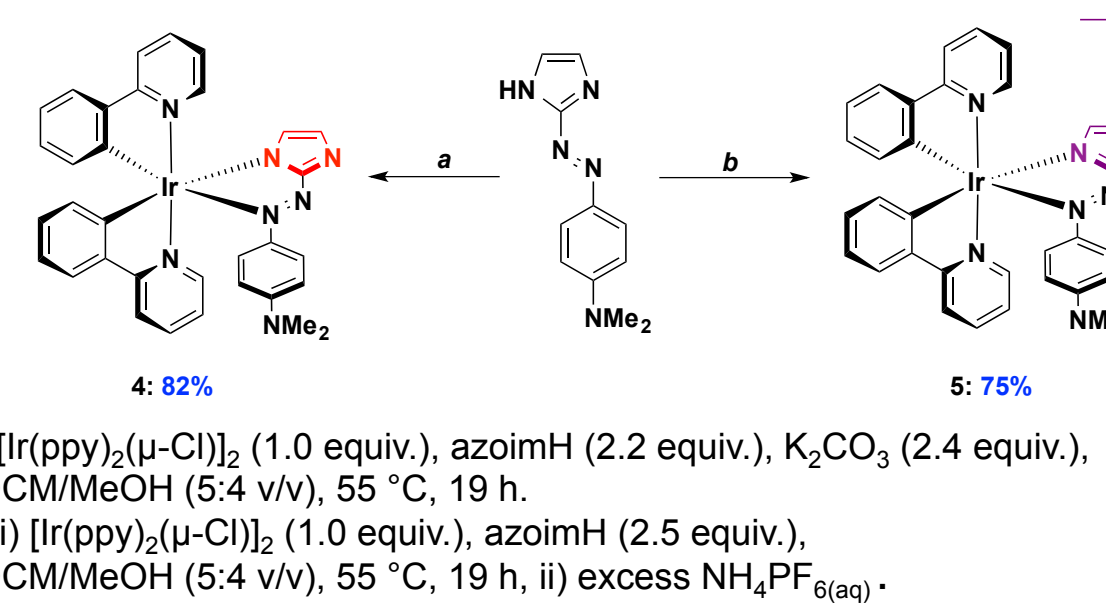
The high chemical and thermal stability of iridium(III) complexes are attractive features; however, no high performance dye has been developed, primarily due to the poor absorption characteristics of most iridium(III) complexes.

We have incorporated ligands with strong charge-transfer character designed to overcome this weakness and to materials with more favourable absorption properties.
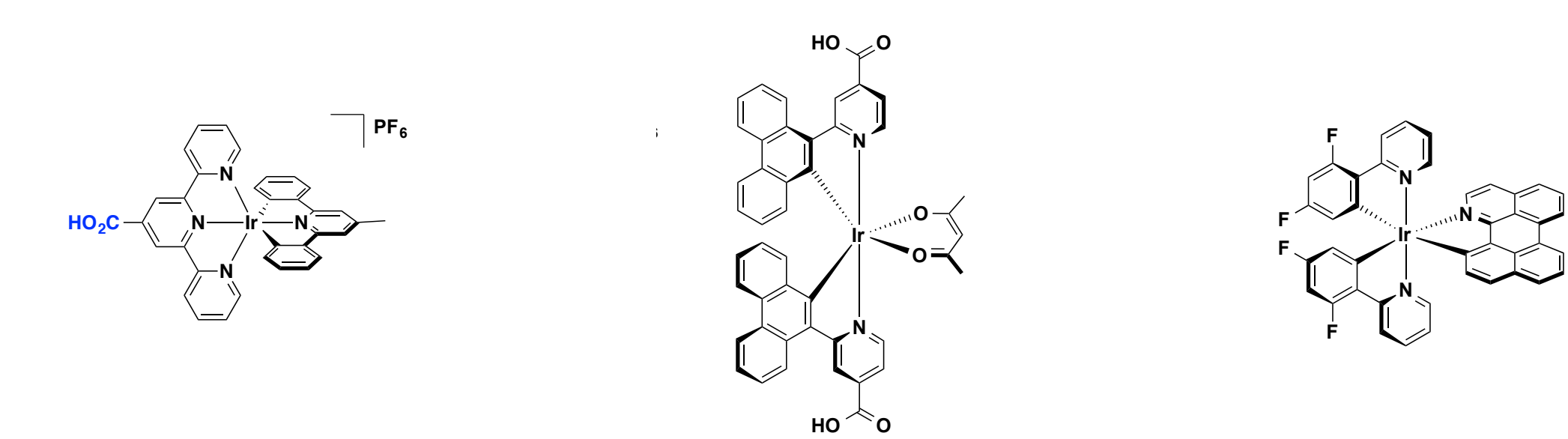

ACIE, 2006, 45, 2338

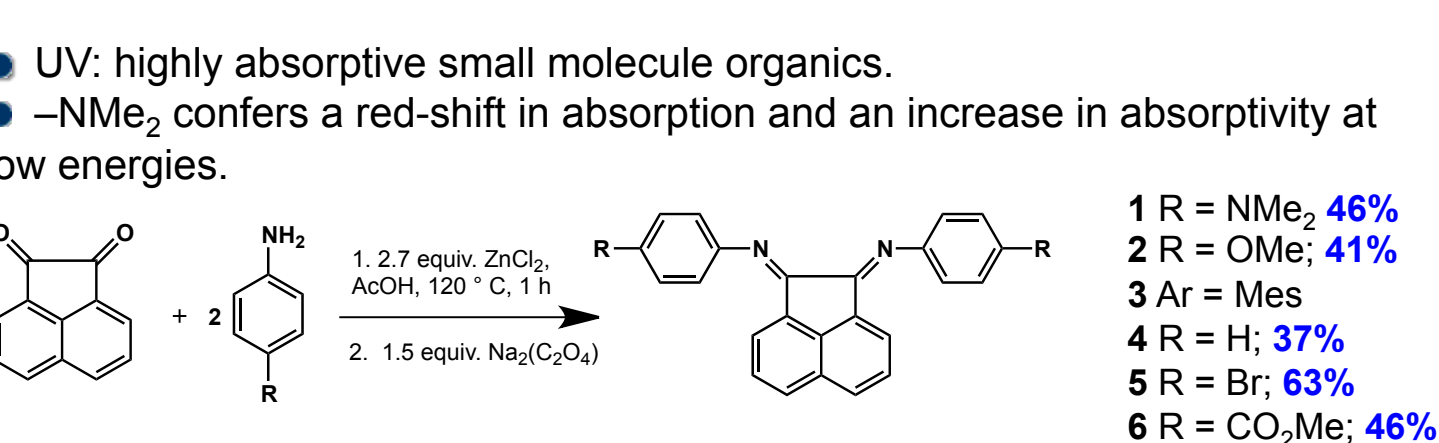## Literature Dyes and Panchromic Absorbers

J. Photochem. Photobiol. A, 2011, 222, 203
λ_{max} /nm [ε (x10³) /M⁻¹ cm⁻¹]: ca. 526 [ca. 2.9]
DSSC: J_{sc}: 8.2 mA cm²; V_{oc}: 456 mV;
FF: 0.58 PCE: 2.2%

Chem. Asian J. 2010, 5, 496
λ_{max} /nm [ε (x10³) /M⁻¹ cm⁻¹]: ca. 475 [ca. 8.0]
DSSC: J_{sc}: 5.8 mA cm²; V_{oc}: 491 mV;
FF: 0.72 PCE: 2.0%

Inorg. Chem. 2013, 52, 7338
λ_{max} /nm [ε (x10³) /M⁻¹ cm⁻¹]: ca. 530 [ca. 8.0]
OPV: J_{sc}: 4.5 mA cm²; V_{oc}: 990 mV;
FF: 0.62 PCE: 2.8%

Aryl-BIAN Ligands

- UV: highly absorptive small molecule organics.
- –NMe₂ confers a red-shift in absorption and an increase in absorptivity at low energies.

1 R = NMe₂ 46%
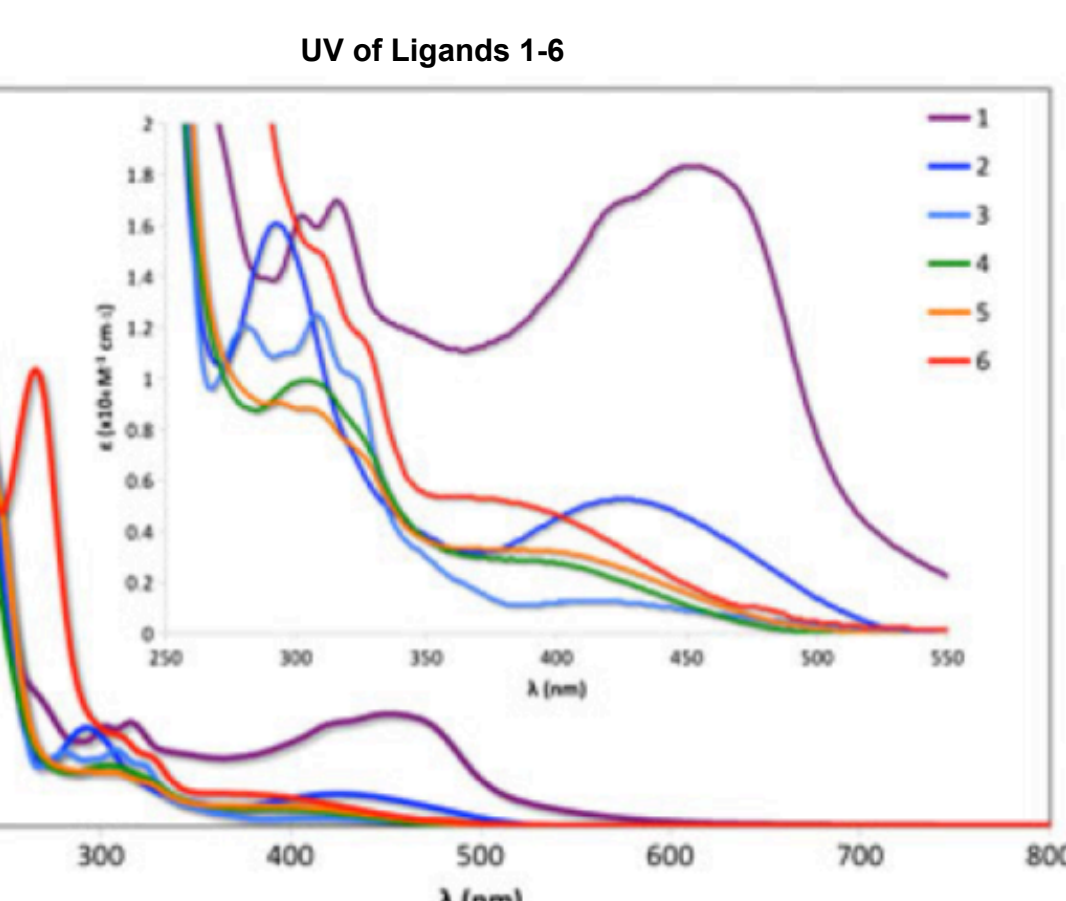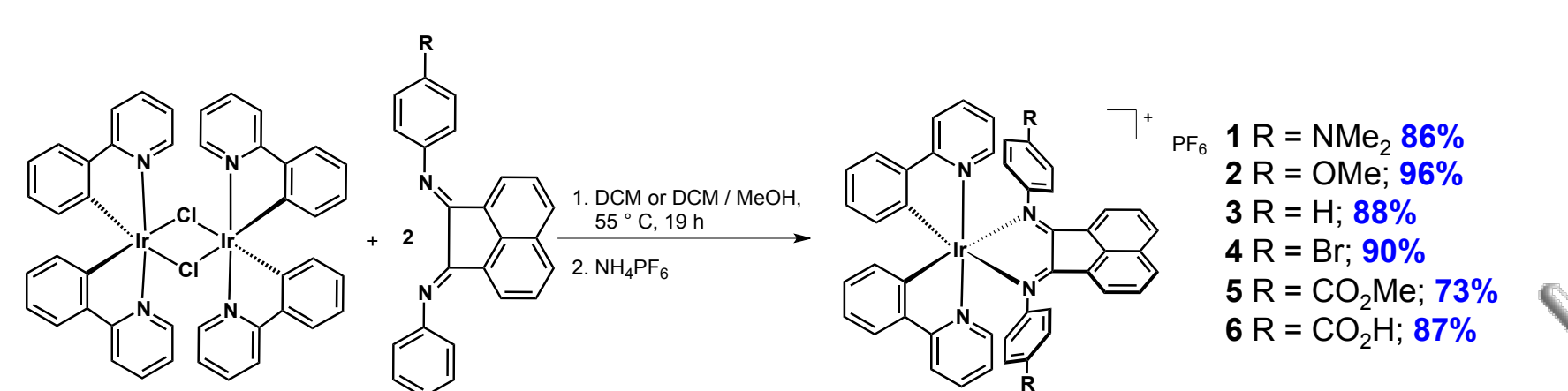2 R = OMe 41%
3 Ar = Mes
4 R = H 37%
5 R = Br; 63%
6 R = CO₂Me; 46%

K. Hasan and E. Zysman-Colman, *J. Phys. Org. Chem.*, 2013, 26, 274.
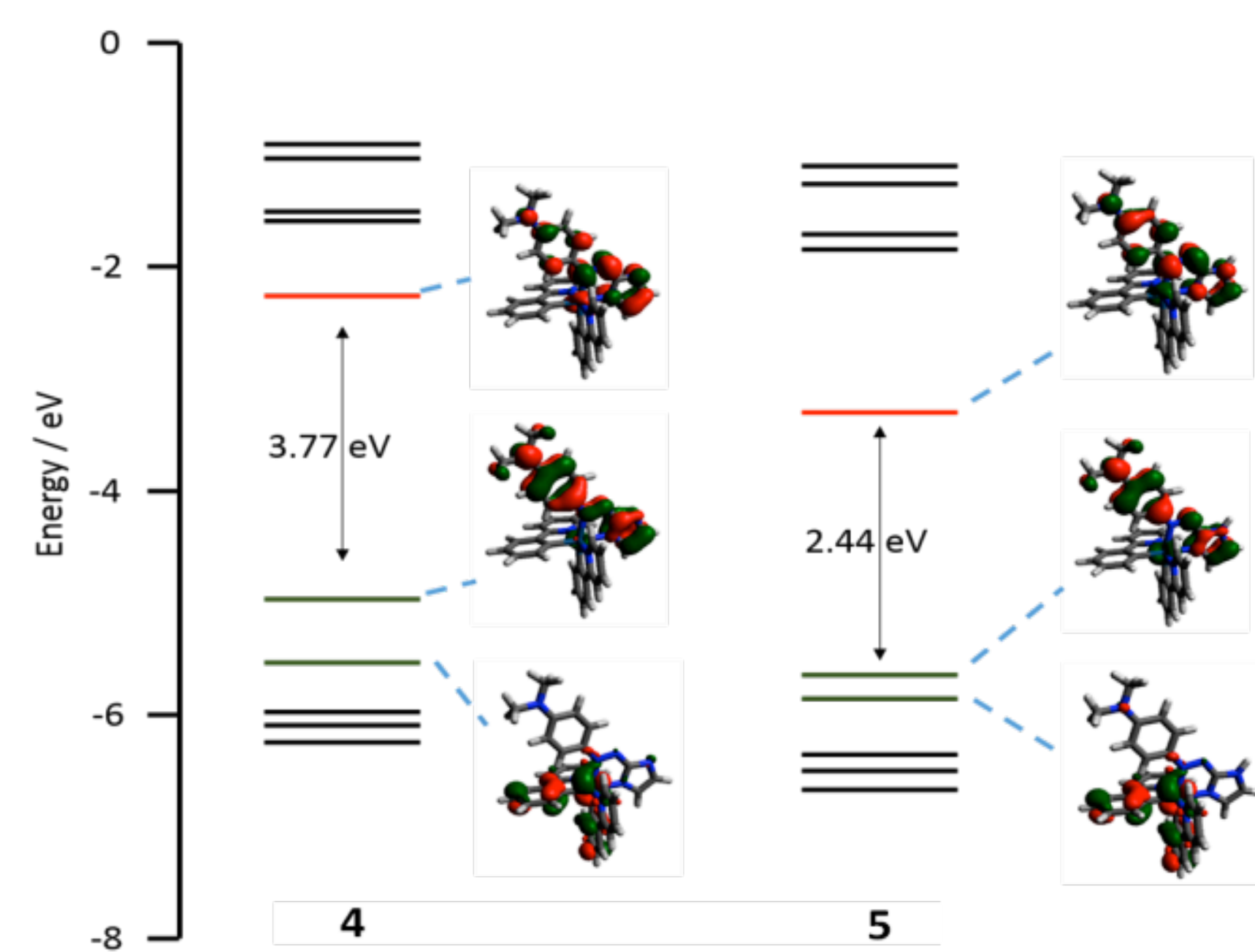
Aryl-BIAN Iridium Complexes

- Exploration of Aryl-BIAN ligands **1-6** as ancillary ligands in [Ir(C^N)₂(N^N)](PF₆)-type complexes.
- UV: As with the free ligand, greatest absorptivity and red-shifting of absorption is conferred by -NMe₂ functionality.
- CV: -NMe₂ introduces an additional oxidation wave at 1.22 V, leading to the narrowest HOMO-LUMO gap. Reduction waves are largely reversible and centred on the π* orbitals of the Ar-BIAN ligands, undergoing significant shifts as a function of ligand decoration.
- DFT: -NMe₂ introduces a change in the excited state. While **2** is mixed CT between the ppy and Ar-BIAN ligands, **1** is ILCT on the Ar-BIAN.
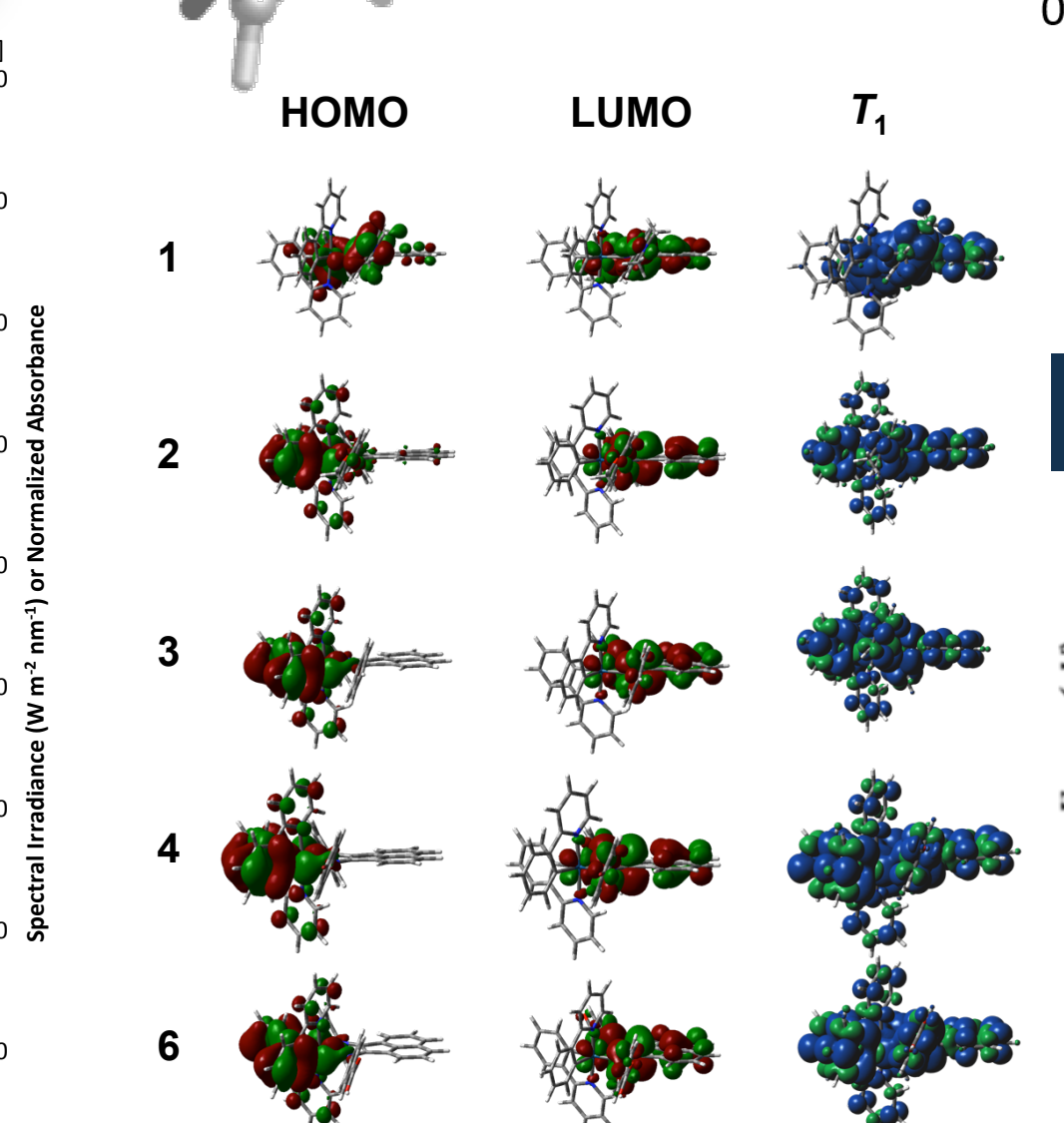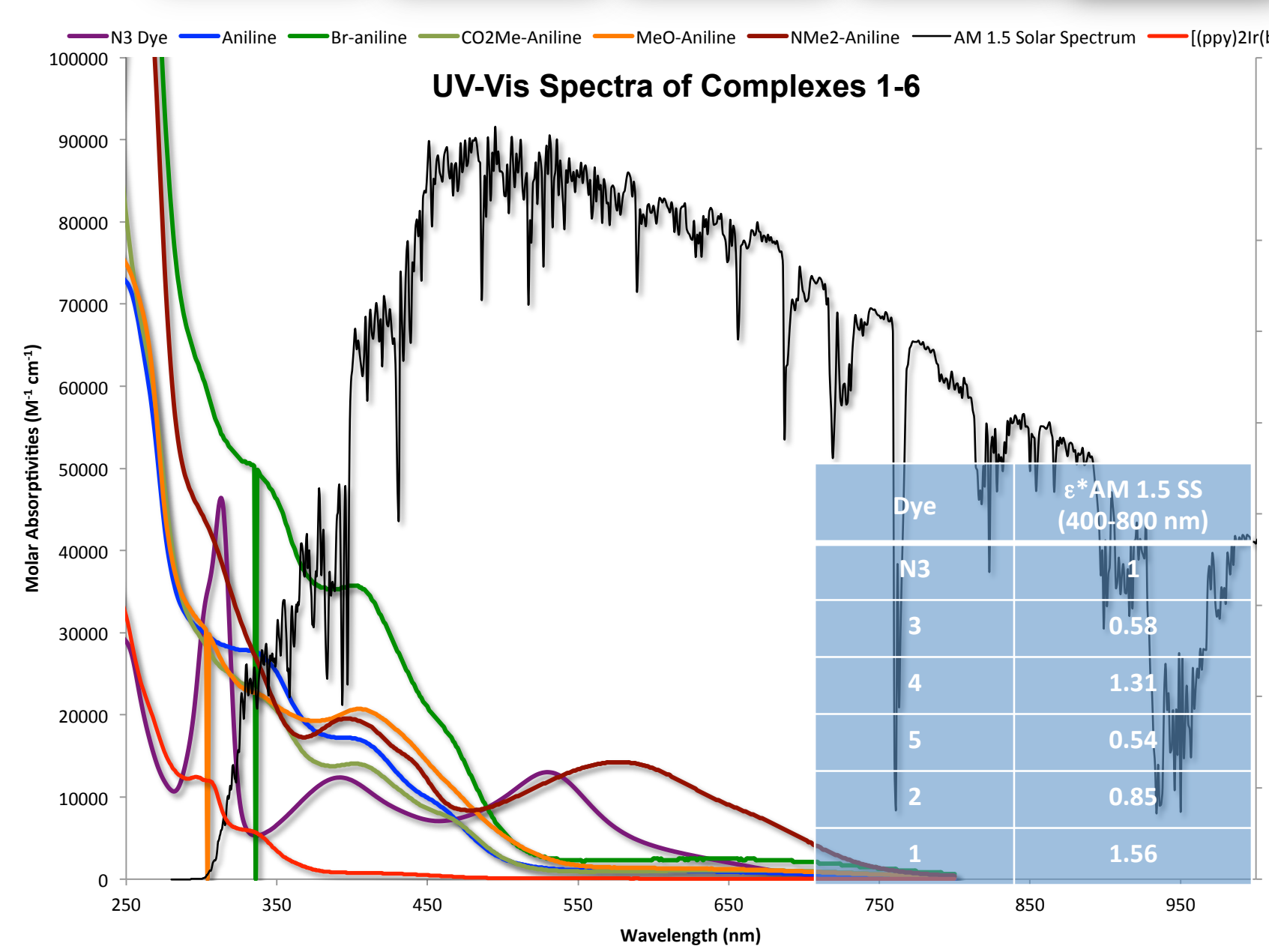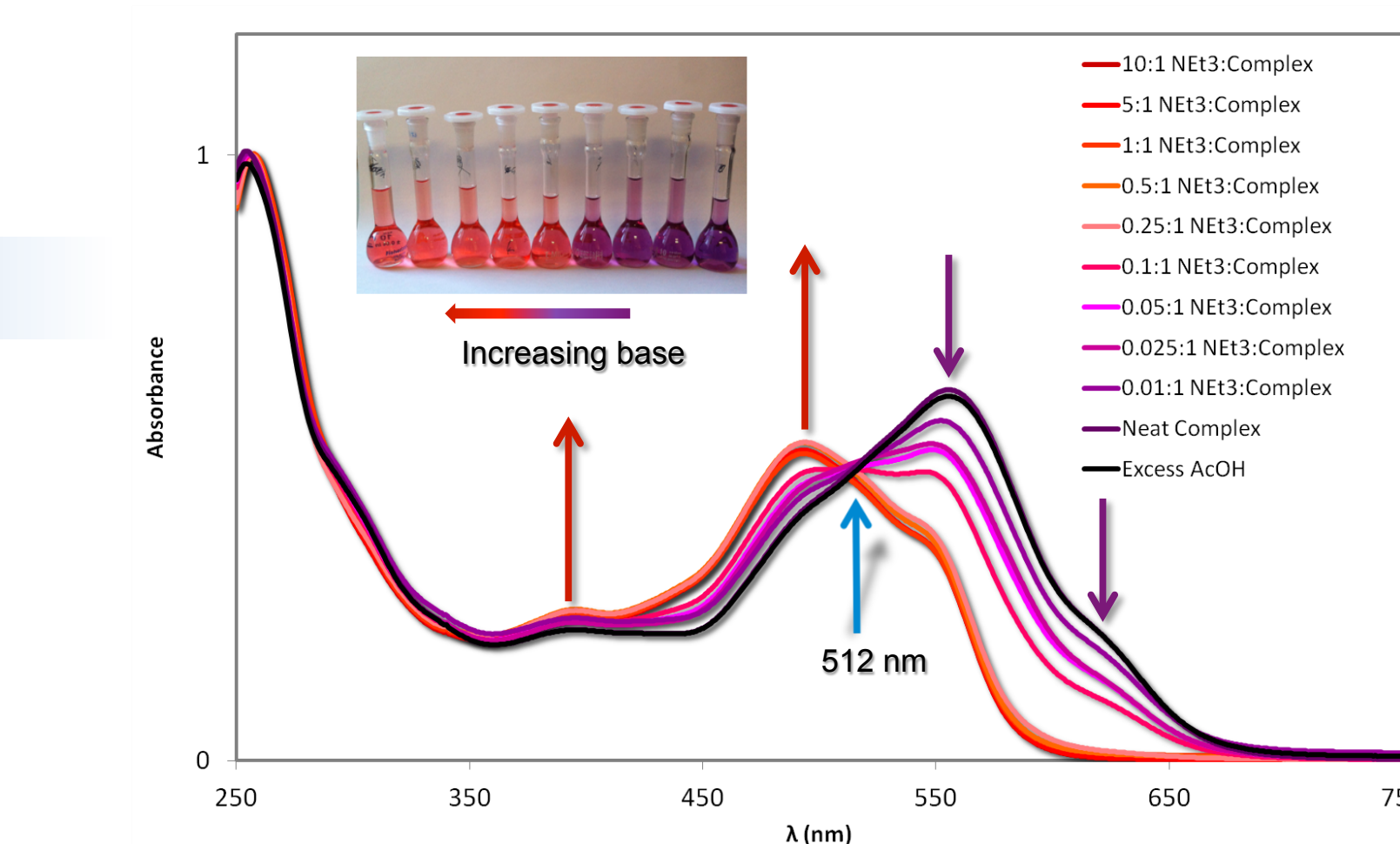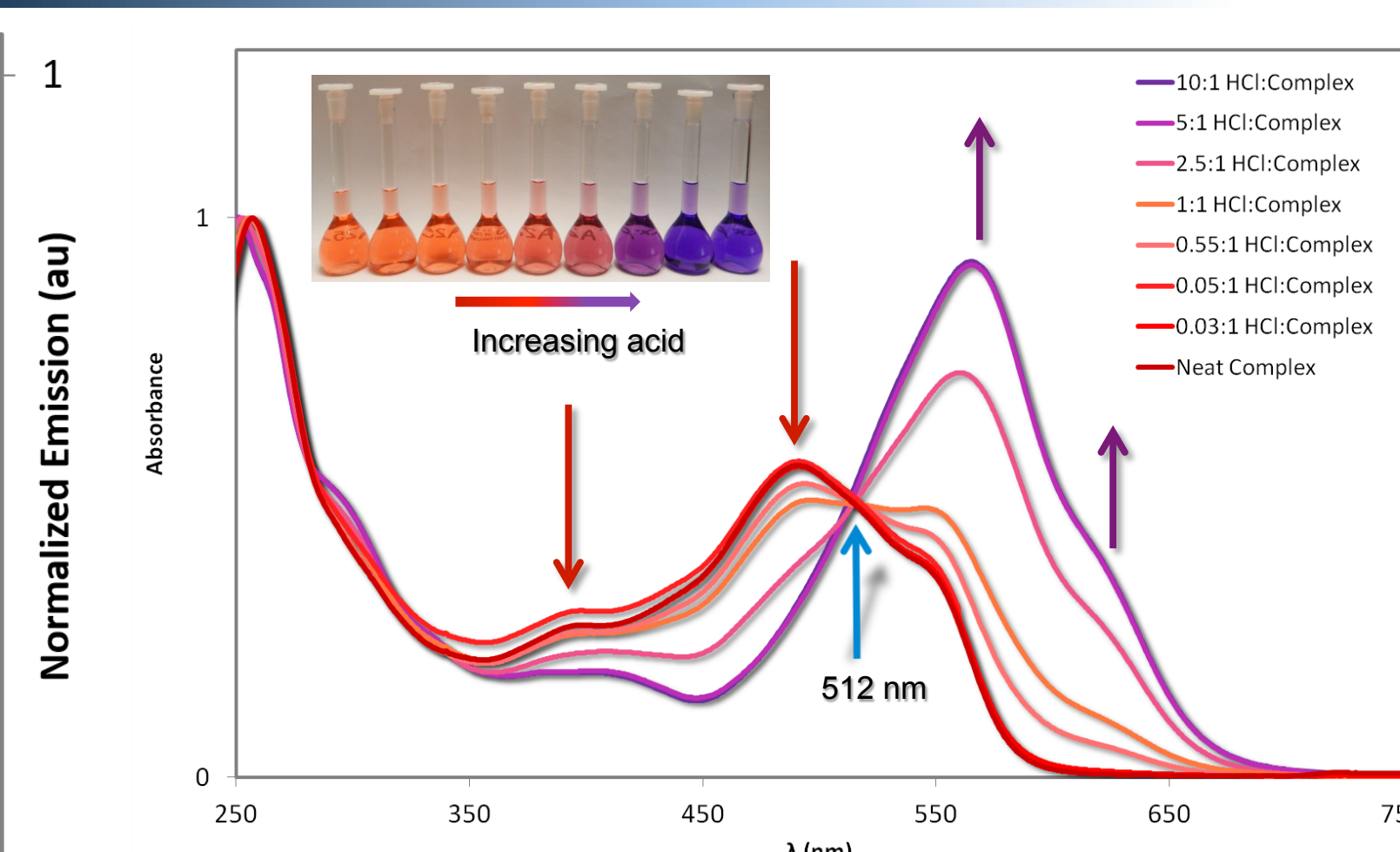

1 R = NMe₂ 86%
2 R = OMe 96%
3 R = H 88%
4 R = Br; 90%
5 R = CO₂Me; 73%
6 R = CO₂H; 87%

Iridium Diazoimidazole Complexes

Complexes: strong donors (–NMe₂) and acceptor (imidazole) facilitate charge transfer and deep red absorption.
- UV: less accepting deprotonated imidazole in **4** results in reduced charge transfer and blue-shifting absorption.

4: 82%   5: 75%

[a] [Ir(ppy)₂(μ-Cl)]₂ (1.0 equiv.), azoimH (2.2 equiv.), K₂CO₃ (2.4 equiv.), DCM/MeOH (5:4 v/v), 55 °C, 19 h.
[b] i) [Ir(ppy)₂(μ-Cl)]₂ (1.0 equiv.), azoimH (2.5 equiv.), DCM/MeOH (5:4 v/v), 55 °C, 19 h, ii) excess NH₄PF₆(aq).

33.7°   -12.6°

4   5

Optoelectronic Characterization

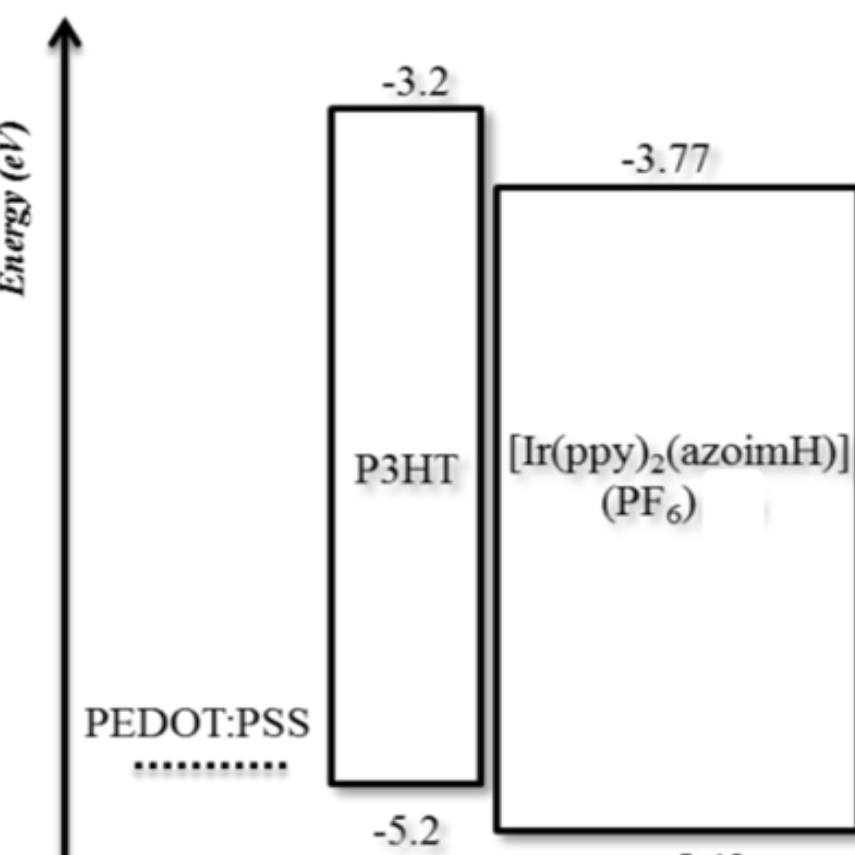|	4 [Ir(ppy)₂(azoim)]	5 [Ir(ppy)₂(azoimH)](PF₆)
λ_{abs} /nm [ε (×10⁴ / M⁻¹ cm⁻¹)]	256 [4.08], 304sh [1.55], 392 [1.04], 493 [2.21], 546sh [1.55]	252 [4.00], 297sh [1.98], 406 [0.80], 565 [3.38], 616sh [1.50]
λ_{em} (nm)[b]	580	625
Φ_{PL} (%)[b, c]	0.03	0.08
τ_e (ns)[d]	4.82 (11%), 163 (19%), 1403 (69%)	108.7 (22%), 1215 (78%)
τ_e aerated (ns)[d]	0.405 (19%), 4.57 (41%), 45.2 (40%)	8.46 (15%), 31.5 (85%)
$E_{1/2}^{ox}$ (V)	0.19	0.62
$E_{1/2}^{red}$ (V)	-1.82	-1.03
E_{HOMO} (eV)[e]	-4.99	-5.42
E_{LUMO} (eV)[f]	-2.98	-3.77

[a] Measurements were carried out at 298 K in degassed MeCN, except for UV-Vis absorption and aerated lifetimes, which were conducted under air. Electrochemical measurements were performed at 100 mV s⁻¹, using Fc/Fc⁺ as an internal standard and are referenced to the Fc/Fc⁺ redox couple. [b] λ_{exc}: 360 nm. [c] Quinine sulfate was used as the reference (Φ_{PL} = 54.6% in 0.5 M H₂SO₄ at 298 K).[2,d] λ_{exc}: 375 nm. [e] E_{HOMO} = -[E$^{ox}_{vs Fc/Fc+}$ + 4.8] eV. [f] E_{LUMO} = -[E$^{red}_{pa vs Fc/Fc+}$ + 4.8] eV.

3.77 eV   2.44 eV

4   5

Acid/Base Titration

Increasing acid — 512 nm

Increasing base — 512 nm

4 (left) and 5 (right) in MeCN solution

HOMO   LUMO   T₁

UV-Vis Spectra of Complexes 1-6

Dye	ε*AM 1.5 SS (400-800 nm)
N3	
3	0.58
4	1.33
5	0.54
2	0.85
1	1.56

CV of Complexes 1-6

V vs NHE (V)

Hammett Relationship

ρ = 0.2164σₚ - 0.4027
R^2 = 0.9476
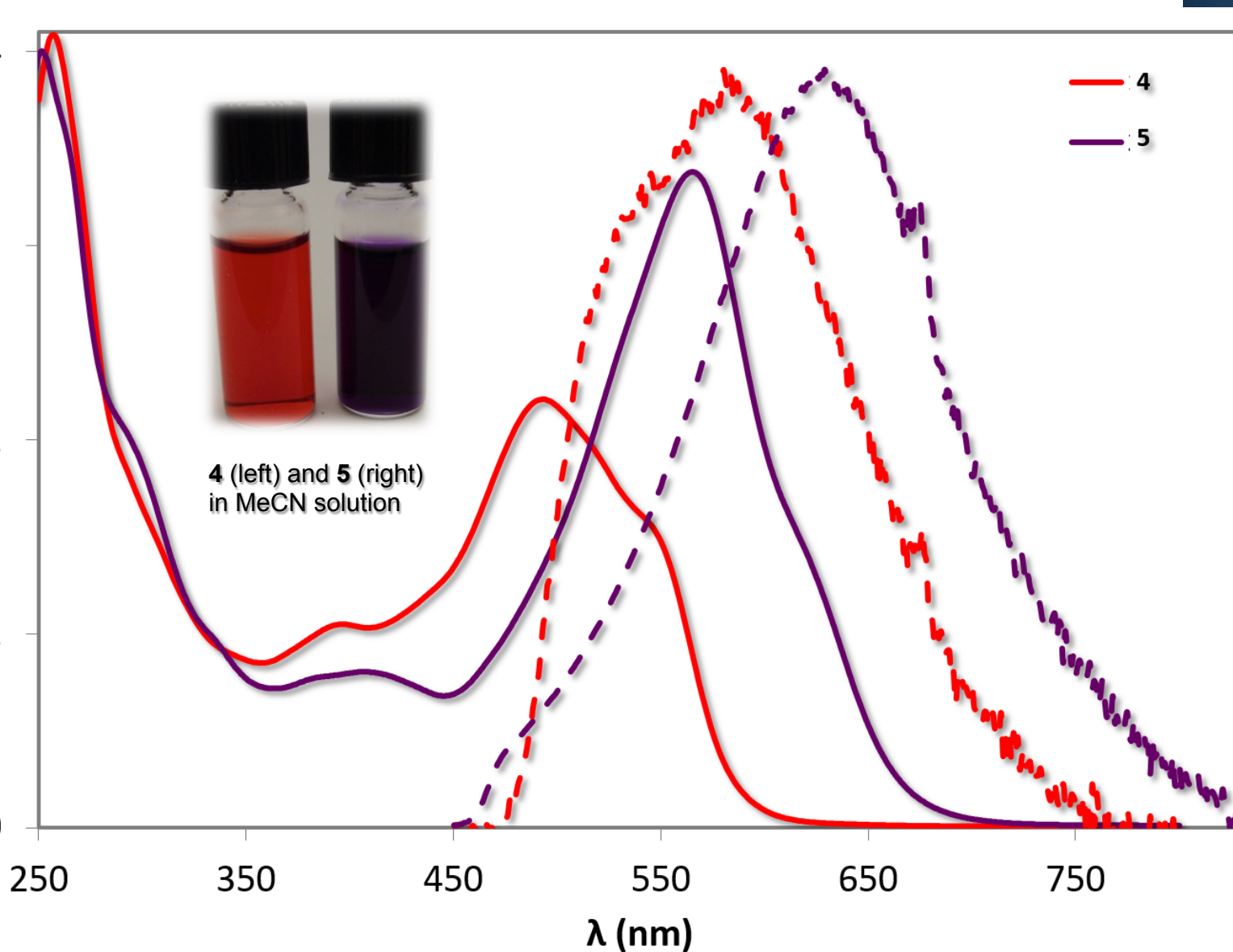
Organic Photovoltaics

Device	J_{sc} mA cm⁻²	V_{oc} (V)	FF (%)	η_{ext} (%)
P3HT	0.015	0.93	37	0.005
P3HT:5 (1:0.5)	0.021	1.12	26	0.006
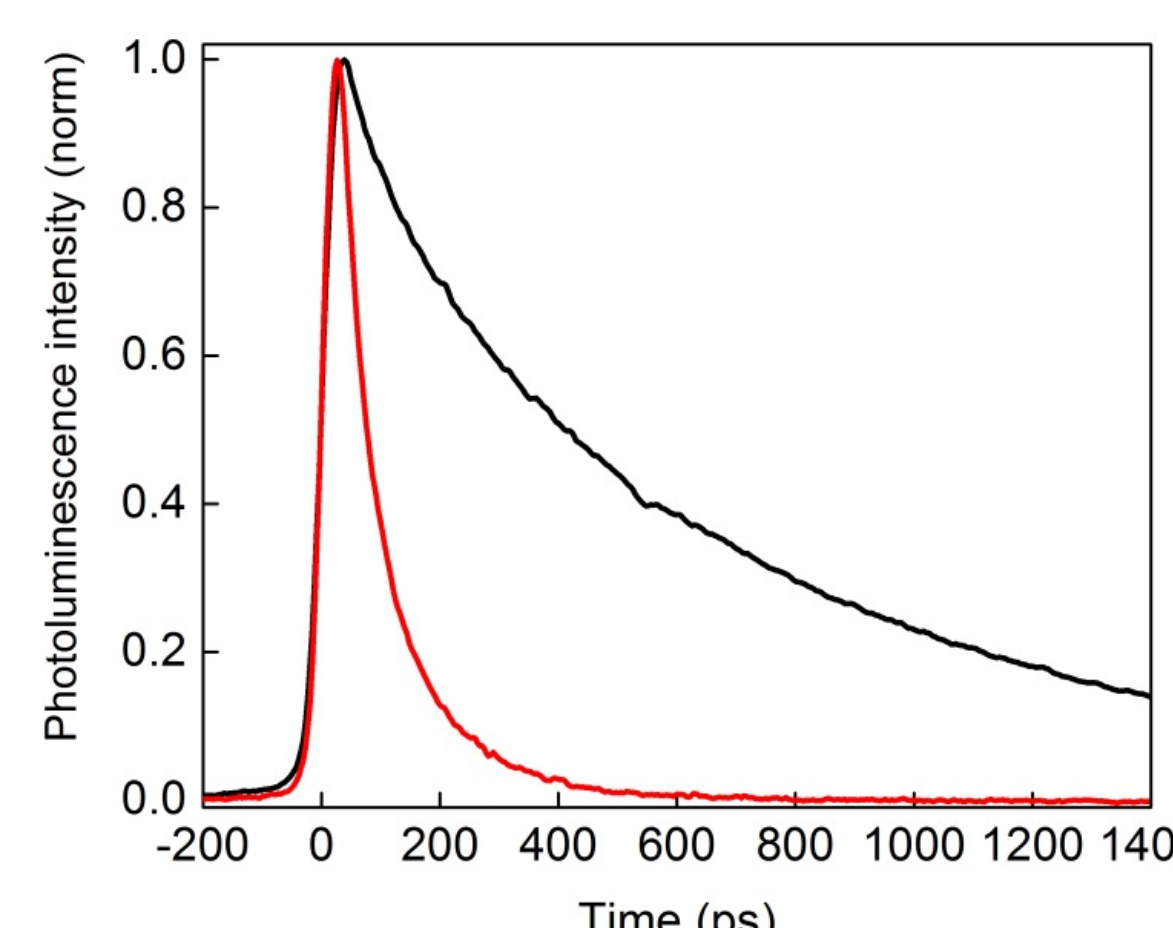
TRPL spectra of pristine P3HT(—) and P3HT:5 (1:0.5) (—) films on quartz substrates. The films were excited at 400 nm and spectra detected at 650 nm.
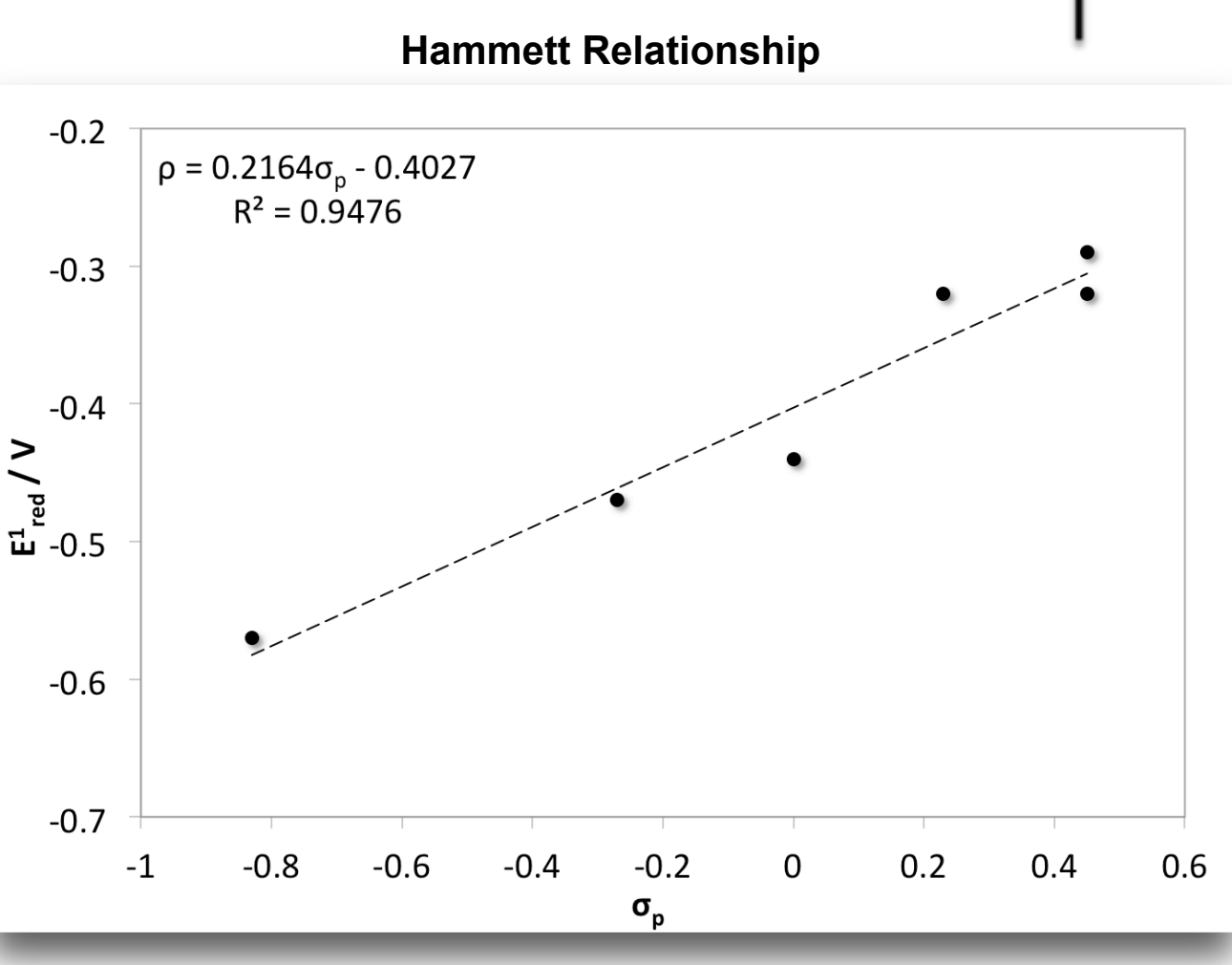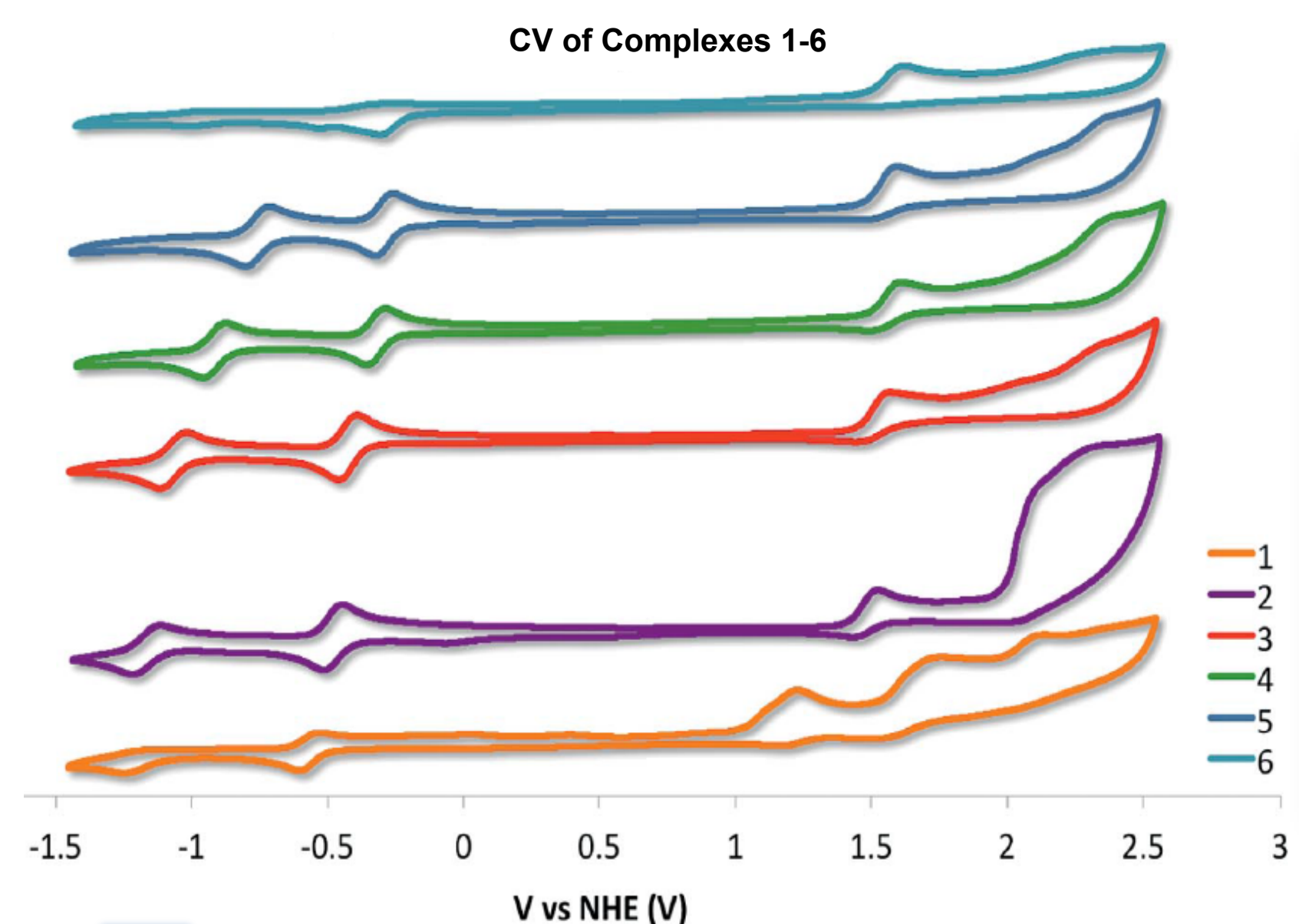
K. Hasan and E. Zysman-Colman, *Inorg. Chem.,* 2012, 51, 12560.
K. Hasan and E. Zysman-Colman, *Eur. J. Inorg. Chem.,* 2013, 4421.

Conclusions

We have developed two families of panchromic iridium dyes.

We are presently adapting the Ar-BIAN- containing Ir complexes to be compatible within a DSSC architecture through the incorporation of anchoring groups.

We are exploring in greater detail how to improve the OPV performance of the aryl-diazo-imidazole-containing Ir complexes.

Team Members and Collaborators

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