

Enhancing the Photoluminescent Quantum Yields of Blue-Emitting Cationic Iridium(III) Complexes Bearing Bisphosphine Ligands

Diego Rota Martir,^a Vincent Di Mascio,^a Ashu Bansal,^a David B. Cordes,^a Adam F. Henwood,^a Alexandra M. Z. Slawin,^a Paul C. J. Kamer,^a Laura Martínez-Sarti,^b Antonio Pertegá,^b Henk J. Bolink,^b Ifor Samuel,^a Eli Zysman-Colman*^a

^aOrganic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife, UK, KY16 9ST, eli.zysman-colman@st-andrews.ac.uk, http://www.zysman-colman.com

^bInstituto de Ciencia Molecular, Universidad de Valencia, C/ Catedrático J. Beltrán, ES-46980 Paterna, Valencia, Spain. E-mail: henk.bolink@uv.es



Introduction

During the last decade, cyclometalated Iridium(III) complexes have been drawing tremendous interest as emitters for lighting applications due to their relatively short-lived triplet excited states (τ_e), high photoluminescence quantum yields (Φ_{PL}), and their facile emission color tunability, which are crucial properties for emitters employed in organic light emitting diodes (OLEDs) or light-emitting electrochemical cells (LEECs).

Bisphosphine ligands have been extensively used in organometallic catalysis but their use as ligands for luminescent Ir(III) complexes remains underexplored, despite their potentially high chemical stability and good tunability of the optoelectronic properties, particularly for achieving blue emission. [1,2]

Given the paucity of photoluminescent iridium complexes bearing P[∧]P chelators and their promising properties, herein we report a structure-property relationship study of thirteen cationic iridium (III) complexes of the form of [Ir(C[∧]N)₂(P[∧]P)]PF₆, in both solution and the solid state, through systematic evaluation of six bisphosphine (P[∧]P) ligands (xantphos, nixantphos, dpephos, dppe, Dppe and isopropantphos) and four C[∧]N cyclometalating ligands (ppy, mesppy, dFppy and dFmesppy) (figure 1).

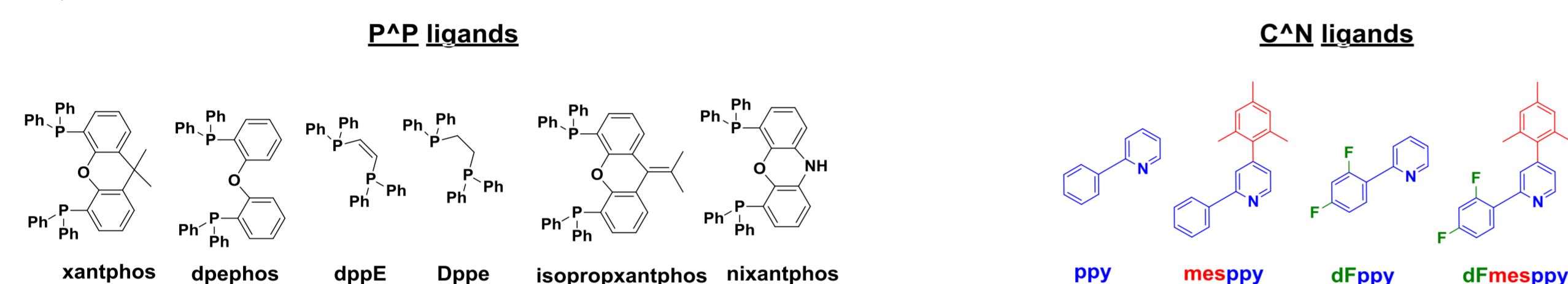
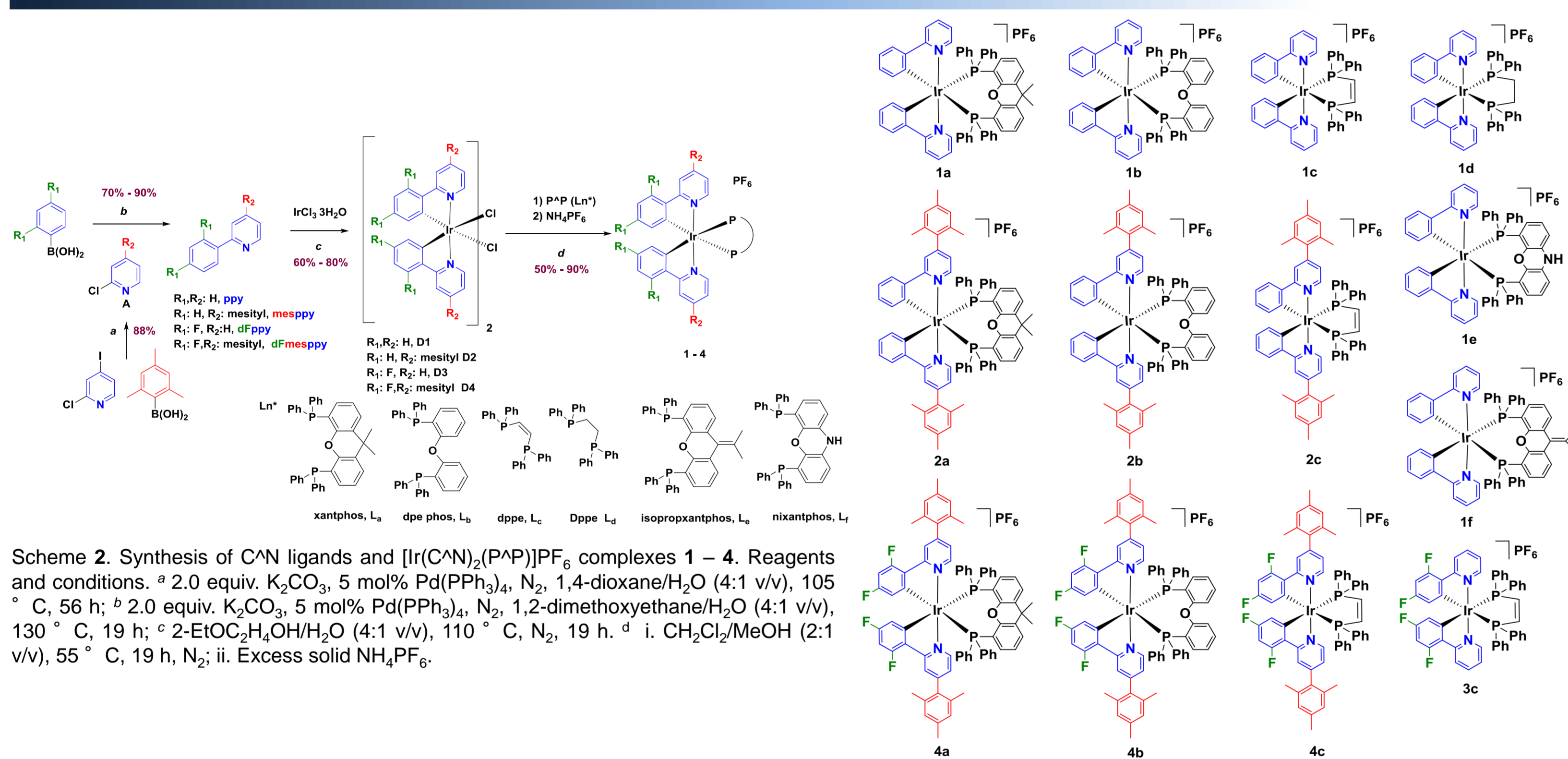


Figure 1. P[∧]P and C[∧]N ligands explored in this study

By optimizing the bite angle of the P[∧]P chelate and coupling it with bulky C[∧]N ligands, bright blue emitters with high photoluminescence quantum yield and long-lived excited states have been obtained. Light-Emitting Electrochemical Cells (LEECs) and Organic Light-Emitting Diodes (OLEDs) have been fabricated using lead complexes from this study and their performances in device have been investigated.

Synthesis and chemical structures



Scheme 2. Synthesis of C[∧]N ligands and [Ir(C[∧]N)₂(P[∧]P)]PF₆ complexes 1 – 4. Reagents and conditions: ^a 2.0 equiv. K₂CO₃, 5 mol% Pd(PPh₃)₄, N₂, 1,4-dioxane/H₂O (4:1 v/v), 105 °C, 56 h; ^b 2.0 equiv. K₂CO₃, 5 mol% Pd(PPh₃)₄, N₂, 1,2-dimethoxyethane/H₂O (4:1 v/v), 130 °C, 19 h; ^c 2-EtOC₂H₄OH/H₂O (4:1 v/v), 110 °C, N₂, 19 h. ^d i. CH₂Cl₂/MeOH (2:1 v/v), 55 °C, 19 h, N₂; ii. Excess solid NH₄PF₆.

Chart 2. Chemical structures of complexes 1 – 4.

Optoelectronics

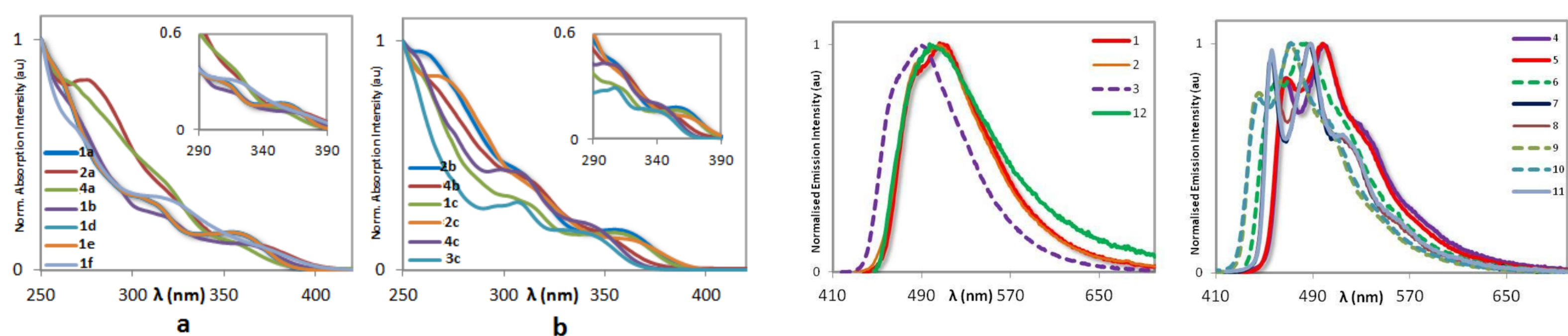


Figure 3. UV-Vis spectra of complexes 1a, 2a, 4a, 1b, 1d, 1e, 1f (a) and 2b, 4b, 1c, 2c, 4c, 3c (b) recorded in MeCN at 298 K.

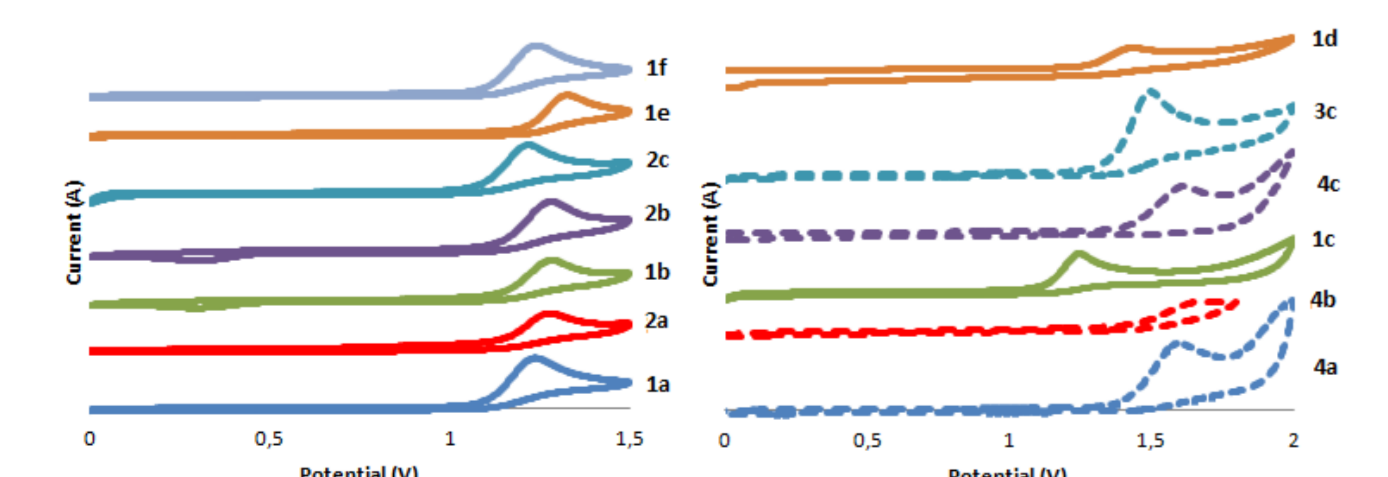


Figure 4. Normalized luminescence spectra of complexes 1a, 2a, 4a, 1f (a) and 1b, 2b, 4b, 1c, 2c, 4c, 3c, 1d (b) recorded in degassed MeCN at 298 K.

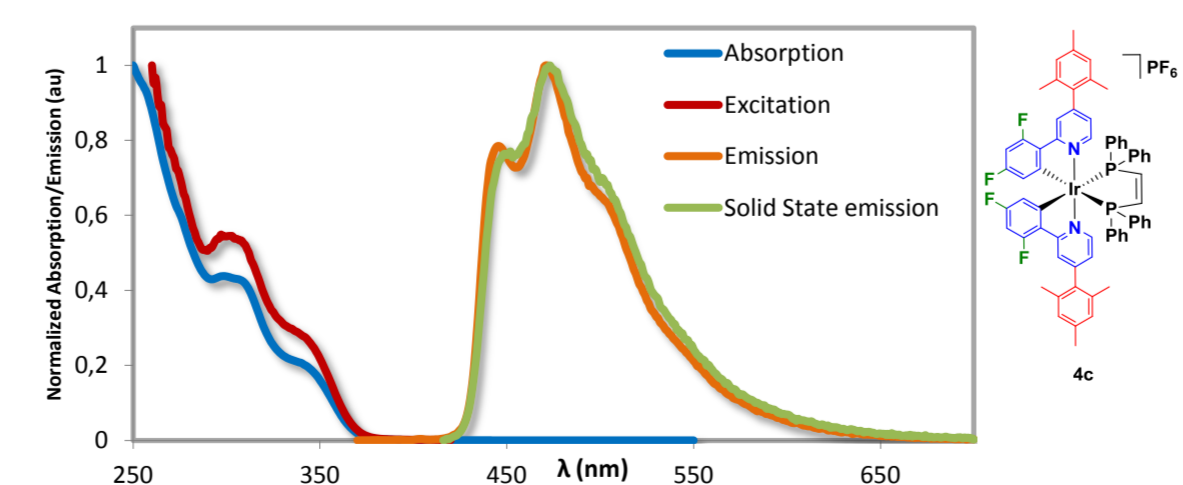


Figure 5. UV-Vis (in blue, in MeCN at 298 K), excitation (in red) and emission spectra (in orange, excitation wavelength: 360 nm, in degassed acetonitrile at 298 K) and solid state emission spectrum (in green, excitation wavelength: 360 nm, dip-coating deposition on pristine quartz substrate) of [Ir(dFmesppy)₂(dppe)]PF₆ (4c).

ACKNOWLEDGEMENTS AND FUNDING



Structure-property relationships

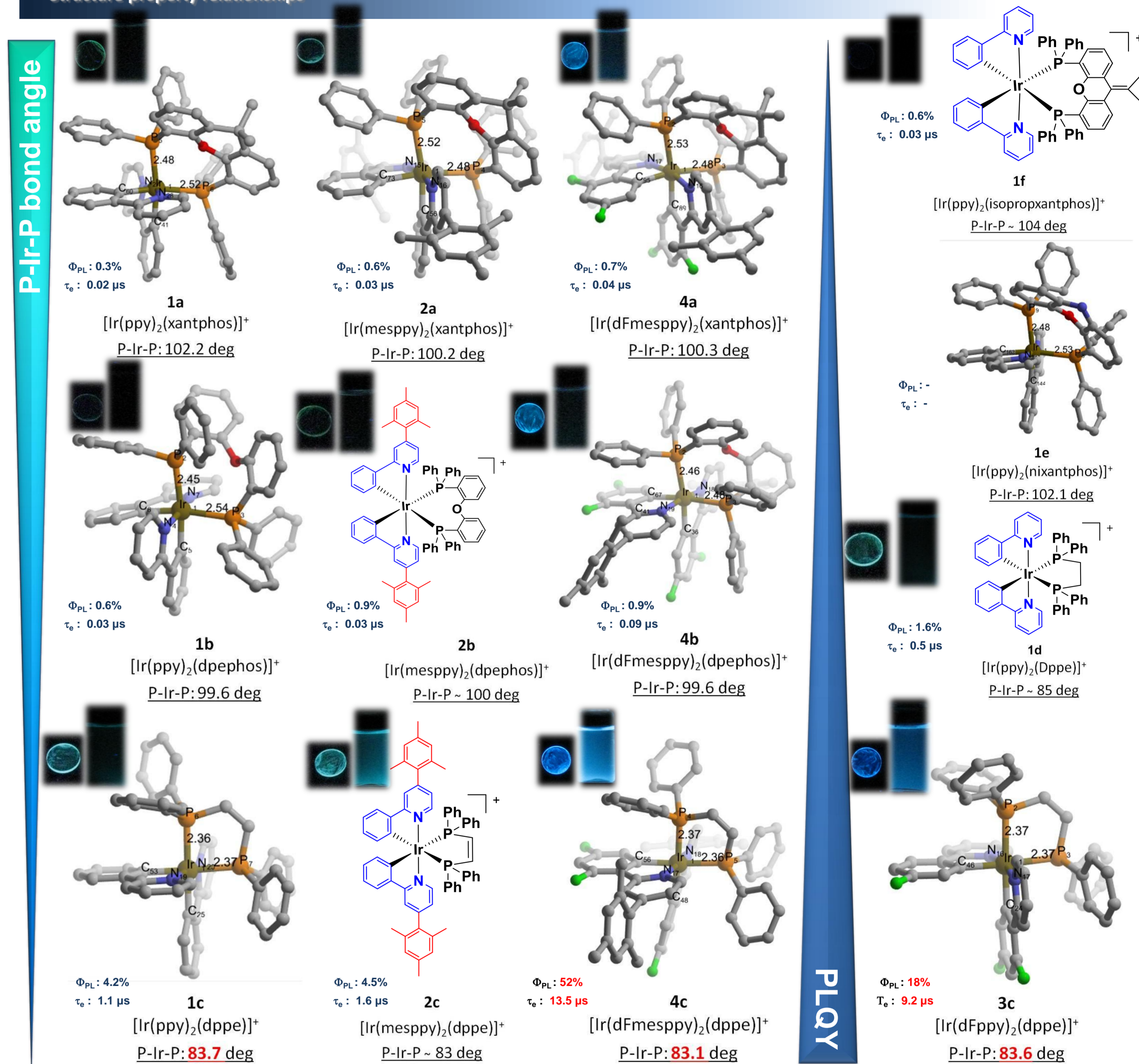
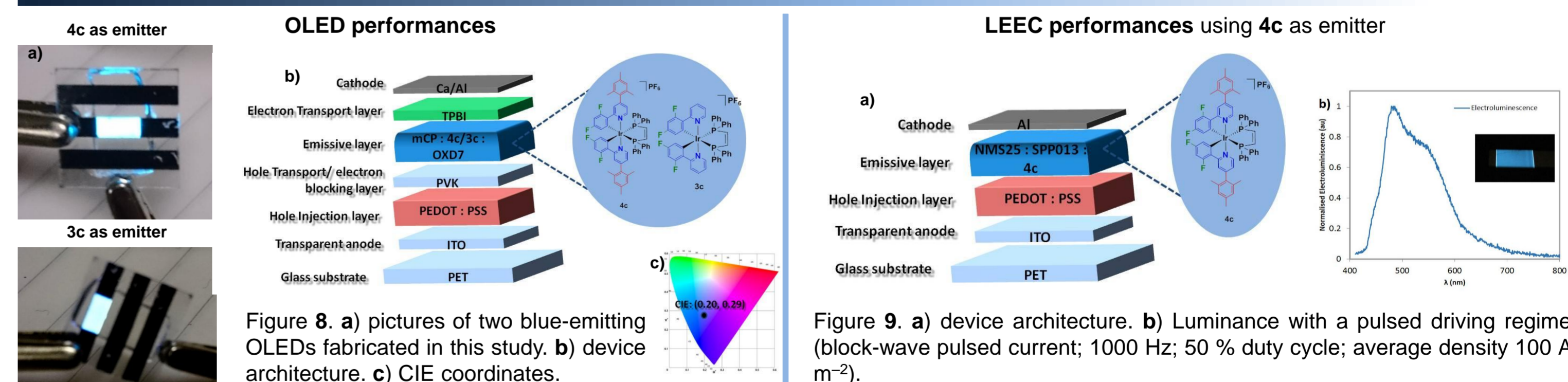


Figure 7. Crystal structures or chemical structures of the thirteen targeted [Ir(C[∧]N)₂(P[∧]P)]⁺ complexes with their solution and solid state emissions and their solution photoluminescent quantum yields (Φ_{PL}) and excited states lifetimes (τ_e) (in deaerated MeCN at 298 K). Ir-P-Ir bond angle values for each of the complexes are underlined. PF₆ counterions, solvent molecules and hydrogen atoms are omitted for clarity.

OLED and LEEC devices



REFERENCES

- S.-X. Luo, L. Wei, X.-H. Zhang, M. H. Lim, K. X. V. Lin, M. H. V. Yeo, W.-H. Zhang, Z.-P. Liu, D. J. Young and T. S. A. Hor, *Organometallics*, **2013**, 32, 2908.
- M. S. Lowry, W. R. Hudson, R. A. Pascal Jr. and S. Bernhard, *J. Am. Chem. Soc.*, **2004**, 126, 14129.
- V. N. Kozhevnikov, Y. Zheng, M. Clough, H. A. Al-Attar, G. C. Griffiths, K. Abdullah, S. Raisys, V. Jankus, M. R. Bryce and A. P. Monkman, *Chem. Mater.*, **2013**, 25, 2352.

CONCLUSIONS

In summary, thirteen blue to blue-green emitting (λ_{em} 477 - 510 nm) cationic heteroleptic iridium(III) complexes bearing bisphosphine ancillary ligands have been synthesized and their optoelectronic properties investigated. Through optimization of the bite angle of the P[∧]P chelate and introduction of bulky and fluorinated C[∧]N ligands, we have rationally designed the brightest reported blue-emitting (λ_{em} : 471 nm) complex of this class in **4c** (Φ_{PL} : 52%). However, these complexes exhibit irreversible electrochemistry, which perhaps accounts for the poor LEEC performances observed using complexes **1b**, **4a**, **4b** and **4c**. OLED devices have been fabricated using complexes **4c** and **3c** as emitters but unfortunately low External Quantum Efficiencies (EQE) of 0.23% and 0.17%, respectively have been achieved.