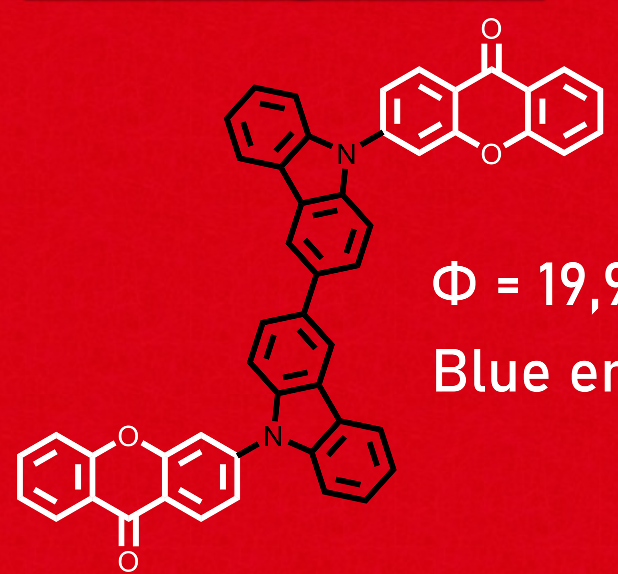
DESIGN AND SYNTHESIS OF 3,3-BICARBAZOLE-TRIAZINE DERIVATIVES AS POTENTIAL EMITTERS FOR OLED DEVICES

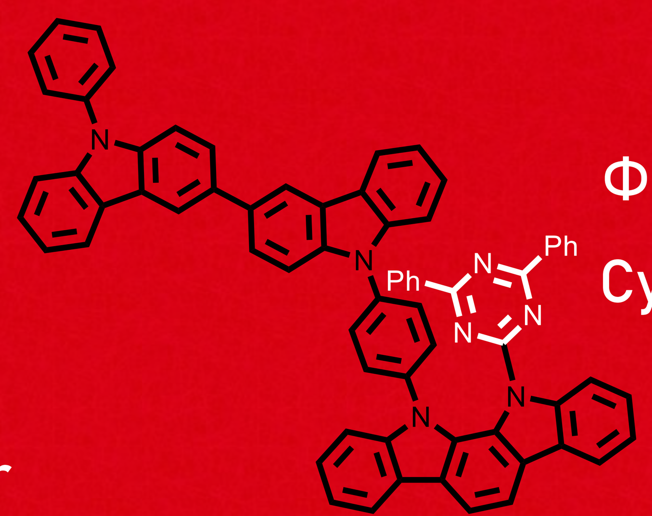
Laureano Marín Oliva, María A. El Ain, Marcelo Puiatti and María E. Budén
Instituto de Investigaciones en Físico-Química de Córdoba, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba, XHUA5000, Argentina.
laureano.marin.oliva@unc.edu.ar

1. Background



Φ = 19,9%
Blue emitter

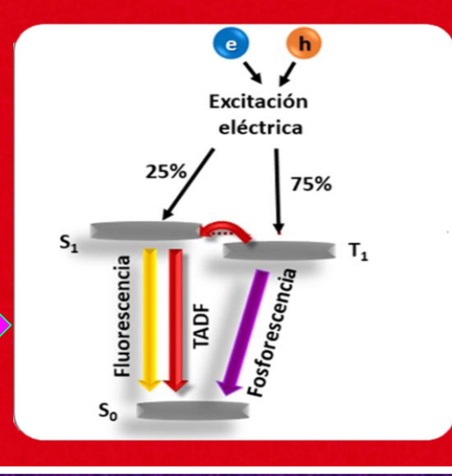
J. Photopol. Sci. Technol. **2017**, *30*, 475.



Φ = 22,8%
Cyan emitter

Adv. Funct. Mater. **2019**, *29*, 1808022.

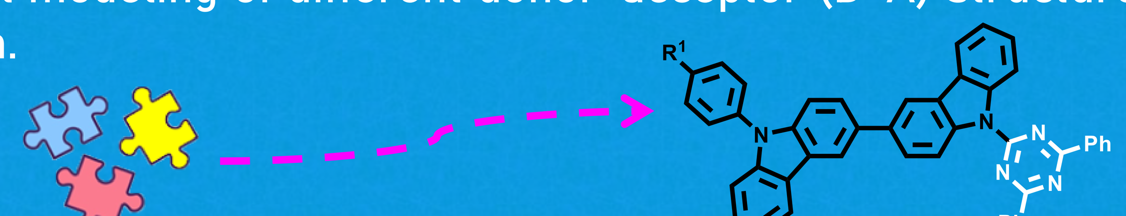
Thermally Activated Delayed Fluorescence (TADF)



Context:
- Blue OLEDs are expensive and short-lived.
- Vacuum-process fabrication is costly and energy demanding.
- TADF emission harvest "wasted" energy from non-fluorescent states.

2. Goals

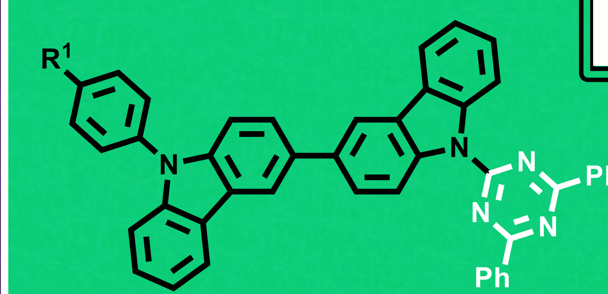
- Perform the rational design of new TADF emitters assisted by computational modeling of different donor-acceptor (D-A) structures with blue emission.



- Develop the synthesis of TADF emitting molecules, selected through computational calculations, using sustainable "Green Chemistry" synthesis strategies.
- Characterize the photophysical and photochemical properties of the newly obtained materials, both in solution and in the solid state, and evaluate their feasibility as emitters in electrochemiluminescent devices

3. Computational calculations

Predicting photophysical properties from molecular modeling



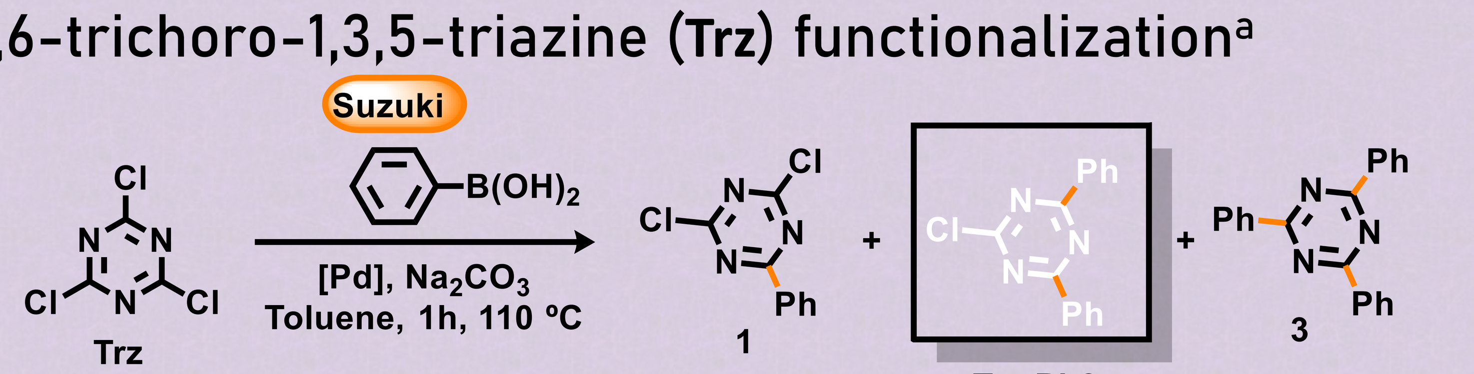
R^1	ΔE_{S-T} (meV)	λ_{em} (nm)
OCH_3	293	416
CF_3	298	404
$C(CH_3)_3$	293	415
NPh_2	294	416
CH_3	292	415
H	292	413

Criterion:
1) ΔE_{S-T} < 300 meV
2) λ blue

3 candidates chosen to synthezise

4A. Acceptor motif synthesis

2,4,6-trichoro-1,3,5-triazine (**Trz**) functionalization[a]



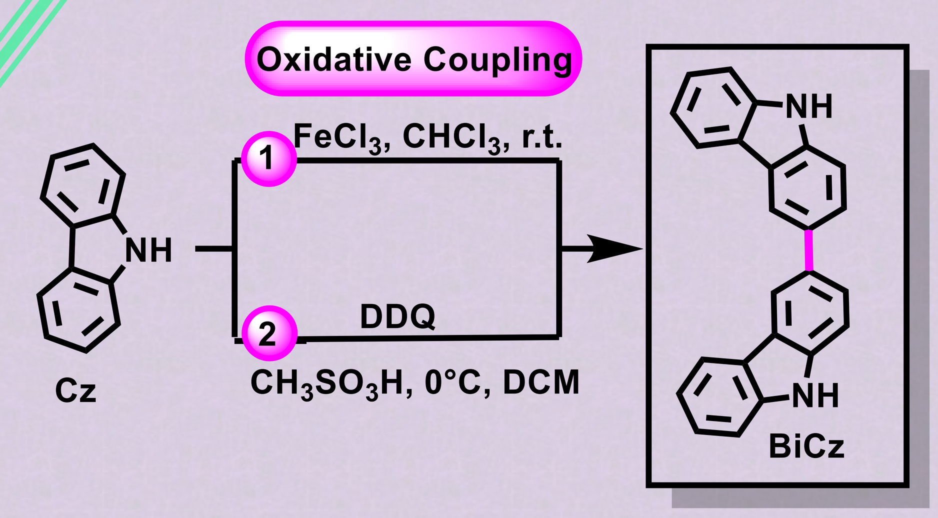
Projection: Develop a metal free synthesis of the acceptor motif.

Entry	Conditions	Yield (Trz-Ph2)
A	$PhB(OH)_2$ (2,2 eq), Pd (0,04 eq) y Na_2CO_3(s) (2 eq)	-
B	$PhB(OH)_2$ (2,2 eq), Pd (0,04 eq) y Na_2CO_3 2M	-[b]
C	$PhB(OH)_2$ (2 eq), Pd (0,04 eq) y Na_2CO_3 2M	6%

[a]Reaction conditions: Trz (1 eq, 2 mmol) in 15 mL of toluene under innert atmosphere.
[b]Only **3** was obtained.

4B. Donor motif synthesis

i) Bicarbazole synthesis (**BiCz**)



Reference conditions:
(1) $FeCl_3 \cdot 6H_2O$ (4 eq) in 17 mL of $CHCl_3$, 24 h. yield: 71%
Synth. Commun. **2019**, *18*, 2330–2341

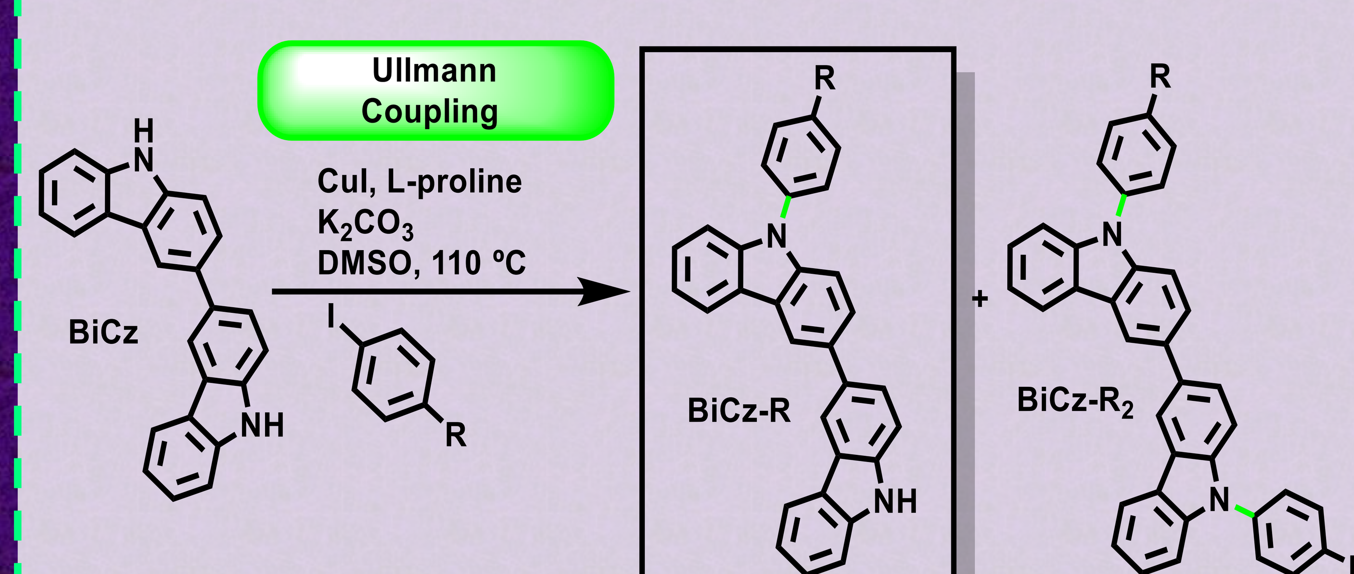
(2) DDQ (2 eq) in 100 mL of CH_2Cl_2 and 10 mL of MSA. Yield: 93%.
J. Org. Chem. **2019**, *84*, 73–93

Entry	Conditions	Extraction	Yield
A	$FeCl_3 \cdot 6H_2O$ (4 eq), $CHCl_3$, 24 h.	Methanol, ethyl acetate and wáter	-
B	Anhydrous $FeCl_3$ (4 eq), $CHCl_3$, 3 h	Methanol and saturated NaOH solution	25%
C	Anhydrous $FeCl_3$(4 eq), CH_2Cl_2, 3 h	Ethanol, ethyl acetate, Zn poder and acetic acid	29%
D	Anhydrous $FeCl_3$(3 eq), CH_2Cl_2, 1.5 h	Ethanol, ethyl acetate, Zn poder and acetic acid	43%
D	DDQ (2 eq) en 100 mL de CH_2Cl_2 y 10 mL de MSA	Saturated $Na_2CO_{3(ac)}$ and brine	37%

Optimized conditions for reaction 1:
- Less metal oxidant
- Less reaction time
- Less toxic and cheaper solvent
- No yield compromise

Metal free synthesis of BiCz with comparable yields via reaction 2.

ii) **BiCz** functionalization

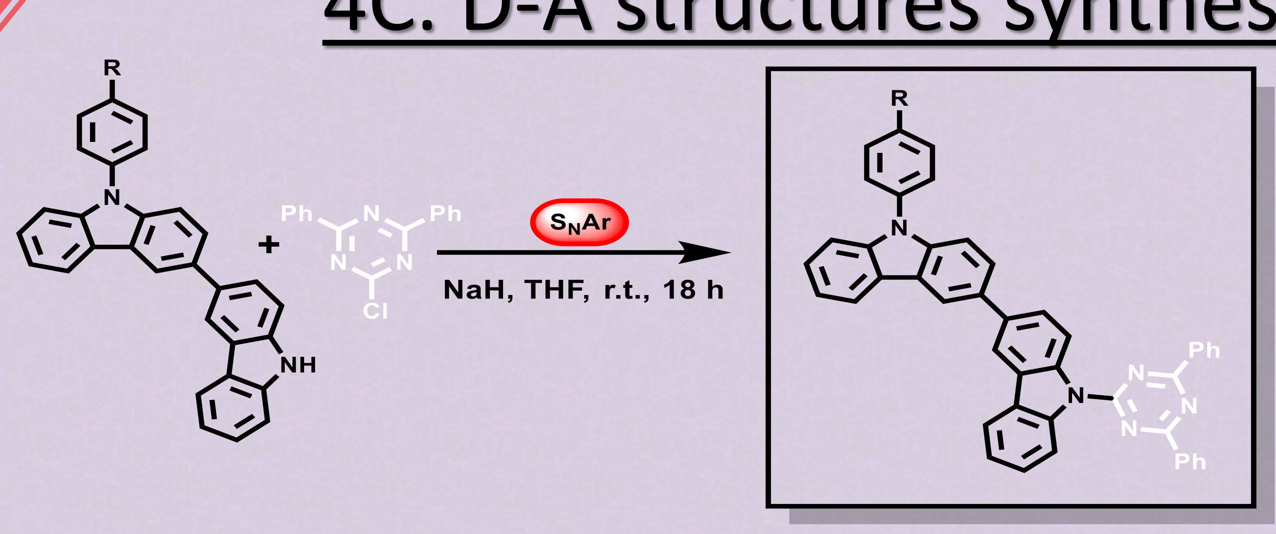


En.	R	Condiciones	Yield*
A	CH_3	$CH_3C_6H_4I$ (1,1 eq), 40 h	60%
B	CH_3	$CH_3C_6H_4I$ (1 eq), 24 h	10%
C	OCH_3	$OCH_3C_6H_4I$ (1,1 eq), 40 h	18%
D	$C(CH_3)_3$	$C(CH_3)_3C_6H_4I$ (1,1 eq), 40 h	27%

*Isolated yield for **BiCz-R**

Projection:
Find reaction conditions to obtain selectively BiCz-R with better yields.

4C. D-A structures synthesis



BiCz-R-TrzPh2

Reaction conditions: Trz-Ph2 (2 eq), BiCz-R (1 eq). 1 h reflux. Cool at r.t. and add Trz slowly

Entry	R	Yield
A	CH_3	16%
B	OCH_3	13%
C	$C(CH_3)_3$	9%

All 3 products are soluble in chloroform and dichloromethane

Conclusion

✓ A synthetic pathway was proposed and employed for obtaining potential TADF emitters.
✓ Each reaction was tested and optimized, resulting in the synthesis of 3 target molecules.

Projections

📖 Characterize and compare experimental data with calculated ones.
📖 Determine if the methodology proposed is an efficient and greener way to predict novel target molecules