# FROM THE COMPUTER TO THE LAB: RATIONAL DESIGN AND SYNTHESIS OF LIGHT - EMITTING MATERIALS

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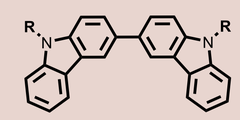
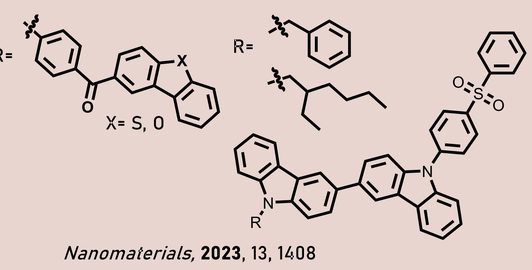
## BACKGROUND AND GOALS

OLEDs

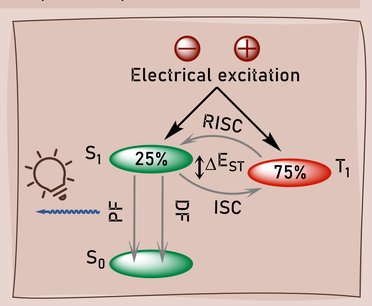
- Use of organic molecules instead of gallium and arsenic compounds
- Better efficiency and brightness than other light-emitting devices using thermally activated delayed fluorescence (TADF)



*Org. Electron*, **2021**, 96, 106199




*Nanomaterials*, **2023**, 13, 1408




- Perform a rational design of light – emitting materials based on predictions of photophysical features
- Synthesize the best candidates and do the photophysical and electrochemical characterization

**1) *Rational design***: use computational methods (DFT and TD-DFT) to predict HOMO – LUMO distribution, emission wavelength and $\Delta E_{S-T}$ of materials

**2) *Synthesis***: develop methodologies of heterocyclic synthesis under mild conditions (room temperature, metal – free and visible light)

## GREEN CHEMISTRY PRINCIPLES

Rational design of molecules that could work as emitters, leads to prevent large amounts of waste products being produced in synthesis → **1** Prevention

Synthesis of organic molecules for emitters instead of metallic compounds → **4** Designing Safer Chemicals

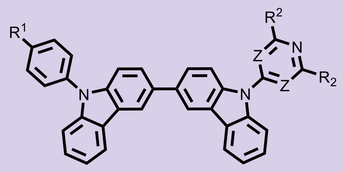
Synthesis of different nitrogen heterocycles under mild conditions: room temperature, metal – free reactions, visible light and non-toxic solvents

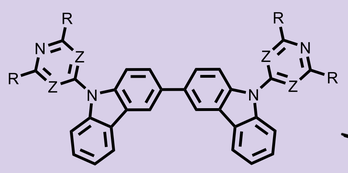
- **5** Safer Solvents and Auxiliaries
- **6** Design for Energy Efficiency
- **9** Catalysis

## RESULTS

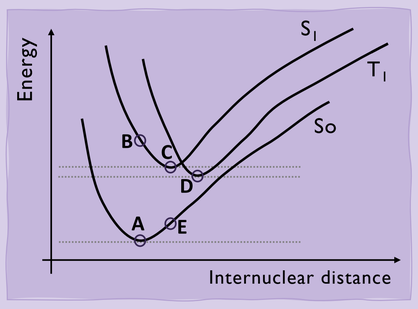
### 1) Rational design using computational methods

Light – emitting materials based on bicarbazoles




Prediction of photophysical properties with computational chemistry to choose the best candidate




**What properties are we looking for?**

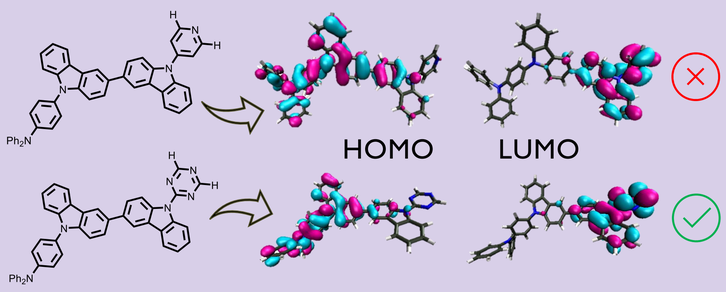
- HOMO – LUMO distribution
- $\Delta E_{S-T}$ (difference between $S_1$ and $T_1$)
- Emission wavelength

**How do we do it?**

Analyzing geometries and energies in ground state (So), first excited state ($S_1$) and triplet state ($T_1$) with DFT and TD-DFT calculations

Chosen molecules as the best candidates for TADF materials

#### 1- HOMO – LUMO distribution analysis



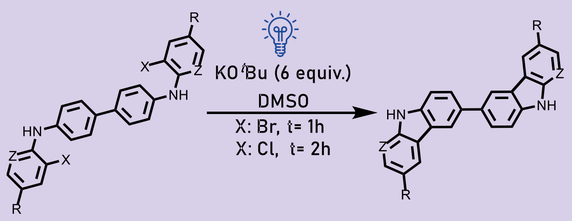

HOMO – LUMO overlap is inversely proportional to RISC speed

**2, 3, 4-** Optimization of $S_1$ and $T_1$, prediction of $\Delta E_{S-T}$ and emission λ

| Molecule | Z | $R^1$ | $R^2$ | $\Delta E_{S-T}$ | $\lambda_{em}$ (nm) |
|---|---|---|---|---|---|
| **2** | N | H | Ph | 362 | 413 |
| **3** | N | $CF_3$ | Ph | 369 | 404 |
| **4** | N | $C(CH_3)_3$ | Ph | 362 | 415 |
| **5** | N | $NPh_2$ | Ph | 496 | 417 |

### 2) Synthesis of *N*-containing heterocycles

Synthesis of BiCz by $S_{RN}1$ reaction

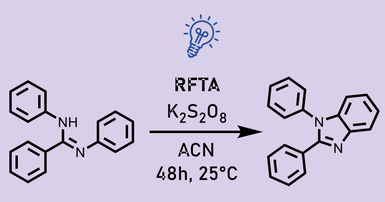



- Optimization of conditions
- Analysis of scope
- Reaction mechanism studied by spectroscopy and computational chemistry

**1a**, Z: CH, R: H, X: Br **2a = 59%**
**1b**, Z: CH, R: $CH_3$, X: Br **2b = 50%**
**1c**, Z: CH, R: $OCF_3$, X: Br **2c = 45%**
**1d**, Z: N, R: $CH_3$, X: Br **2d = 41%**

**1e**, Z: CH, R: H, X: Cl **2a = 65%**
**1f**, Z: CH, R: $CF_3$, X: Cl **2f = 52%**
**1g**, Z: N, R: H, X: Cl **2g = 55%**
**1h**, Z: CH, R: $OCH_3$, X: Cl **2h = 43%**
**1i**, Z: CH, $R^1$: $CH_3$, $R^2$: H, X:Br **2i = 65%**

Synthesis of bencimidazoles by photocatalysis



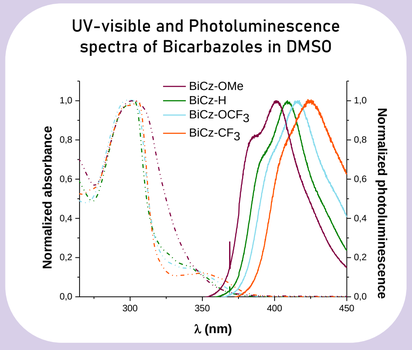

In both methodologies mild reaction conditions are used:

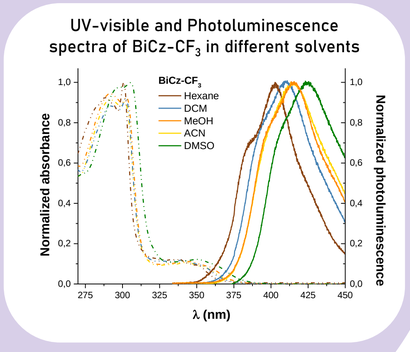
- Visible light
- Room temperature
- Non-toxic solvents (ACN, DMSO)

### 3) Photophysical characterization

Study of photophysical properties of bicarbazoles and the effect of different substituents

- UV-visible spectroscopy
- Photoluminescence spectroscopy
- Photoluminescence Quantum Yields
- Lifetimes

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## CONCLUSIONS AND PROJECTIONS

✓ Choice of best candidates for TADF emission to be synthesized

✓ Synthesis of N-containing heterocycles using visible light ($S_{RN}1$ and photocatalysis)

✓ Photophysical characterization of BiCz to understand the excited state and dual emission

✓ Continue with the photophysical characterization of Bicarbazoles and bencimidazoles

✓ Functionalization of Bicarbazoles to obtain light-emitting materials and do photophysical characterization of final molecules