

Supporting Information

Bipolar Luminescent Azaindole Derivative Exhibiting Aggregation-Induced Emission For Non-doped Organic Light-Emitting Diodes

Cristina Martin,^a Carlos Borreguero,^b Koen Kennes,^a Mark Van der Auweraer,^a J. Hofkens,^a
Gustavo de Miguel,^{*,c} and Eva M. García-Frutos.^{*,b}

^aChem&Tech - Molecular Imaging and Photonics, KU Leuven, Celestijnenlaan 200F, B-3001

^b Instituto de Ciencia de Materiales de Madrid (ICMM), CSIC, Cantoblanco, Madrid, Spain, E-28049.

^cDepartamento de Química Física, Instituto Universitario de Química Fina y Nanoquímica Universidad de Córdoba, Campus de Rabanales, Edificio Marie Curie, E-14071, Córdoba, Spain.

*Corresponding Authors: emgfrutos@icmm.csic.es, gmiguel@uco.es

Table of contents:

| | Page |
|--|------|
| 1. Experimental Details | S2 |
| 2. Thermogravimetric analysis | S2 |
| 3. Photophysical studies | S3 |
| 4. Electroluminescence studies | S7 |
| 5. Copy ¹ H NMR spectra of compound 2 | S7 |

1. Experimental Section

2-Cyano-3-[5-(4-diphenylamino-phenyl)-1-dodecyl-1H-pyrrolo[2,3-b]pyridin-3-yl]-acrylic acid

(2)

A solution of 179 mg (0.313 mmol) of carbaldehyde **1** was dissolved in 1 mL of dichloromethane and 10 mL of anhydrous acetonitrile under nitrogen atmosphere and then, 21.6 mg (0.241 mmol) of cyanoacetic acid, and 6 μ L of piperidine was added. The mixture was refluxed for 24 hours under nitrogen atmosphere and then cooled down to room temperature. The yellow solid is filtered and washed with acetonitrile to afford **2** with a 49% yield, mp 255-258 $^{\circ}$ C, 1 H NMR (300 MHz, CDCl_3) δ 8.70 (s, 1H), 8.67 (d, $J = 2.0$ Hz, 1H), 8.59 (s, 1H), 8.30 (d, $J = 2.0$ Hz, 1H), 7.53-7.50 (m, 2H), 7.29 (m, 4H), 7.22-7.14 (m, 6H); 7.14-7.09 (m, 2H); 4.43 (d, $J = 7.38$ Hz, 2H), 2.0 (m, 2H), 1.25 (m, 18H), 0.87 (t, $J = 6.61$ Hz, 3H), UV-vis (CH_2Cl_2 , 25 $^{\circ}$ C) λ_{max} (ϵ) 290 (26164), 308 (27338), 379 (25217); MALDI MS m/z 625 (M+H) $^+$; HRMS (MALDI) $\text{C}_{41}\text{H}_{44}\text{N}_4\text{O}_2$: calculated: 625.3491, found: 625.3512.

2. Thermogravimetric analysis

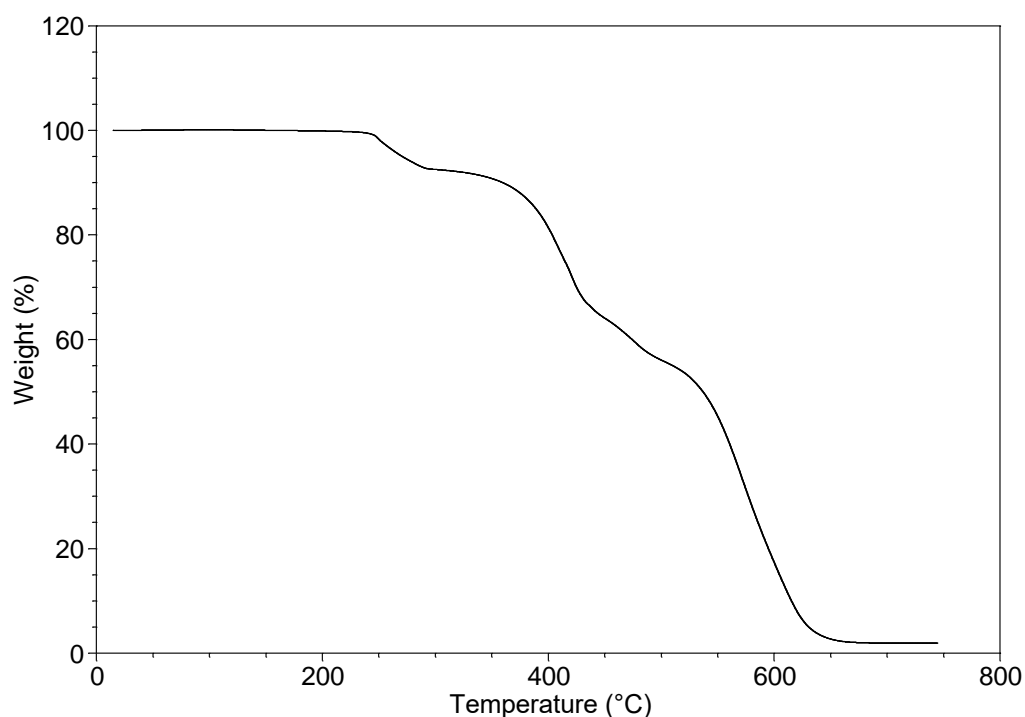


Figure S1: Thermogravimetric (TG) curve of compound **2**

3. Photophysical studies

The emission spectra of **2** in solvents with moderate polarity (toluene, anisole, THF and CH₂Cl₂, high solubility of **2**) were also recorded to analyze the influence of the solvent polarity on the relaxation mechanism after photoexcitation. Figure S3A shows that the intensity of the emission spectra tend to decrease with increasing polarity of the solvents. Figure S3B exhibits the normalized emission spectra indicating a shift of the maximum of the emission peak to lower energies upon increasing the solvent polarity. The red-shift of the spectra points out a decrease of the energy of the emissive state due to the interaction with the polar solvents. Indeed, the S₁ state populated after the excitation has a strong charge transfer character as shown in the theoretical calculations. Thus, the combination of a reduction and red-shift of the emission signal with increasing solvent polarity has been previously identified as an experimental evidence of a non-radiative deactivation process *via* a conical intersection involving a twisting of a single bond followed by a complete charge separation between the donor and acceptor units (ICT state).

To further demonstrate the influence of the solvent polarity on the deactivation mechanism of **2**, different emission spectra were measured in mixtures of CH₂Cl₂/cyclohexane. Figure S4 displays the changes in the spectra when increasing the percentage of cyclohexane in a CH₂Cl₂ solution from 0 to 100% (10% each step). The sequential addition of cyclohexane (non-polar solvent) produces a blue-shift of the emission spectrum due to the destabilization of the ICT state followed by the increase of the emission intensity. The variable polarity of the mixed solvent enables to monitor the continuous shift of the ICT emission, showing the intense charge transfer character of this excited state.

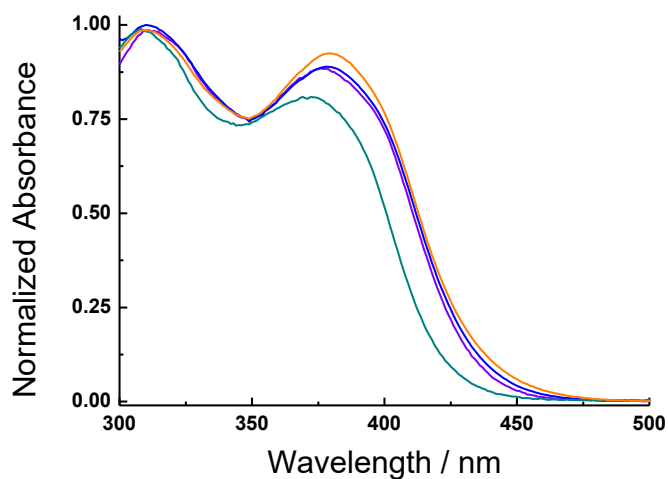


Figure S2. Normalized absorbance spectra of **2** in solvents with increasing polarity. Toluene (violet line), Anisole (blue line), THF (green line), and CH_2Cl_2 (orange line).

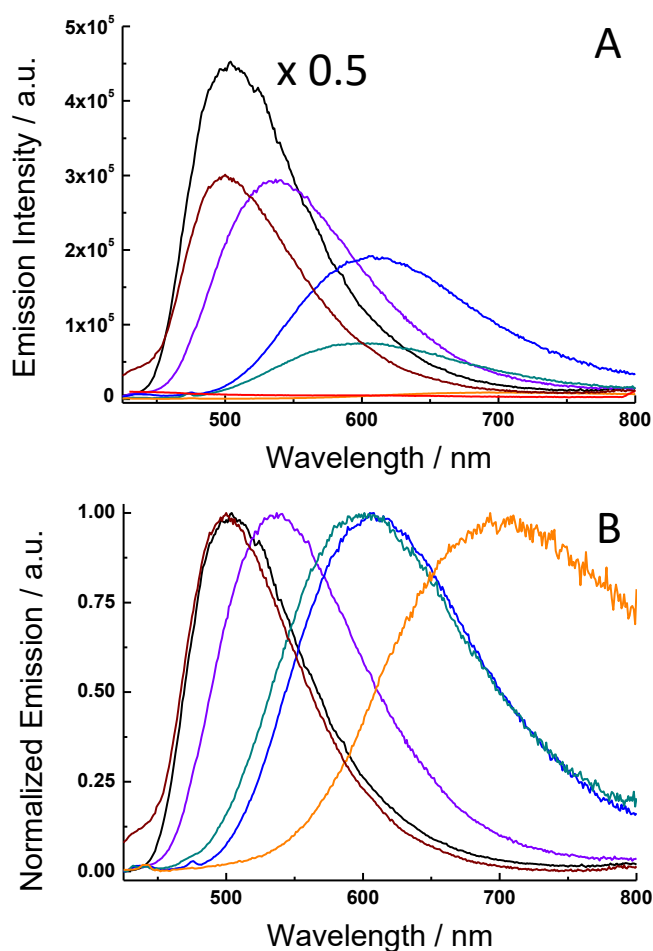


Figure S3. Regular (A) and normalized (B) emission spectra of **2** in solvents with increasing polarity. Cyclohexane (black line), Toluene (violet line), Anisole (blue line), THF (green line), CH_2Cl_2 (orange line) and ACN (brown line). $\lambda_{\text{exc}} = 415 \text{ nm}$.

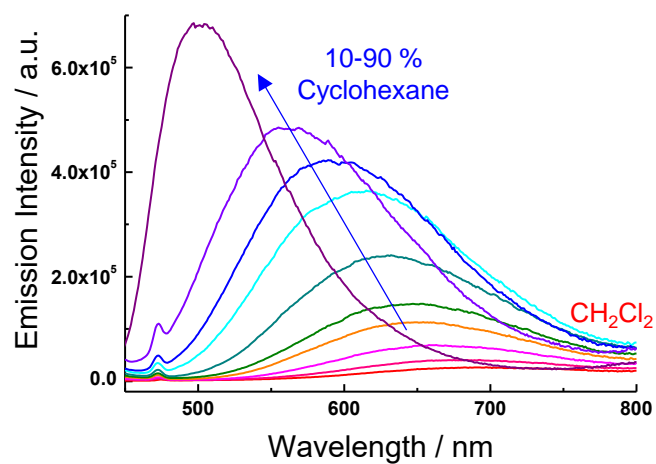


Figure S4. Emission spectra of **2** in CH_2Cl_2 /cyclohexane mixtures. $\lambda_{\text{exc}} = 415$ nm.

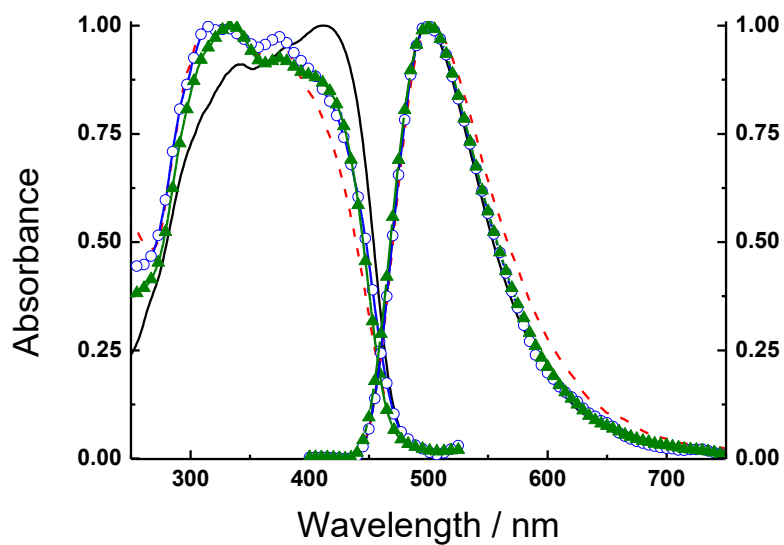


Figure S5. Normalized absorption and emission spectra of **2** in thin films prepared with spin-coating using different solvents: cyclohexane (solid black line), CH_2Cl_2 (dash red line), ACN (blue empty circles) and toluene (green empty triangles). $\lambda_{\text{exc}} = 400$ nm.

Table S1. Fluorescence lifetimes values derived from mono- or bi-exponential fit of the experimental data of **2** in six different solvents. $\lambda_{exc} = 406$ nm. The parameter of the solvents are also given (dielectric constant, ϵ , Lippert-Mataga solvent polarity parameter Δf and viscosity η at 293 K).

| Solvent | $\lambda_{em} =$ 500-610 nm | | | | Solvent properties | | |
|---------------------------------|--------------------------------|-------|---------------|-------|--------------------|------------|-------------|
| | τ_1 / ns | a_1 | τ_2 / ns | a_2 | ϵ | Δf | η / cp |
| Cyclohexane | 3.00 | 0.75 | 10.2 | 0.25 | 2.02 | 0.001 | 0.98 |
| Toluene | 1.02 | | | | 2.38 | 0.013 | 0.56 |
| Anisole | 1.43 | | | | 4.33 | 0.110 | 1.05 |
| THF | 1.16 | | | | 7.58 | 0.211 | 0.55 |
| CH ₂ Cl ₂ | 0.15 | | | | 8.93 | 0.217 | 0.41 |
| ACN | 2.6 | 0.52 | 7.5 | 0.48 | 37.5 | 0.305 | 0.37 |

Table S2. Fluorescence lifetimes (τ) and relative fractional amplitudes (a) derived from bi-exponential fit of the experimental emission data of **2** as thin film prepared from four different solvents. $\lambda_{exc} = 420$ nm.

| Solvent | $\lambda_{em} = 500$ nm | | | |
|---------------------------------|-------------------------|-------|---------------|-------|
| | τ_1 / ns | a_1 | τ_2 / ns | a_2 |
| Cyclohexane | 2.42 | 0.62 | 7.21 | 0.38 |
| Toluene | 2.23 | 0.64 | 7.53 | 0.36 |
| CH ₂ Cl ₂ | 2.21 | 0.69 | 7.90 | 0.31 |
| ACN | 2.12 | 0.64 | 7.33 | 0.36 |

4. Electroluminescence studies

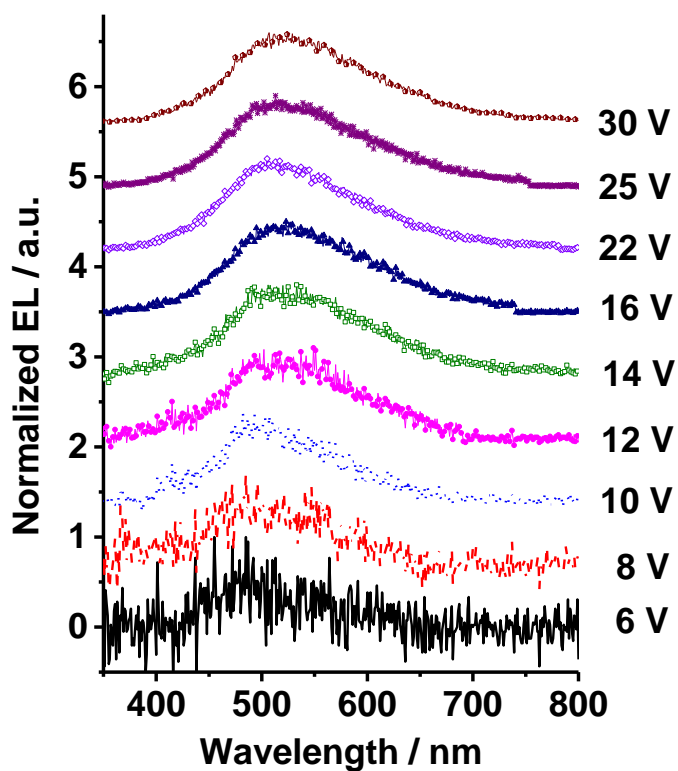


Figure S6. Comparison of the normalized electroluminescence spectra at different driving voltages in device where compound 2 is spin-coated from toluene solution.

5. Copy ^1H NMR spectra of compound 2

