MAKING STUFF GLOW

THERMALLY ACTIVATED DELAYED FLUORESCENCE (TADF) IN SYNTHETIC MACROCYCLIC ANION RECEPTORS

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Outline

Macrocycles comprise an important facet of supramolecular chemistry, with applications spanning from catalysis to chemical sensing.[1] **This project seeks to enhance the viability of using such compounds as anion receptors by incorporating luminophores into their structure**. The traditional mechanism by which these macrocycles stabilise anions is through formal hydrogen bonding between the central anion and highly polarised $^{\delta+}$H-X$^{\delta-}$ bonds in the surrounding ring.[2] These compounds work well in organic solvents, where no other hydrogen bonding competes with the desired interaction, however, this limits their applicability in real-world contexts.[1]

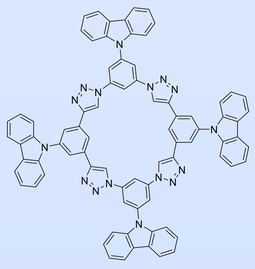


Figure 1: Target compound

Therefore, designing new macrocycles capable of $^{\delta-}$C-H$^{\delta+}$ hydrogen bonding to anions and whose **photophysical properties vary upon complexation** is highly advantageous to anion receptor chemistry. The target compound was inspired by literature,[2] with the addition of carbazole groups which were computationally predicted to make the molecule TADF active.

Computation

According to DFT calculation using the PBE0 functional and 6-31G(d,p) basis set for the target molecule in the gas phase, the energy gap between the first excited singlet (S_1) and triplet (T_1) states (ΔE_{ST}) **is estimated to be 0.15 eV.** Geometry optimisation indicated a twisted structure, with the carbazole substituents protruding out of the plane of the central macrocycle. **For appreciable TADF, any value for ΔE_{ST} less than 0.3 eV is adequate.**[3]

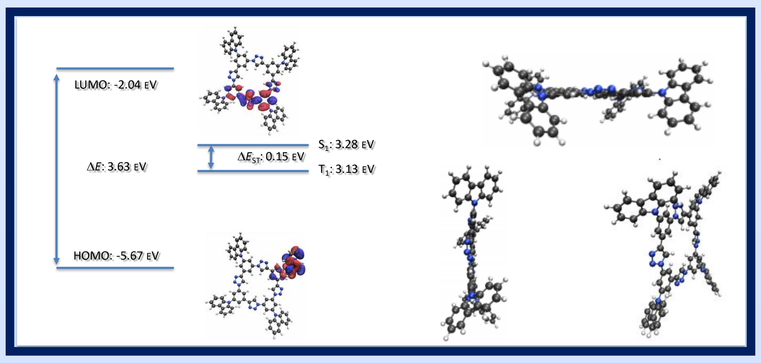
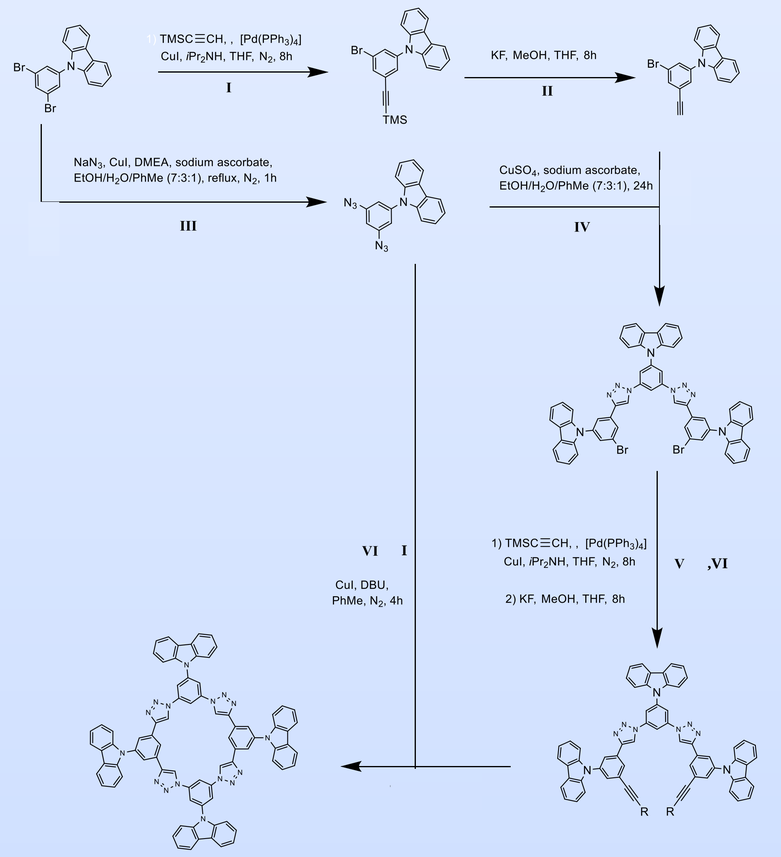


Figure 2: DFT calculated frontier orbital energies and geometry optimisations

Synthesis



Luminescence Potential

The molecule in the literature[2] upon which the project was based is non-emissive, which limits its usefulness for chemical sensing. **Appending carbazole units confers photoluminescence to the target compound**, through a combination of prompt fluorescence (PF) and TADF. Fluorescence involves radiative decay of an exciton (a bound electron-hole pair) from the first singlet (S_1) state to the ground (S_0) state, with the emission of light. PF occurs on a very fast (nanosecond) timescale, whilst TADF occurs more slowly. These can therefore be distinguished, and the delayed fluorescence (DF) can be investigated. **DF is achieved by the thermal up-conversion of triplet (T_1) states to singlet (S_1) states.** This reverse intersystem crossing (RISC) results in radiative decay of all excitons from S_1 back to S_0.[6] If the rate of RISC and the DF profile change upon ion coordination, this would give **valuable sensing information**, and potentially **more informative receptors** than are currently employed.

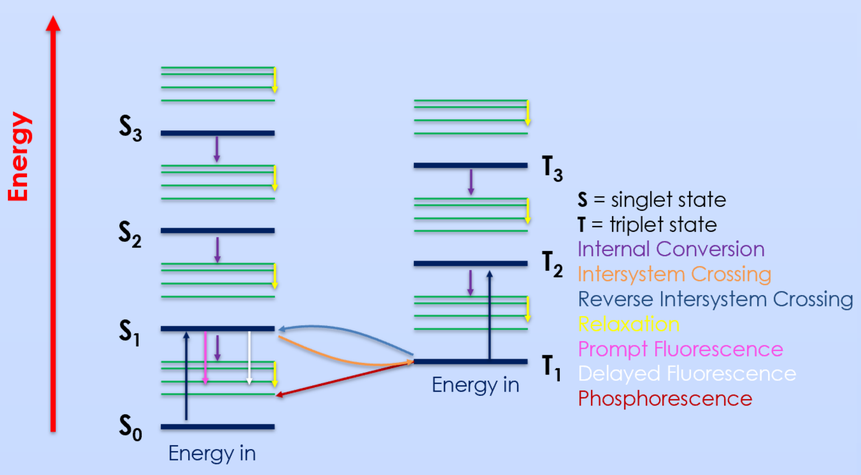


Figure 3: Jablonski diagram illustrating the various radiative and non-radiative decay processes in photoluminescence.

Reaction I: Both $Pd(Ph_3)_2Cl_2$ and $Pd(Ph_3)_4$ were screened as catalysts. Et_3N and $^{i}Pr_2NH$ were also screened as bases. (47%). The mono-coupled and di-coupled products were formed.

Reaction II: Successful TMS deprotection using a fluoride source to give terminal alkyne (86%).

Reaction III: Conducted by supervisor in the interest of time.

Reaction IV: Unsuccessful in the absence of a ligand for Cu(I), reaction repeated with phenyl azide and $^{i}Pr_2NEt$ (3.5 eq.) successfully in a 5:3:3 ratio of the same solvents.

Reactions V, VI and VII: Still to be completed by supervisor.

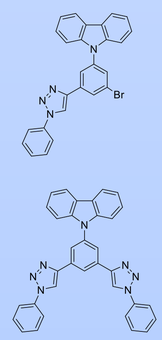
The reactions were taken from literature[2] and the products were purified by flash chromatography using silica.

Results

Compounds II – IV were synthesised using procedures either given in, or inspired by, literature.[2] All intermediates were characterised by some combination of gas-chromatography mass spectrometry (GCMS), ^{1}H nuclear magnetic resonance (NMR) and ^{13}C DEPTQ NMR spectroscopy, and the expected structures were fully supported by the data. The catalyst used for the Sonogashira coupling given in literature [$Pd(Ph_3)_2Cl_2$] did not enable the desired reaction, so a lower oxidation state [$Pd(Ph_3)_4$] complex was used instead. When the reaction was run on a small (400 mg) scale, very low (10%) yields were achieved, however this improved on scaling up the reaction (47%). The very similar polarities of Br and the trimethylsilyl (TMS) group meant that purification was difficult as the retention factors for the dibromo and silylated species were very similar, in a range of different solvent systems.

The deprotections of the desired mono-coupled product and the di-coupled analogue proceeded in high yields as expected (86% and 90%, respectively).

An initial attempt at the theoretically-quantitative click chemistry Reaction IV, under the conditions given above, proved unsuccessful. It was discovered that a ligand for the thermodynamically unstable Cu(I) species is necessary to facilitate this reaction.[7] The reactions between both the deprotected alkyne(1 eq.) and phenylazide (1.5 eq.), and the dialkyne (1 eq.) and phenylazide (2.2 eq.) with the addition of diisopropylethylamine(3.5 eq.) to act as this ligand gave the desired products (shown on the right). The solvent system was altered from a 7:3:1 combination of ethanol: water: toluene to a 5:3:3 combination, to ensure full solubility of the large, aromatic compounds. If more time were available in the lab, Reaction IV would have been repeated in this 5:3:3 solvent system, with the addition of diisopropylethylamine (3.5 eq.). Due to time constraints, the subsequent reactions were not attempted.



Future Work

The outstanding portions of the synthesis of the target compound will be carried out by Dr John Marques Dos Santos and the intermediates will also be characterised by ^{1}H and ^{13}C DEPTQ NMR spectroscopy. Both the photophysical properties of the target compound and its anion binding ability will also be measured, for a range of halide anions, in a range of different solvents. The catalysts involved in the cross-coupling steps could also be varied, in order to identify the best candidate for maximum mono-coupling. If the results are encouraging, alternative donor substituents could be screened to investigate how the binding affinity of these macrocycles, as well as their TADF responses, changes.

References

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Acknowledgments

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LAIDLAW SCHOLARS

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