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DOC-FAM DOCtoral training programme in Functional Advanced Materials H2020-MSCA-COFUND-2016 MARIE CURIE ACTIONS

Carborane Based π- Conjugated Systems for Two Photon Absorption (TPA)

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INTRODUCTION

Carboranes or dicarba-*closo*-dodecaboranes ($C_2B_{10}H_{12}$) are known to have geometrically diversified 3D structure, σ-aromaticity, [1] high thermal and chemical stability. Due to the unique structural and electronic properties, carboranes are highly versatile moieties that could produce a large impact when attached to aromatic systems.[2] There are three isomers, *o*- (Fig 1), *m*- and *p*-carborane depending on the position of C atoms in the cluster.

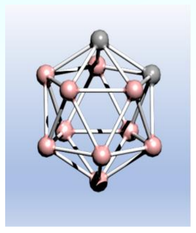
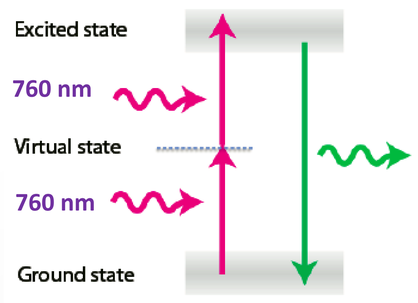


Fig 1. ***ortho*-carborane ($1,2\text{-}C_2B_{10}H_{12}$)**

With the advent of initial use in organometallic chemistry and catalysis, boron clusters have proved its immense attention in photoluminescence and biological applications.[2-4] Two photon absorption (TPA, Fig 2)) is a non-linear optic phenomenon in which a molecule can simultaneously absorb two photons of same energy to reach a stable excited state via virtual state (of very short lifetime).



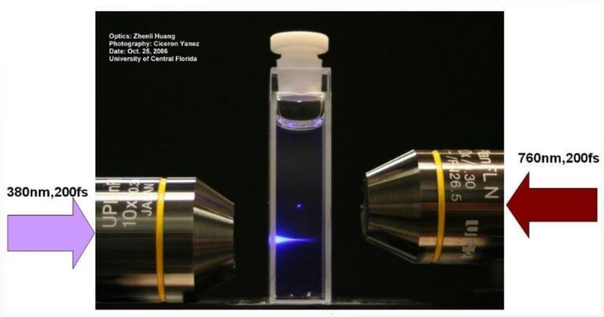


Fig 2 Z scan Technique (TPA signature: a single blue dot)

OBJECTIVE

The strong electron-withdrawing properties of the carborane cage through C atoms and the highly polarizable σ-aromatic character lead to intramolecular charge transfer (ICT) between the *π*-conjugated aromatic groups and *o*-carborane. *The aim is to develop acceptor-donor-acceptor (example in Fig 3) or donor-acceptor systems that act efficiently as two-photon-absorbing fluorophores and find their applications in microfabrication or bioimaging*. In these systems the *o*-carborane cage acts as an acceptor group.

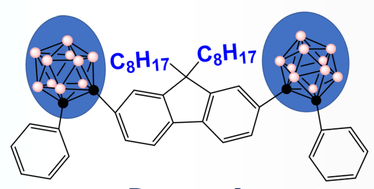


Fig 3 Acceptor–Donor-Acceptor system

PHOTOPHYSICAL ACTIVITY

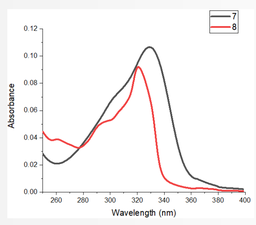
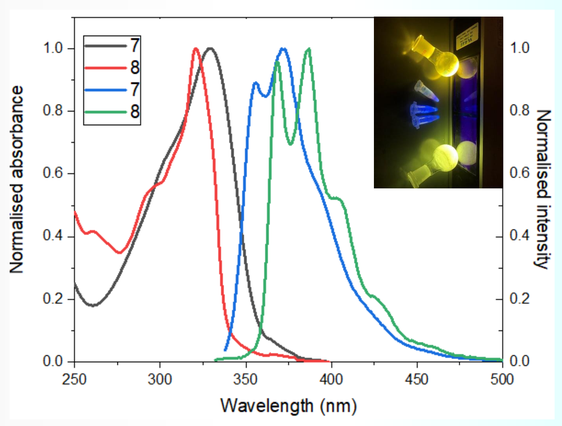


Fig 7

Absorption spectra of compounds 7 & 8



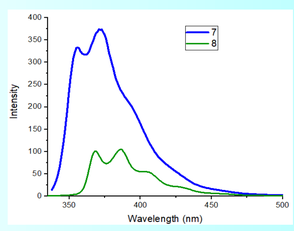


Fig 8

Fluorescence quenching (in THF) in 8 compared to 7 due to *o*-carborane units.

Fig 6 Normalised absorption & emission spectra of 7 & 8

SYNTHESIS & CHARACTERIZATION

The acetylene precursors for fluorene and thiophene derivatives were synthesized by Sonogashira reaction using standard conditions and corresponding phenylacetylene derivatives. After purification and isolation, the acetylene derivatives [1], [3], [5], [7] and [9] were further used in insertion reaction with decaborane ($B_{10}H_{14}$) using Et_2S as a Lewis base in toluene (Scheme 1). This reaction was stirred for 72 h at 90 °C. Thus, the respective *closo*-carborane containing acceptor-donor-acceptor systems were isolated. All of them were fully characterized using ^1H, ^{11}B, ^{13}C NMR and FT-IR spectroscopy (Fig 4 and 5) and photophysical properties (UV-Vis and fluorescence spectroscopy) were analyzed (Fig 6-8).

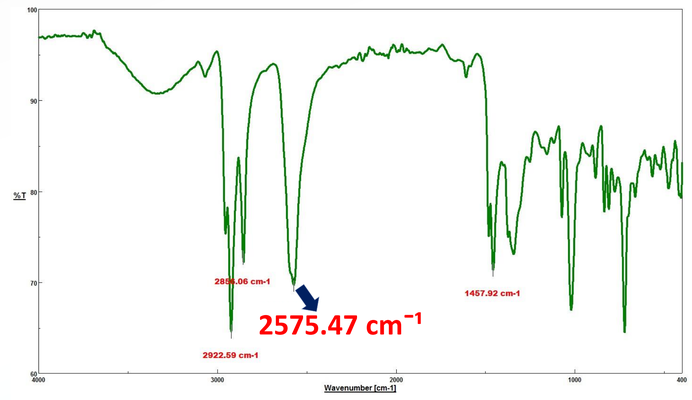
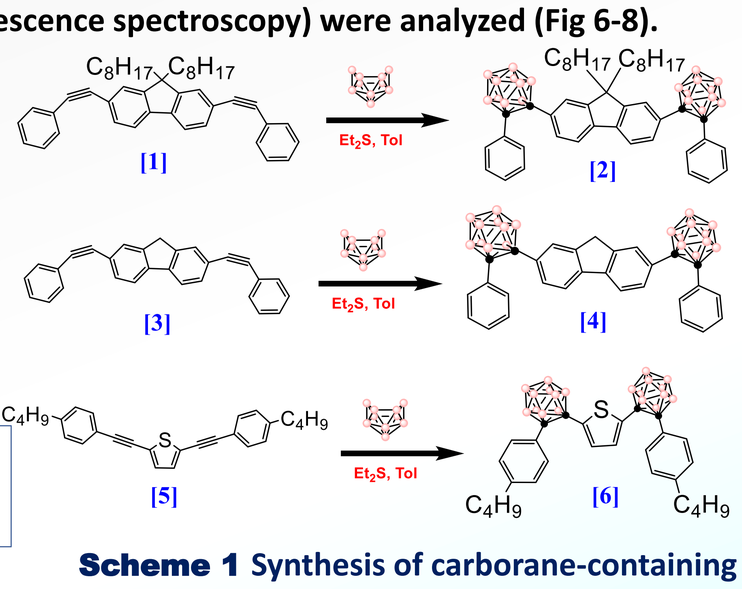
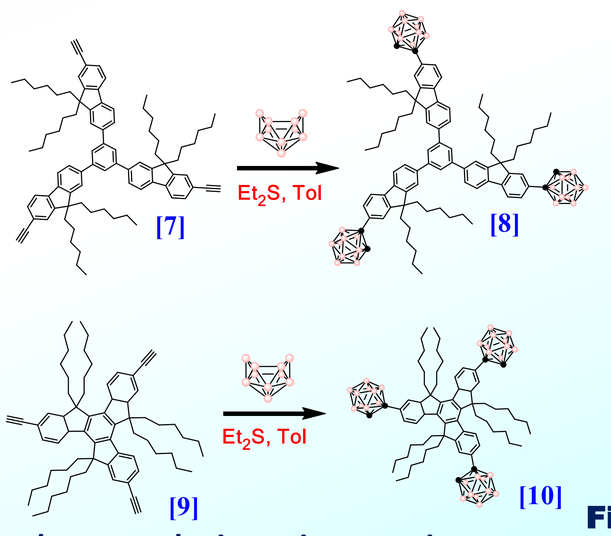


Fig 4 FT-IR confirms ν(B-H) band of *o*-carborane





Scheme 1 Synthesis of carborane-containing π-conjugated systems by insertion reaction

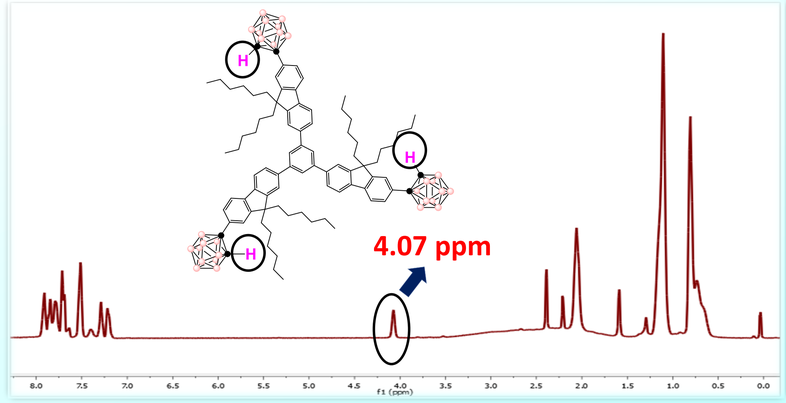


Fig 5 ^1H NMR confirms $C_{cluster}$-*H* resonance of *o*-carborane

CONCLUSION

A set of fluorene and thiophene-based compounds containing *o*-carborane was synthesized and fully characterized. The role of acceptor and donor groups in the electron transfer process was further studied which suggested quenching of fluorescence on addition of *o*-carborane units. This behavior was observed for rest of the compounds based *o*-carborane. The fluorescence quantum yield of compound 8 was observed to be 24.7% whereas that of compound 7 was 95.57%, the reference used was quinine sulphate in 0.5 M H_2SO_4 (ϕ = 0.54%). Some of these compounds have been submitted for TPA measurements (using Z scan technique) and the results are awaited.

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REFERENCES

[1] J. Poater, C. Viñas, I. Bennour, S. Escayola, M. Solà, F. Teixidor, J. Am. Chem. Soc. 2020, 142, 9396.
[2] a) R. Núñez, M.Tarrés, A. Ferrer-Ugalde, F. Fabrizi de Biani, F. Teixidor, Chem. Rev. 2016, 116, 14307-14378. b) R. Núñez, M.I. Romero, F. Teixidor, C. Viñas Chem. Soc. Rev. 2016, 45, 5147-5173.
[3] a) M. Chaari, Z. Kelemen, J. G. Planas, F. Teixidor, D. Choquesillo-Lazarte, A. Ben Salah, C. Viñas, R. Núñez, J. Mater. Chem C 2018, 6, 11336-11347. b) M. Chaari, Z. Kelemen, D. Choquesillo-Lazarte, F. Teixidor, C. Viñas, R. Núñez, Inorg. Chem. Front, 2020, 7, 2370.
[4] P. Labra-Vázquez, R. Flores-Cruz, A. Galindo-Hernández, J. Cabrera-González, C. Guzmán-Cedillo, A. Jiménez-Sánchez, P. G. Lacroix, R. Santillan, N. Farfán, R. Núñez, Chem. – A Eur. J. 2020, 26, 16530.

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