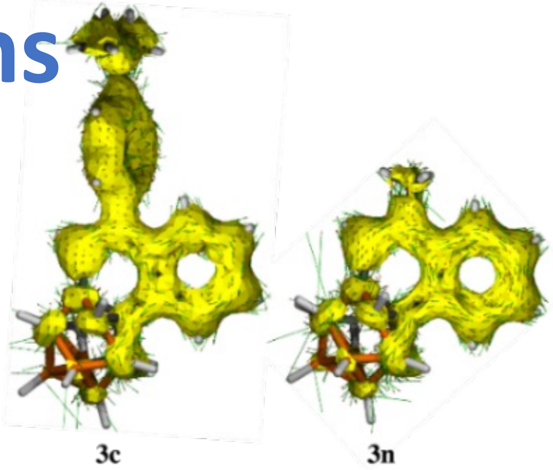
Boron Cage Extension drives to new Hybrid Conjugation between 2D Hydrocarbons and 3D nido-Carborane



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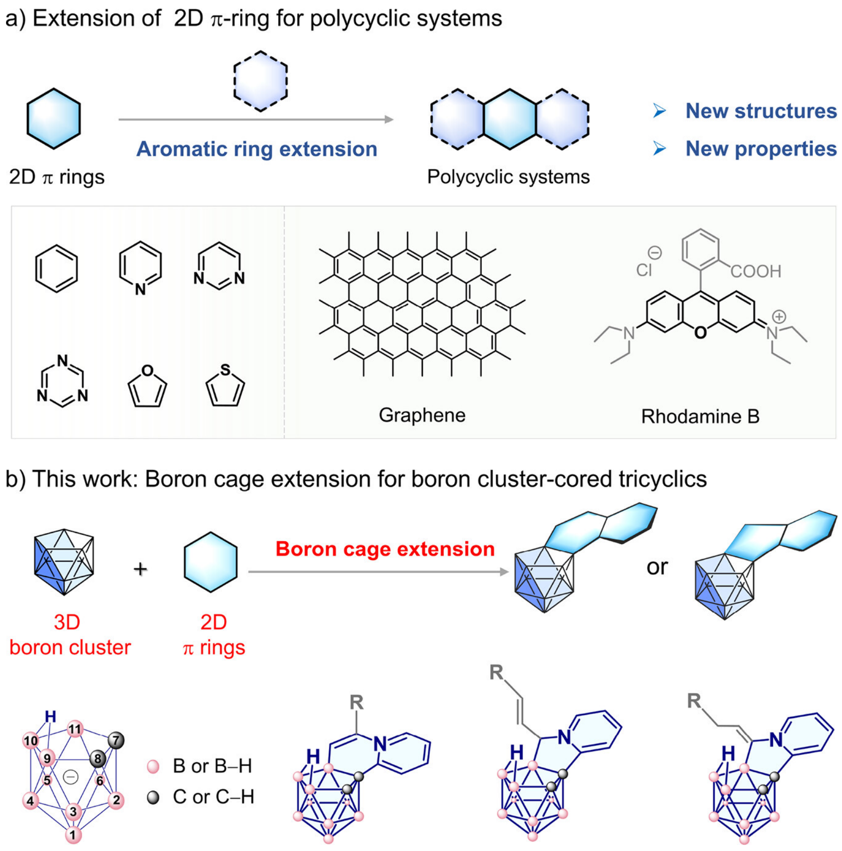
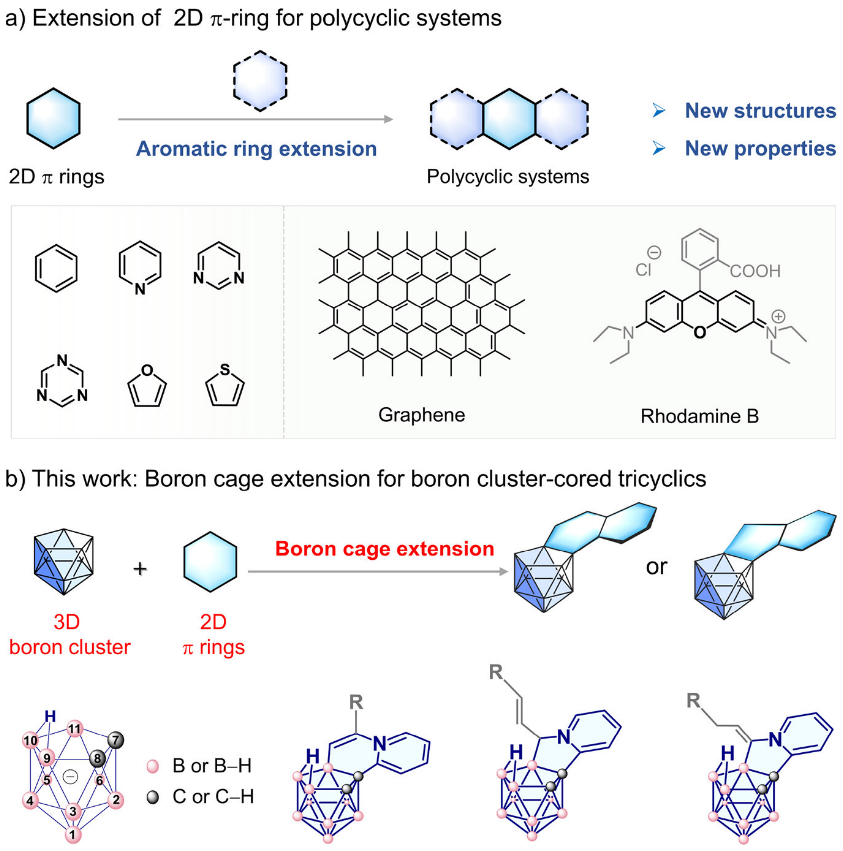
Boron cage extension



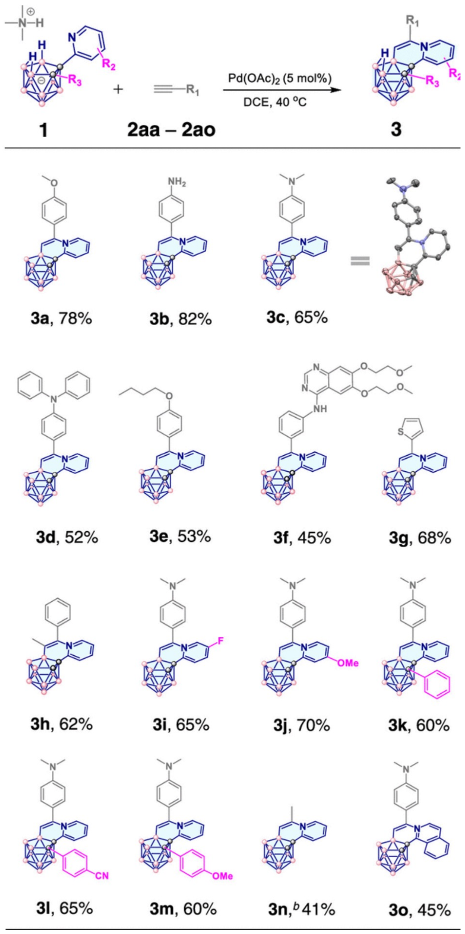
- Carboranes: 3D aromaticity, rigid geometry, high thermal and chemical stability, low toxicity, bulky size, and hydrophobicity.
- Carboranes have been utilized as important building blocks, as appended structural unit, **not central role**.
- A “**cage extension strategy**” to construct boron cluster-cored polycyclics is much less established in contrast to the classical extension of 2D aromatic rings.

Boron cage extension



- We designed and prepared a new hybrid conjugated system, i.e., **fusion between a 2D aromatic ring and a 3D nido-carborane** by facile Pd-catalyzed B–H activation and subsequent cascade heteroannulation of carborane and pyridine with alkynes.
- Distinct properties: enhanced chemical and thermal stability, tunable emission behaviors, and highly efficient solid-state emission.

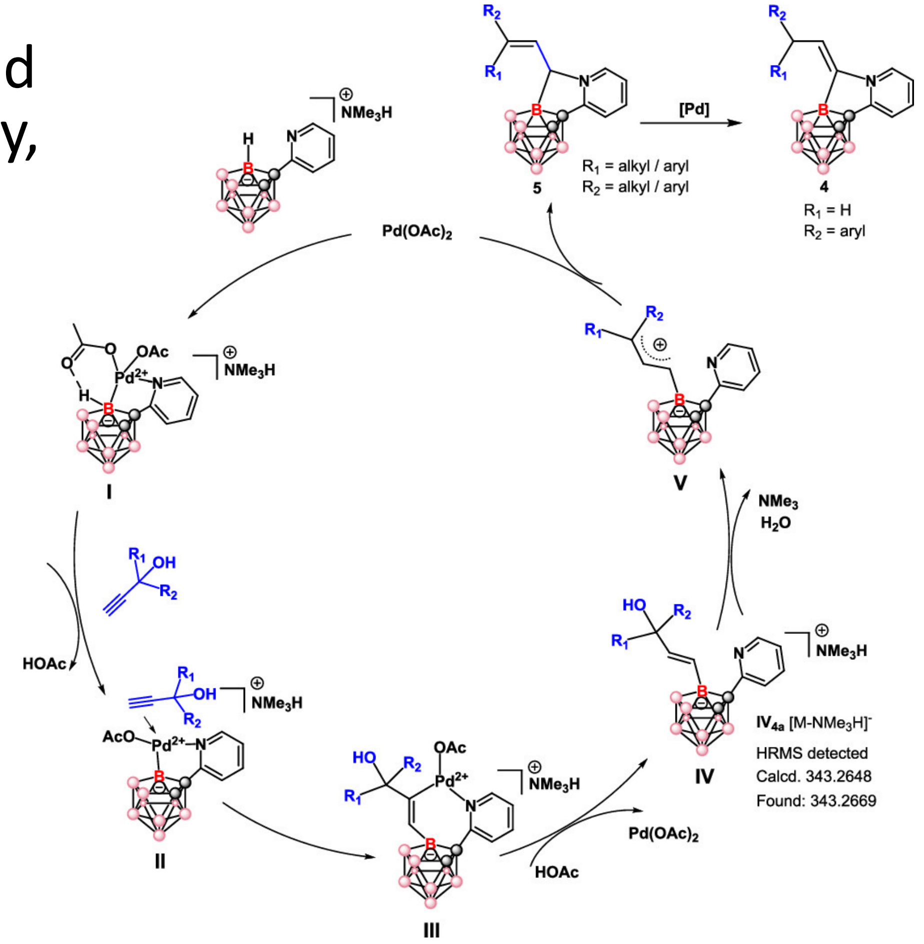
Boron cage extension



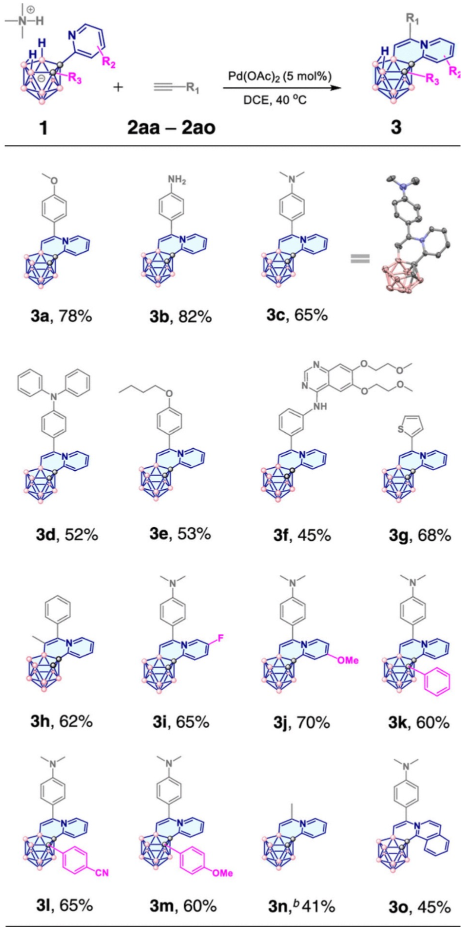
- Challenges for 3D-2D:
  - Site-selective funcionalization.
  - Stepwise reaction in a one-pot manner.
  - Steric hindrance of the cage.
  - B-H side reactions.
- New reaction protocol: Directing group-assisted, metal-catalyzed B-H activation of *nido*-carboranes and cascade cyclization.
- Regioselectivity confirmed by X-ray.

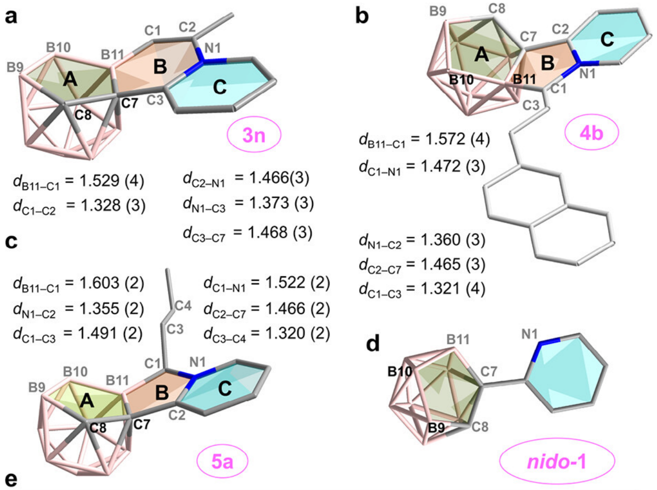
Boron cage extension

- Plausible mechanisms were proposed and validated by gas chromatography, NMR, and HRMS technologies.
  - Coordination of pyridyl to metal.
  - Selective B−H activation and regioselective alkyne insertion into the Pd−B bond.
  - Proto-demetalation.
  - Nucleophilic attack of the N atom of pyridyl.



Boron cage extension





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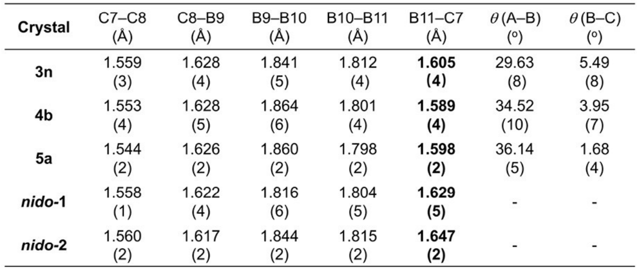
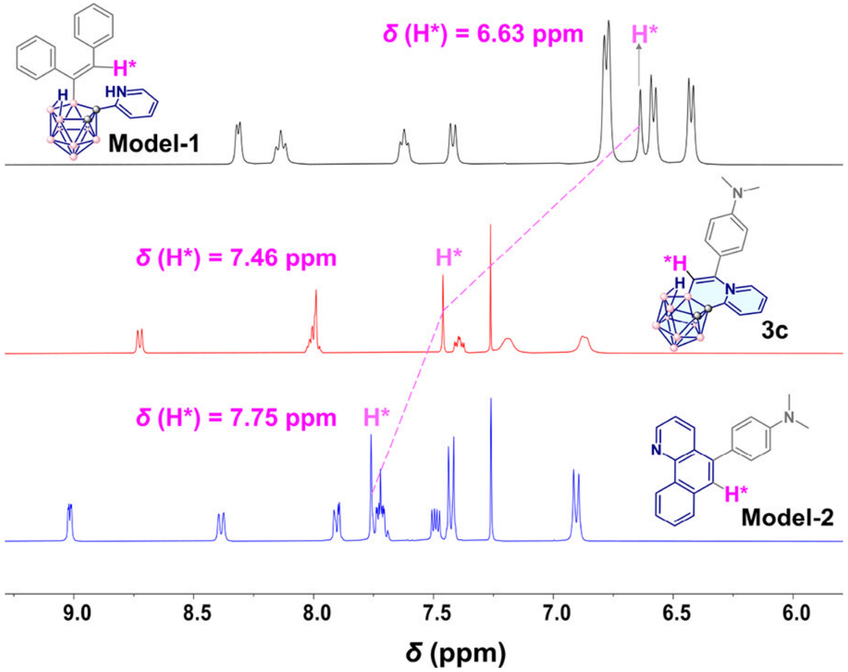


Crystal	C7–C8 (Å)	C8–B9 (Å)	B9–B10 (Å)	B10–B11 (Å)	B11–C7 (Å)	θ (A–B) (°)	θ (B–C) (°)
3n	1.559 (3)	1.628 (4)	1.841 (5)	1.812 (4)	**1.605 (4)**	29.63 (8)	5.49 (8)
4b	1.553 (4)	1.628 (5)	1.864 (6)	1.801 (4)	**1.589 (4)**	34.52 (10)	3.95 (7)
5a	1.544 (2)	1.626 (2)	1.860 (2)	1.798 (2)	**1.598 (2)**	36.14 (5)	1.68 (4)
***nido*-1**	1.558 (1)	1.622 (4)	1.816 (6)	1.804 (5)	**1.629 (5)**	-	-
***nido*-2**	1.560 (2)	1.617 (2)	1.844 (2)	1.815 (2)	**1.647 (2)**	-	-

Boron cage extension



- New fused system has an **unprecedented downfield-shifted 1H chemical shift** (δ) for the olefinic CH in the fused six-membered ring.
- δ(H*) is 7.46 ppm for 3c but the olefinic CH proton in the non-fused compound Model-1 (6.63 ppm) and other vinyl carborane derivatives presents the range of 5.0–6.7 ppm.
- *Is this unprecedented 1H NMR due to aromaticity of new ring?*

3D/3D conditions

- Halves to be merged must be **aromatic**.
- Great **similarity** in the two-connecting atom distances, although in borane clusters, 3D units of different size favor fusion.
- The participating elements in the fusion must have **exocluster bonds**, e.g., C–H, B–H in the starting half or lone pairs.
- These connecting elements will be distinct in the fused molecule from other participating elements and will not have exocluster bonds.

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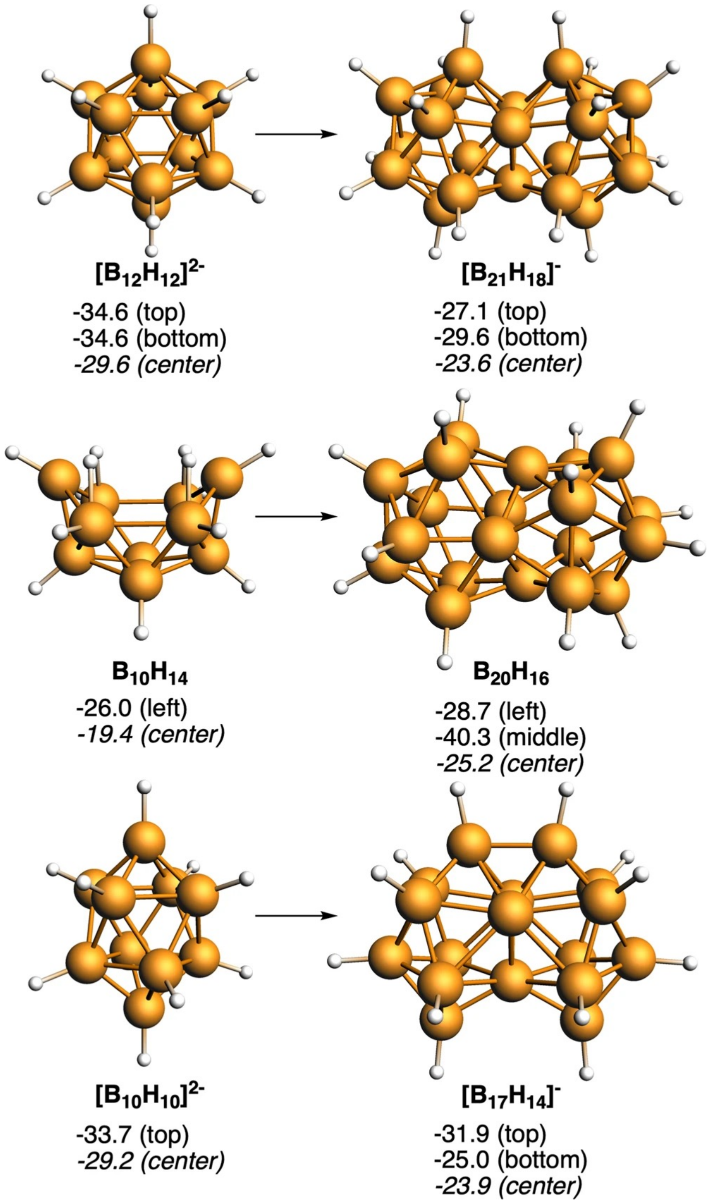


$[B_{12}H_{12}]^{2-}$
-34.6 (top)
-34.6 (bottom)
-29.6 (center)

$[B_{21}H_{18}]^{-}$
-27.1 (top)
-29.6 (bottom)
-23.6 (center)

$B_{10}H_{14}$
-26.0 (left)
-19.4 (center)

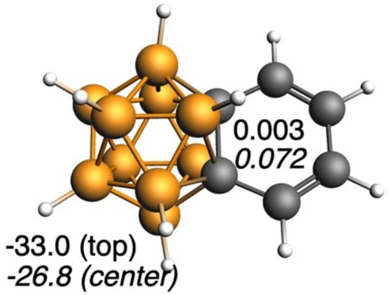
$B_{20}H_{16}$
-28.7 (left)
-40.3 (middle)
-25.2 (center)

$[B_{10}H_{10}]^{2-}$
-33.7 (top)
-29.2 (center)

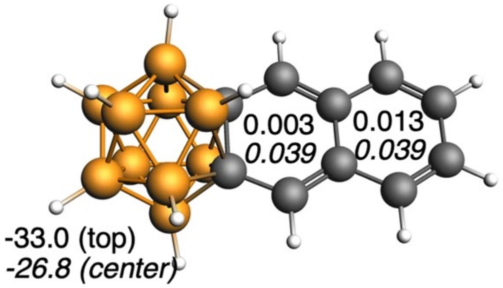
$[B_{17}H_{14}]^{-}$
-31.9 (top)
-25.0 (bottom)
-23.9 (center)

3D/2D fusions

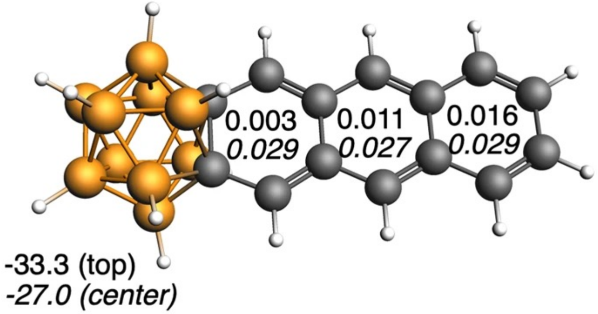
- 3D/2D: **Ineffective overlap** between the π-MOs of the PAH and the $n + 1$ MOs in the cage that deter a higher electronic delocalization between the two fused units.



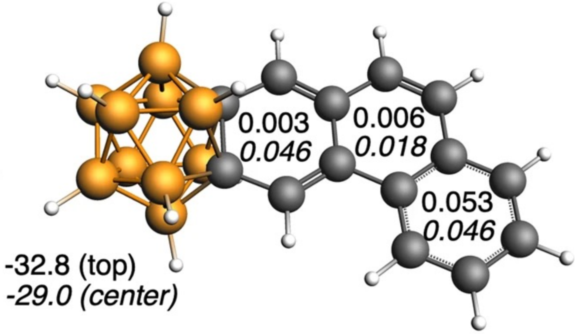
benzene^{CC}



naphthalene^{CC}



anthracene^{CC}



phenanthrene^{CC}

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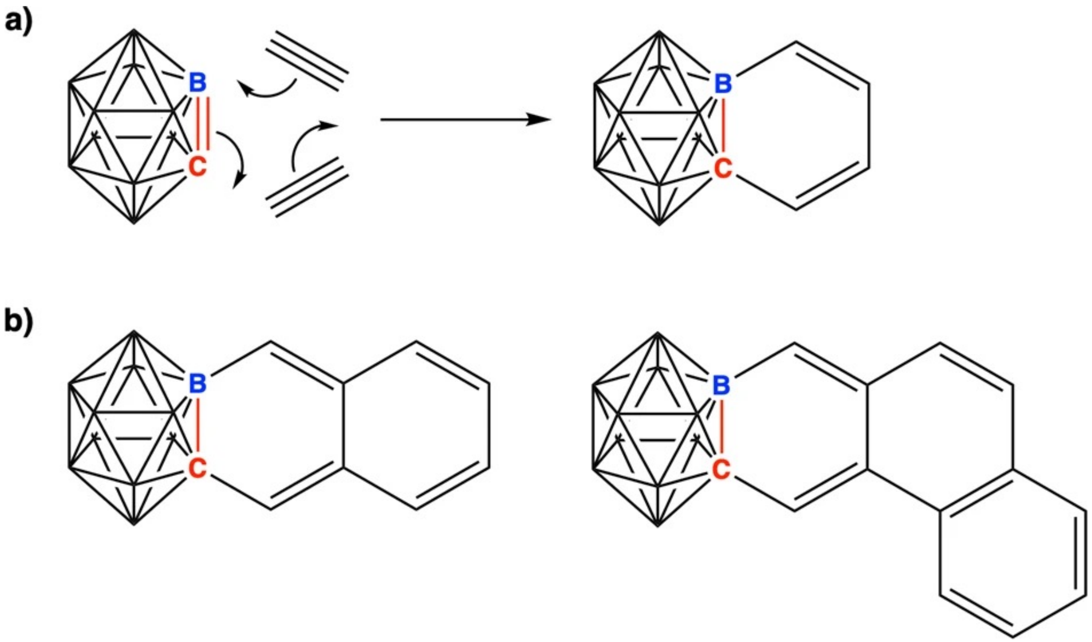
3D/2D fusions

- 3D/2D: **Ineffective overlap** between the π-MOs of the PAH and the *n* + 1 MOs in the cage that deter a higher electronic delocalization between the two fused units.
- **Aromaticity decays** with fusion, this is observed in all 2D/2D, 3D/3D, and 3D/2D cases.



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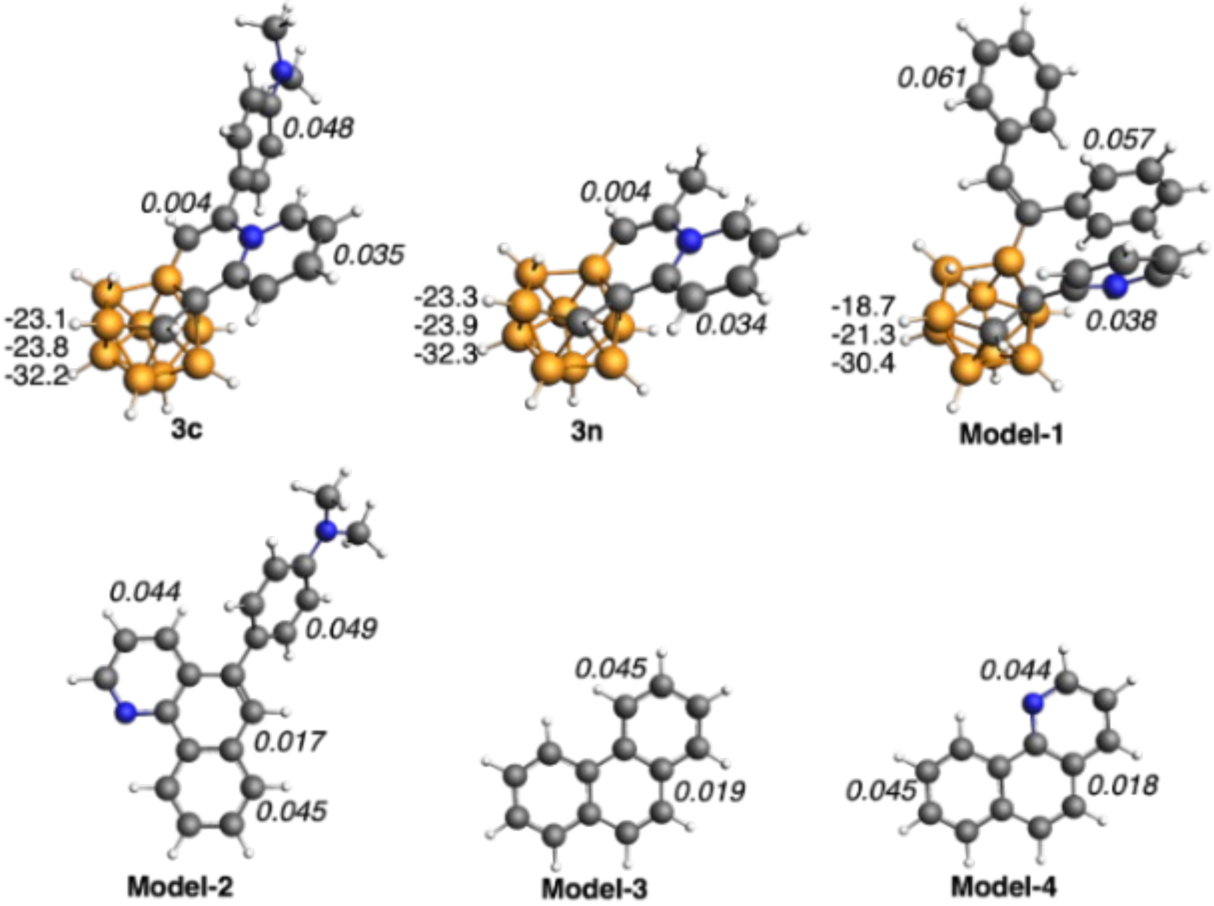
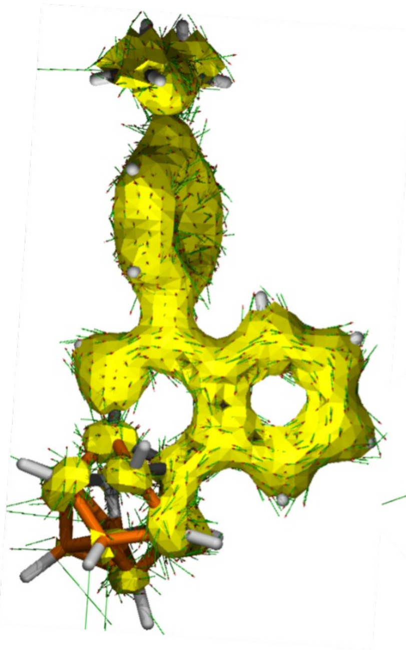
Aromaticity

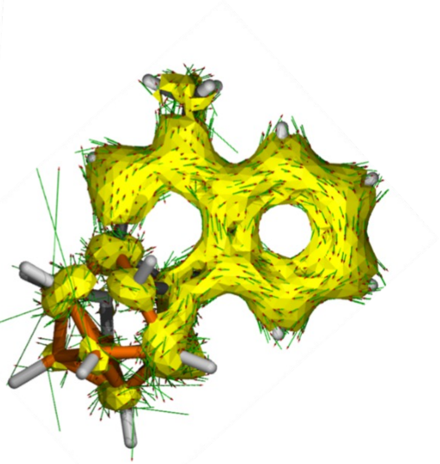
- Once the fused system is obtained, both the 3D carborane and the 2D pyridyl ring **remain aromatic**. However, this is not the case with the newly formed ring between both entities.
- Localization of double and single bond, and non-planarity.



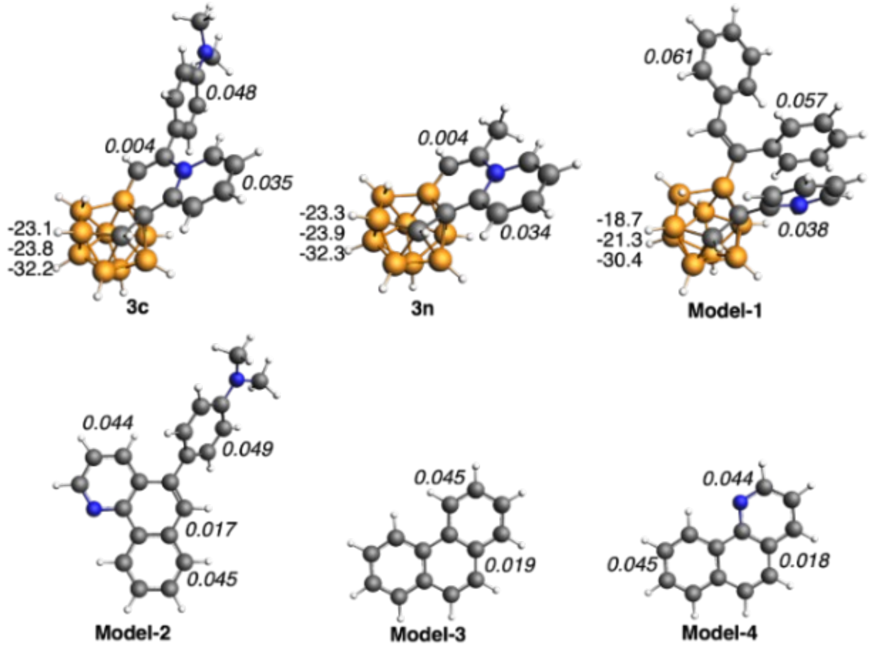
Aromaticity



3c

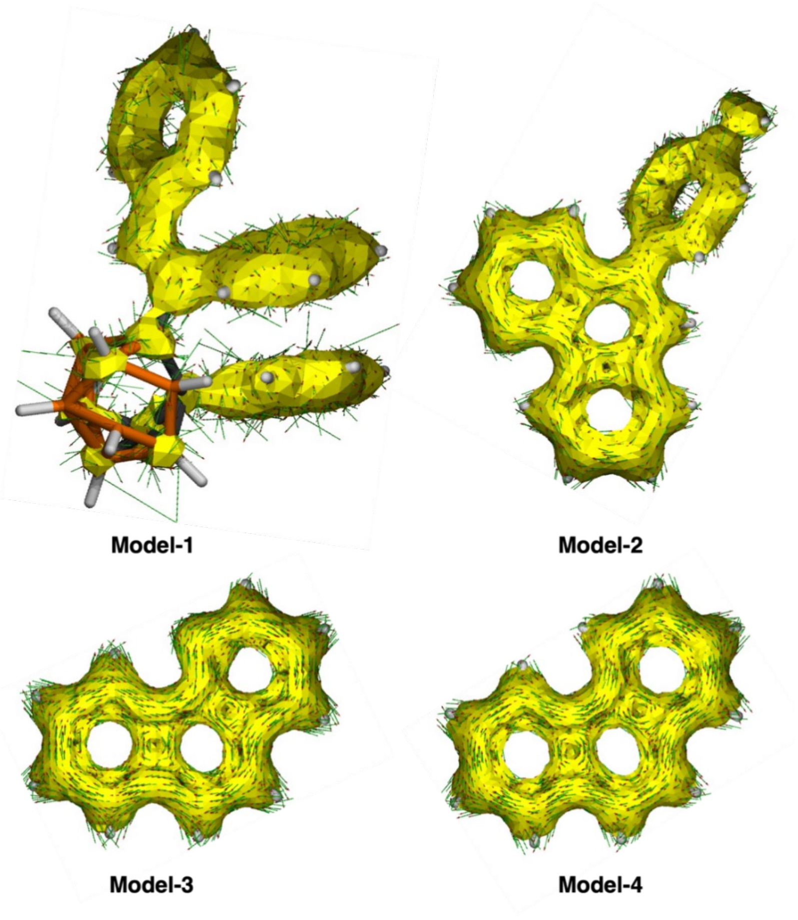


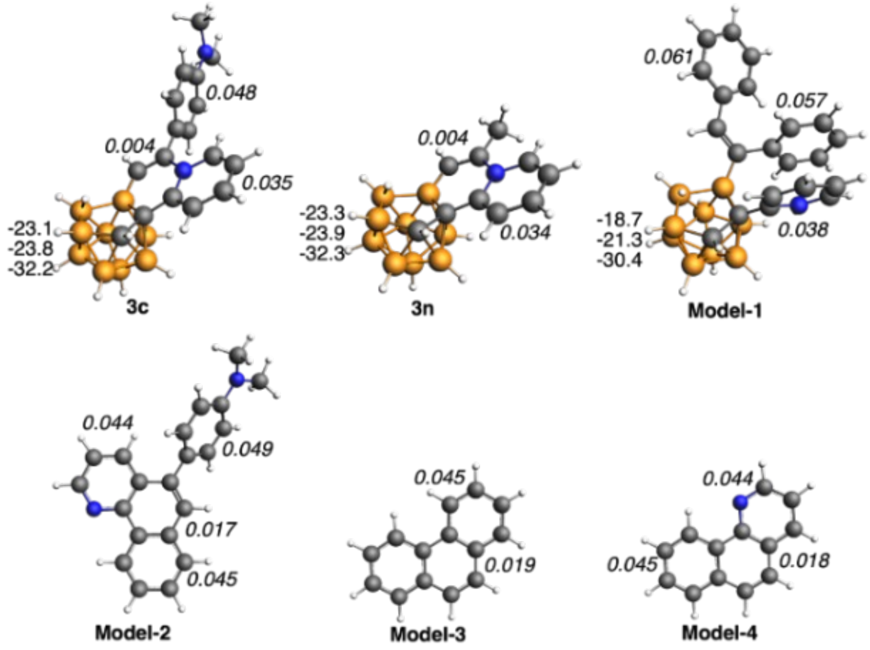
3n



- Hypothesized 2D–3D **global aromaticity** of these compounds **does not take place**, but aromaticity is localized on the 3D carborane and on the 2D pyridyl ring, not on the intermediate-fused six-membered ring.

Aromaticity

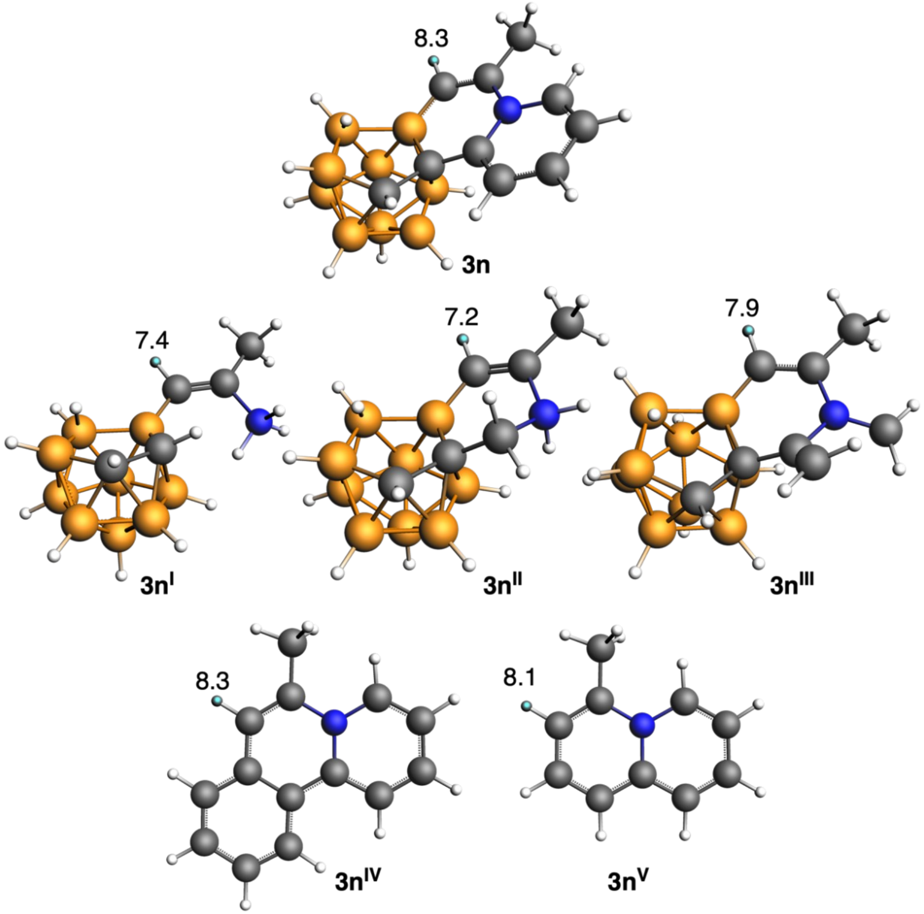




- Hypothesized 2D–3D **global aromaticity** of these compounds **does not take place**, but aromaticity is localized on the 3D carborane and on the 2D pyridyl ring, not on the intermediate-fused six-membered ring.

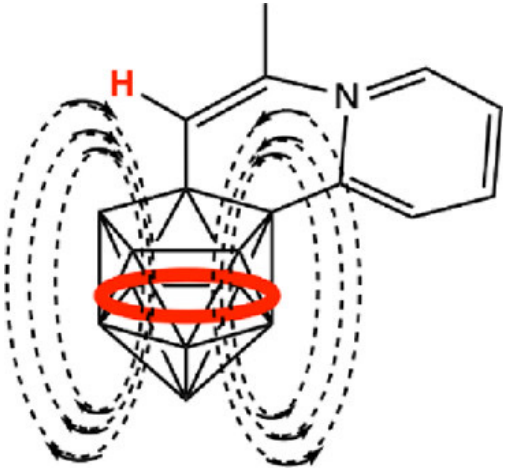
1H NMR chemical shift

- What is the reason for the distinct NMR properties of these systems? In particular, what is the origin of the unprecedented 1H NMR chemical shift of 7.46 ppm for the H atom of the fused six-membered ring δ(H*) of **3c**?
- The downfield chemical shift due to the ring current of the carborane (systems **3n**$^{\text{I}}$, **3n**$^{\text{II}}$, and **3n**$^{\text{III}}$).



1H NMR chemical shift

- Ring currents of the nido-$[C_2B_9H_{12}]^-$ cluster are **diatropic and quite intense**.
- Strongest diatropic ring current of the carborane is located in the middle of the two five-membered rings of the carborane, instead of the initially thought five-membered open face.



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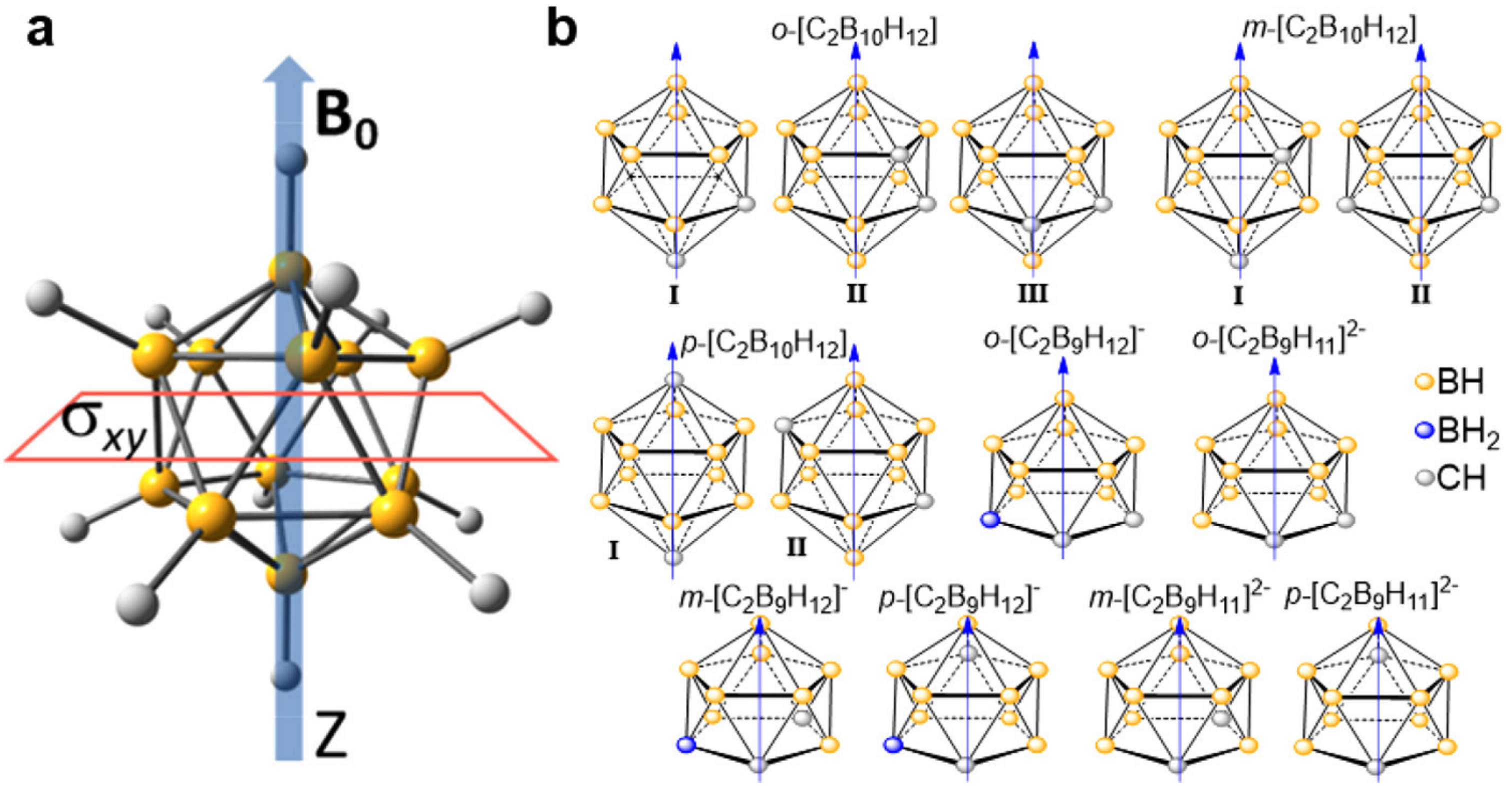
Magnetic induced current densities



- The direction of the diatropic ring currents indicating aromaticity is clockwise.
- Aromatic molecules present paratropic inner and diatropic outer ring currents.

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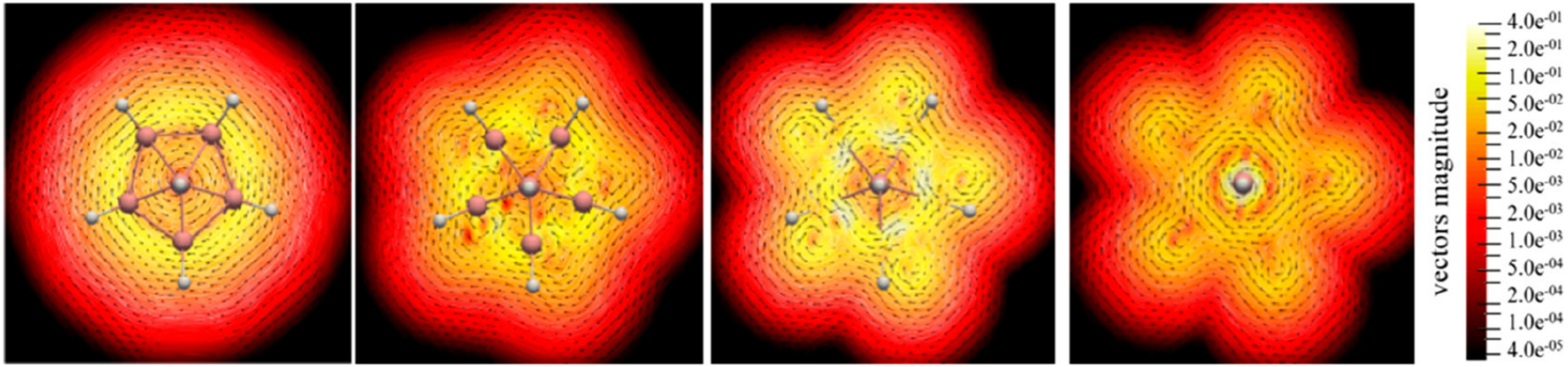
Magnetic induced current densities

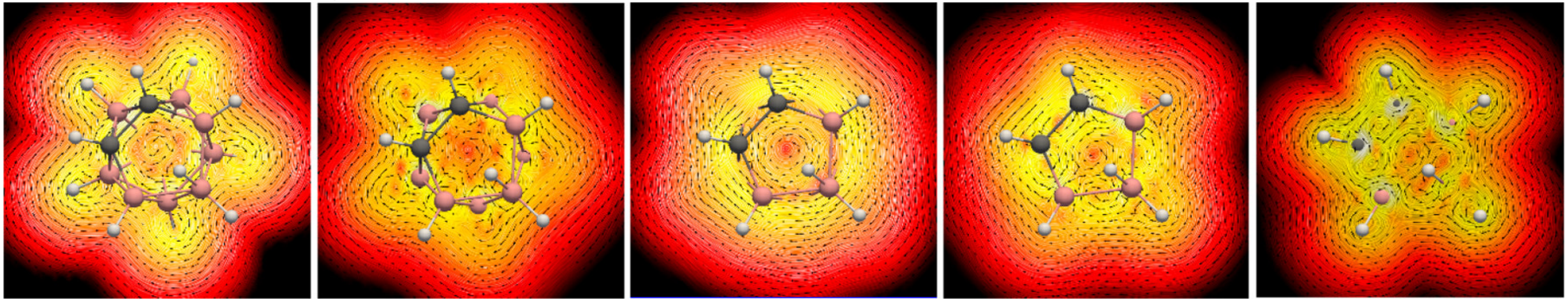
- $[B_{12}H_{12}]^{2-}$:



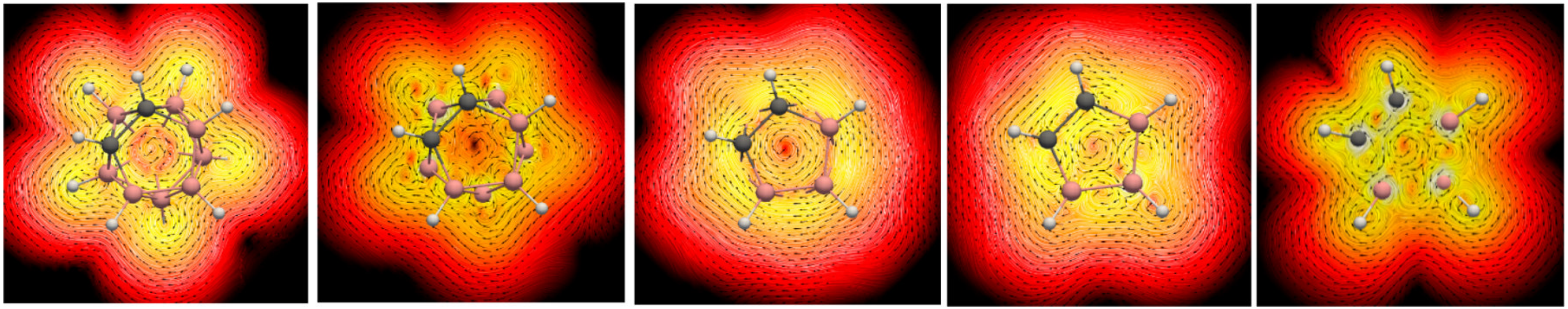
- Maximum in the center of the icosahedron; the most inner ring current in the center is paratropic. Ring currents perpendicular to the external magnetic field at the center are typical of an aromatic compound. Other planes perpendicular to the external magnetic field located at 1, 2, or 3 bohr above or below the central plane show also the same picture, although the intensity of the ring currents is somewhat reduced.

Magnetic induced current densities

- *nido*-o-$[C_2B_9H_{12}]^-$:

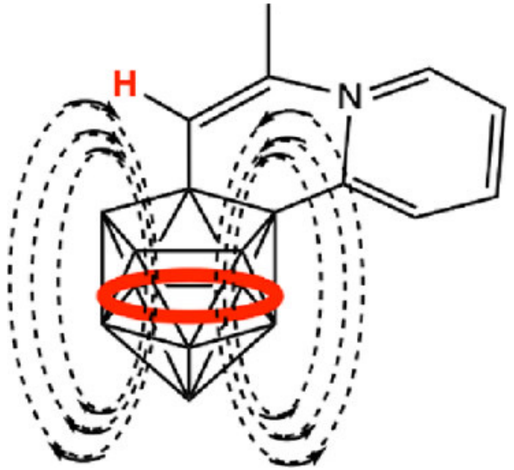


- *nido*-o-$[C_2B_9H_{11}]^{2-}$:



1H NMR chemical shift

- Strong diatropic ring currents in the carborane unit generate an **induced magnetic field** that affects the 1H NMR of the new fused six-membered ring.
- The proton attached to this mid-ring is downfielded not because the ring is aromatic but because of the induced magnetic field created by the carborane unit.



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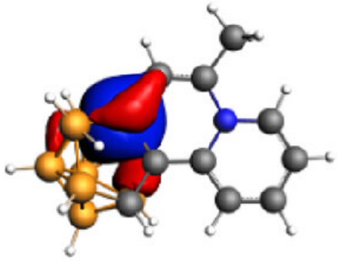
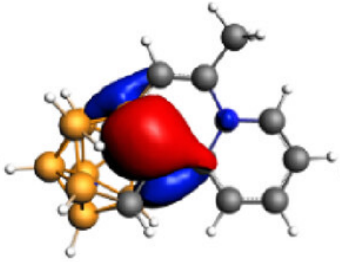
Conjugation

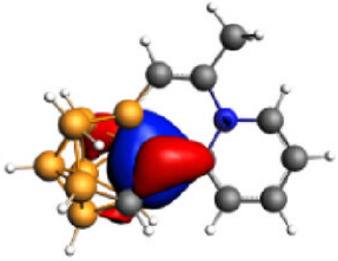
- **Certain conjugation** between the carborane cage and the aromatic ring through the shared atoms.
- Canonical molecular orbitals prove the existence of some conjugation between the carborane and the fused six-membered ring. Such conjugation is also responsible for other abnormal properties for this new series of synthesized species.



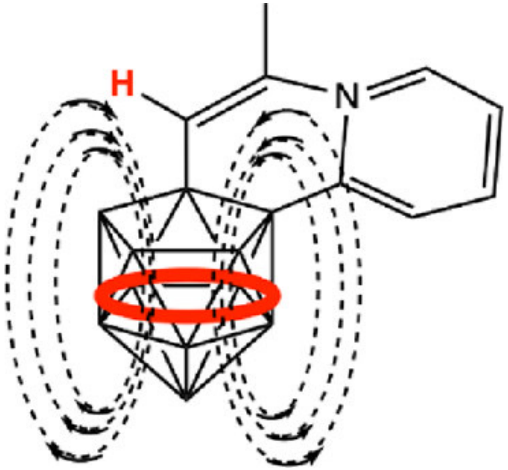
HOMO-10



HOMO-15

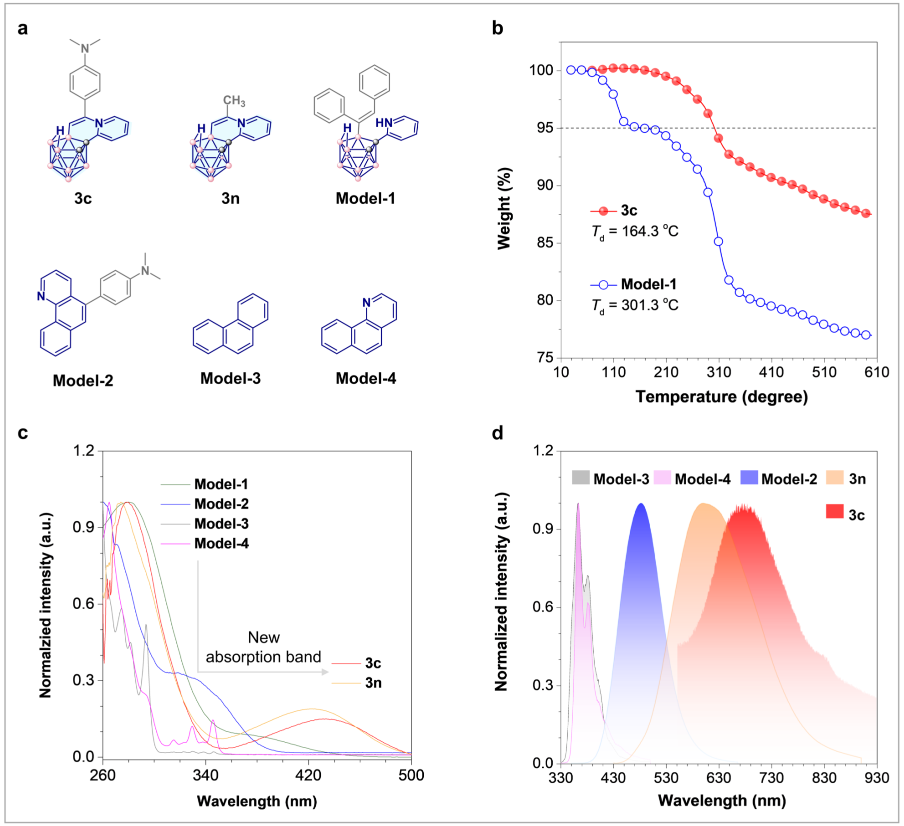


HOMO-22



Physicochemical Properties

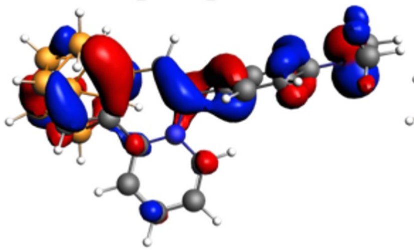
- Owing to the unique conjugation effect between *nido*-carborane and the aromatic pyridyl ring, one can expect **new physicochemical properties**.
- Thermal stability is increased after the fusion between *nido*-carborane and the aromatic ring (thermogravimetric analysis).



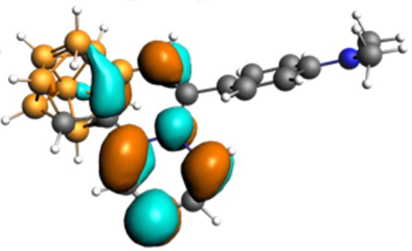
UV-Vis spectra

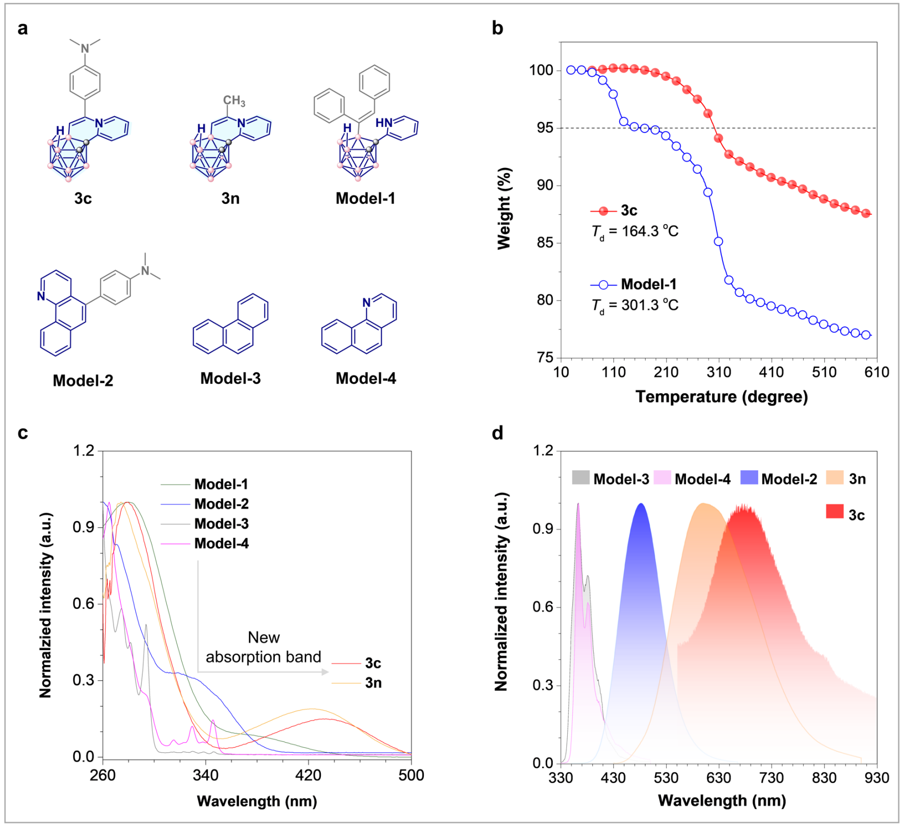
- New absorption band (431nm) for carborane-fused compounds related to the electronic transition in the whole fused system.
- The new absorption band corresponds to the HOMO → LUMO transition.
- Both HOMO and LUMO orbitals involve the atoms of both the carborane and the new fused six-membered ring, further supporting the referred conjugation.

HOMO



LUMO

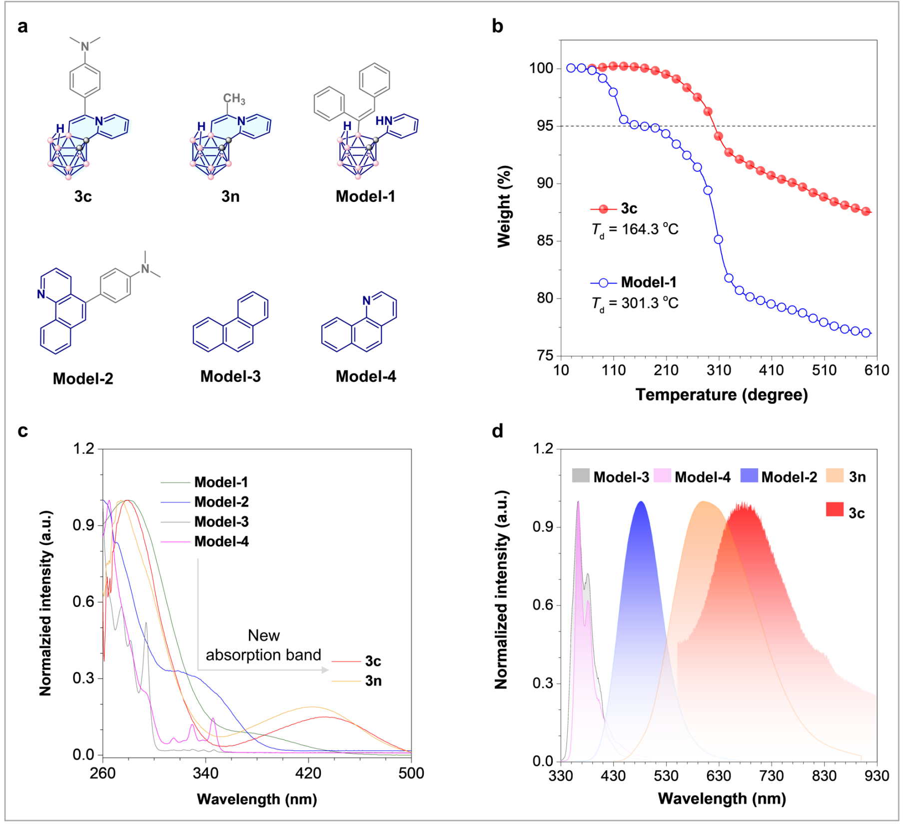




Photoluminescence spectra

- Carborane-fused systems considerably lower down the energy gap between the ground state and the excited state because of the unique conjugated structure.

- Efficient solid state luminescence thanks to restrict the formation of the strong π···π interaction in the solid state, thus reduced aggregation-caused quenching effect. These become new candidates as solid state emitters.

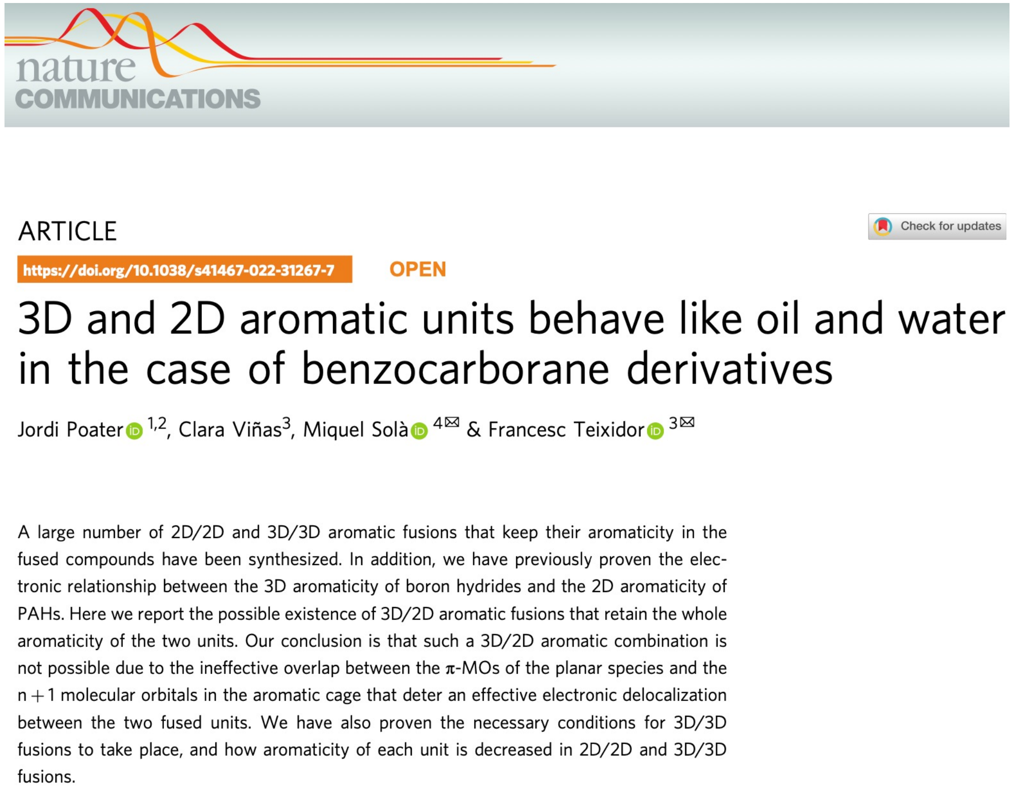


Conclusions

- We report a **new molecular design for conjugation extension**, denoted as fusion from a 2D aromatic ring and a 3D boron cluster.
- By virtue of this **boron cage extension strategy**, a library of boron cluster-cored tricyclic compounds with varying molecular skeletons can be quickly constructed based on one-pot Pd-catalyzed B–H activation and cascade annulation of *nido*-carboranes and N-heterocycles with alkynes.

Conclusions

- These new hybrid tricyclic molecular systems possess an **unusual conjugation** effect that determines excellent properties such as enhanced thermal stability, generation of new absorption bands, extremely red-shifted emissions (up to 230 nm), and tunable emissions covering from blue to red with Φ up to 61% in the solid state. In sharp contrast, these properties are absent for the corresponding non-fused structures and classical 2D-fused aromatic systems.
- The present study provides a paradigm to rationally **construct boron cluster-cored polycyclic molecules** for potential applications.



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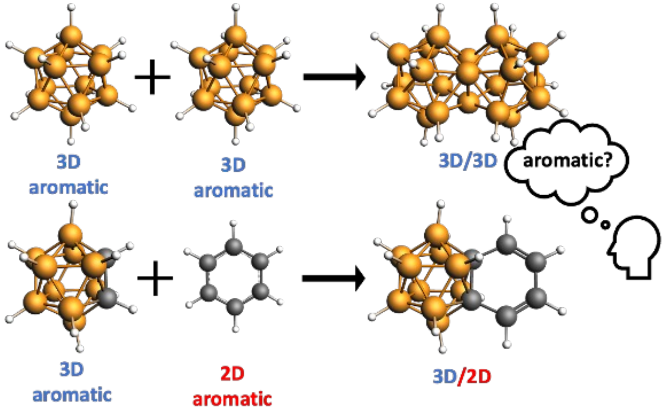
3D and 2D aromatic units behave like oil and water in the case of benzocarborane derivatives

Jordi Poater[1,2], Clara Viñas[3], Miquel Solà[4]✉ & Francesc Teixidor[3]✉

A large number of 2D/2D and 3D/3D aromatic fusions that keep their aromaticity in the fused compounds have been synthesized. In addition, we have previously proven the electronic relationship between the 3D aromaticity of boron hydrides and the 2D aromaticity of PAHs. Here we report the possible existence of 3D/2D aromatic fusions that retain the whole aromaticity of the two units. Our conclusion is that such a 3D/2D aromatic combination is not possible due to the ineffective overlap between the π-MOs of the planar species and the n + 1 molecular orbitals in the aromatic cage that deter an effective electronic delocalization between the two fused units. We have also proven the necessary conditions for 3D/3D fusions to take place, and how aromaticity of each unit is decreased in 2D/2D and 3D/3D fusions.



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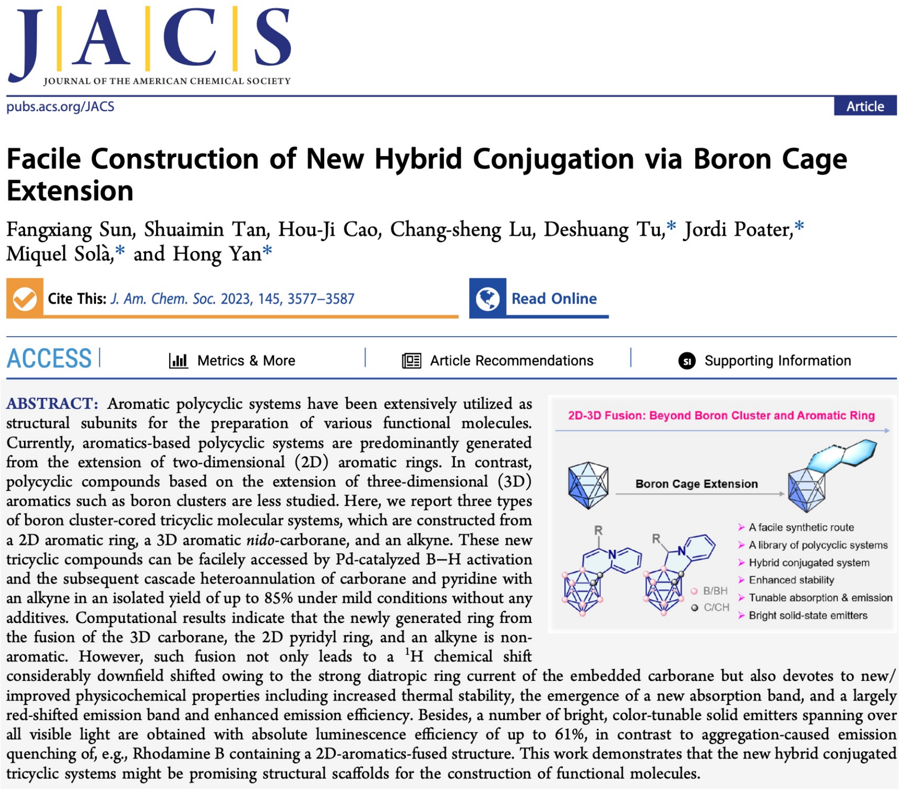

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Facile Construction of New Hybrid Conjugation via Boron Cage Extension

Fangxiang Sun, Shuaimin Tan, Hou-Ji Cao, Chang-sheng Lu, Deshuang Tu,* Jordi Poater,* Miquel Solà,* and Hong Yan*

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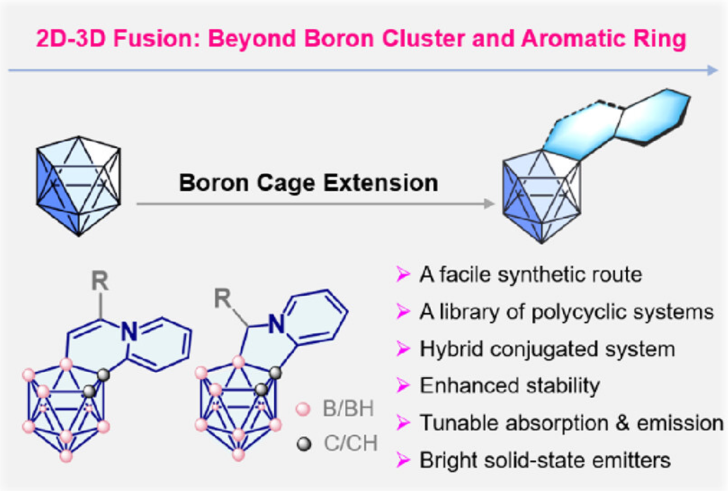
ABSTRACT: Aromatic polycyclic systems have been extensively utilized as structural subunits for the preparation of various functional molecules. Currently, aromatics-based polycyclic systems are predominantly generated from the extension of two-dimensional (2D) aromatic rings. In contrast, polycyclic compounds based on the extension of three-dimensional (3D) aromatics such as boron clusters are less studied. Here, we report three types of boron cluster-cored tricyclic molecular systems, which are constructed from a 2D aromatic ring, a 3D aromatic *nido*-carborane, and an alkyne. These new tricyclic compounds can be facilely accessed by Pd-catalyzed B−H activation and the subsequent cascade heteroannulation of carborane and pyridine with an alkyne in an isolated yield of up to 85% under mild conditions without any additives. Computational results indicate that the newly generated ring from the fusion of the 3D carborane, the 2D pyridyl ring, and an alkyne is non-aromatic. However, such fusion not only leads to a ^{1}H chemical shift considerably downfield shifted owing to the strong diatropic ring current of the embedded carborane but also devotes to new/improved physicochemical properties including increased thermal stability, the emergence of a new absorption band, and a largely red-shifted emission band and enhanced emission efficiency. Besides, a number of bright, color-tunable solid emitters spanning over all visible light are obtained with absolute luminescence efficiency of up to 61%, in contrast to aggregation-caused emission quenching of, e.g., Rhodamine B containing a 2D-aromatics-fused structure. This work demonstrates that the new hybrid conjugated tricyclic systems might be promising structural scaffolds for the construction of functional molecules.



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Hong Yan

The Yan Group @ Nanjing University
The School of Chemistry & Chemical Engineering
Welcome to the wonderful world of carborane!
YAN GROUP

Miquel Solà

iQCC
Institut de Química Computacional i Catàlisi

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