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Supporting Information

Dimerization of Indenocorannulene Radicals:

Imposing Stability through Increasing Strain and Curvature

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I. Materials and Methods

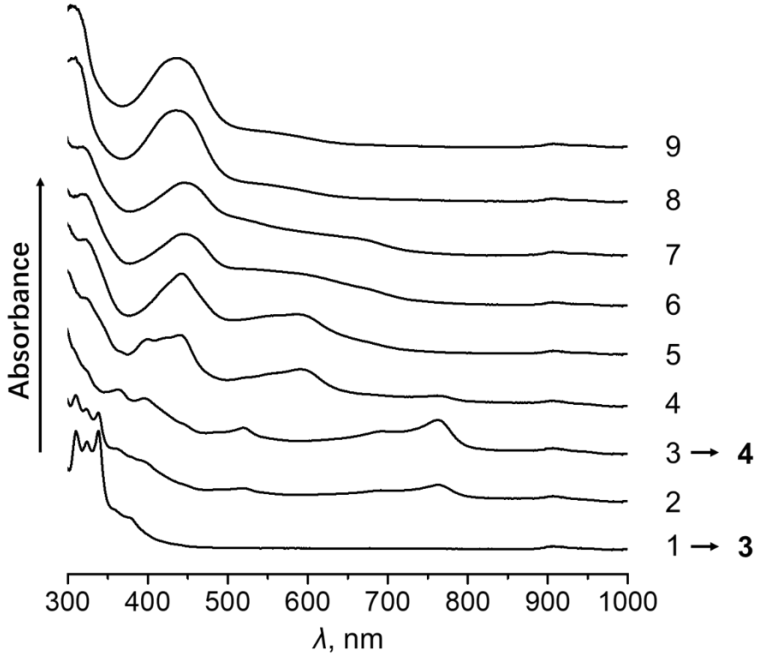
All manipulations were carried out using break-and-seal[1] and glove-box techniques under an atmosphere of argon. Tetrahydrofuran (THF) and hexanes (Sigma Aldrich) were dried over Na/benzophenone and distilled prior to use. THF-d_8 (Sigma Aldrich) was dried over NaK_2 alloy and vacuum-transferred. Rubidium metal (99.6%) and 18-crown-6 ether (99%) were purchased from Sigma Aldrich and used as received. Indenocorannulene ($C_{26}H_{12}$, **3**) was prepared as described previously[2] and sublimed *in vacuo* at 190 °C prior to use. The UV-Vis spectra were recorded on a Thermo Scientific Evolution 201 UV-Visible Spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker Ascend-500 spectrometer and referenced to the resonances of the solvent used. The presence of four loosely bound interstitial THF molecules in **4**·4THF coupled with extreme air- and moisture sensitivity of the crystals prevented obtaining of elemental analysis data.

Crystallization of [{Rb$^+$(18-crown-6)}$_2$($C_{26}H_{12}$–$C_{26}H_{12}$)$^{2-}$]·4THF (4·4THF)

THF (1.5 mL) was added to a customized glass system containing excess Rb (10 eq.), 18-crown-6 ether (1.6 mg, 0.006 mmol), and **3** (2 mg, 0.006 mmol). The mixture was allowed to stir under argon for 1 h at 25 ˚C in a closed system. The initial color of the suspension was yellow (neutral ligand), then it changed to brown after 40 min and remained the same color until the reaction was stopped. The suspension was filtered, the brown filtrate was layered with 1.0 mL of hexanes and placed at 25 °C. Dark brown blocks were present in moderate yield after 4 days. Yield: 4.9 mg, 60%. UV/Vis (THF, nm): λ_{max} 369, 698, 524, 763. ^{1}H NMR (THF-d_8, ppm, 25 ˚C, ($C_{26}H_{12}$–$C_{26}H_{12}$)$^{2-}$): δ = 5.75 (2H), 6.40–6.43 (2H), 6.70–6.74 (2H), 6.94–6.96 (2H), 6.97–6.99 (2H), 7.03 (4H), 7.24–7.31 (4H), 7.5–7.51 (2H), 7.92–7.94 (2H), 7.95 (2H).

UV-Vis Spectroscopic Study

Sample preparation: Rubidium (3 mg, 20 eq.), **3** (0.5 mg, 0.002 mmol, sublimed) and 18-crown-6 ether (0.5 mg, 0.002 mmol) were added into a small storage flask (6.0 mL) in the glove box, followed by the addition of 3.5 mL of anhydrous THF. The UV-Vis spectra of the mixture (0.46 mM in THF) were monitored at different reaction times at room temperature.



Label	Time (min)
1	0
2	4
3	7
4	10
5	14
6	16
7	18
8	24
9	1200

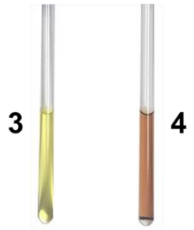
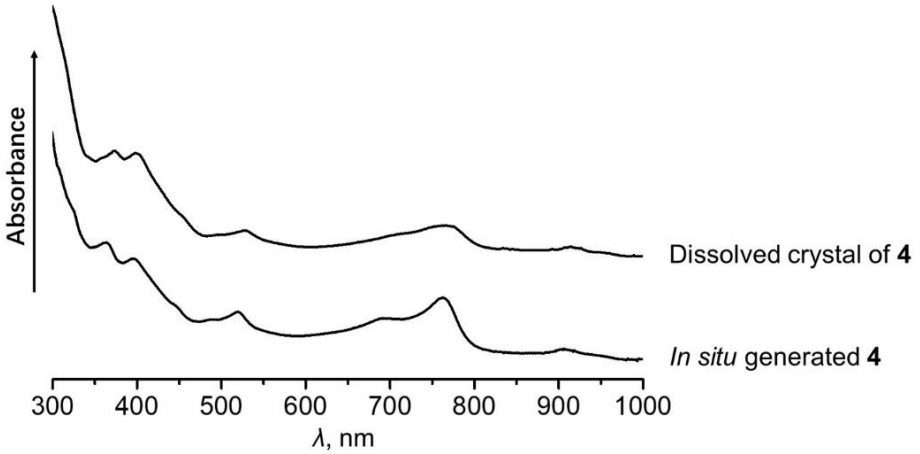


Figure S1. UV-Vis spectra of Rb/18-crown-6/**3** in THF.



Label	**λ_{max} (nm)**
Dissolved crystal	369, 698, 524, 763
In situ generated	367, 396, 521, 764

Figure S2. UV-Vis spectra of *in situ* generated **4** and dissolved crystals of **4**·4THF.

^{1}H NMR Spectroscopic Study

Sample preparation: Crystals of **4** (5 mg, 0.003 mmol) were washed with anhydrous THF (0.5 mL) and anhydrous hexanes several times and dried *in-vacuo*. Crystals were added into an NMR ampule (O.D. 5 mm) in the glove box, followed by the addition of anhydrous THF-d_8 (0.8 mL). A brown solution was obtained. Due to low solubility, some crystals remained at the bottom of the ampule. The NMR tube was sealed under argon.

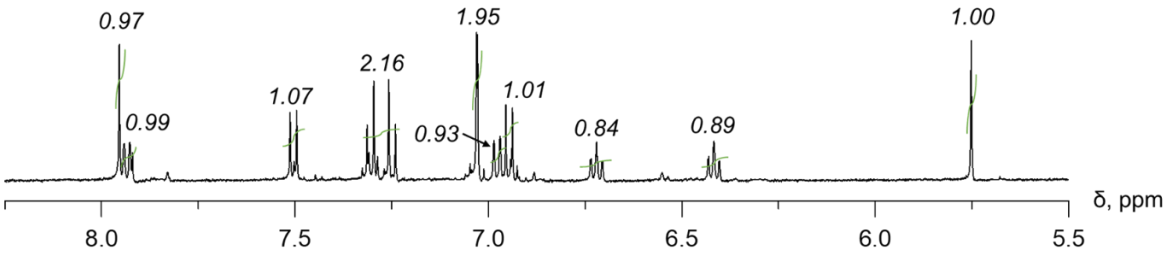


Figure S3. ^{1}H NMR spectrum of **4** in THF-d_8 at 25 ℃ with integrations, aromatic region.

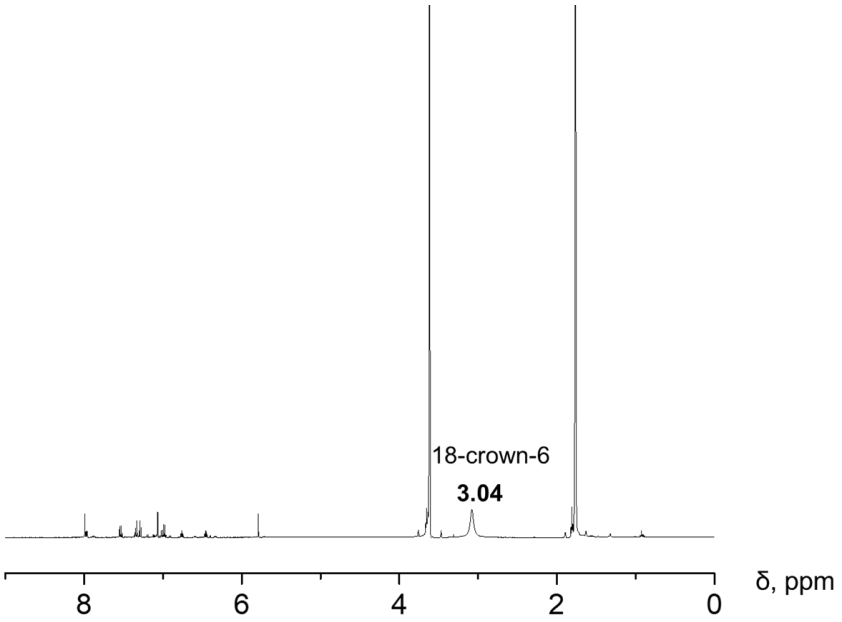


Figure S4. ^{1}H NMR spectrum of **4** in THF-d_8 at 25 ℃.

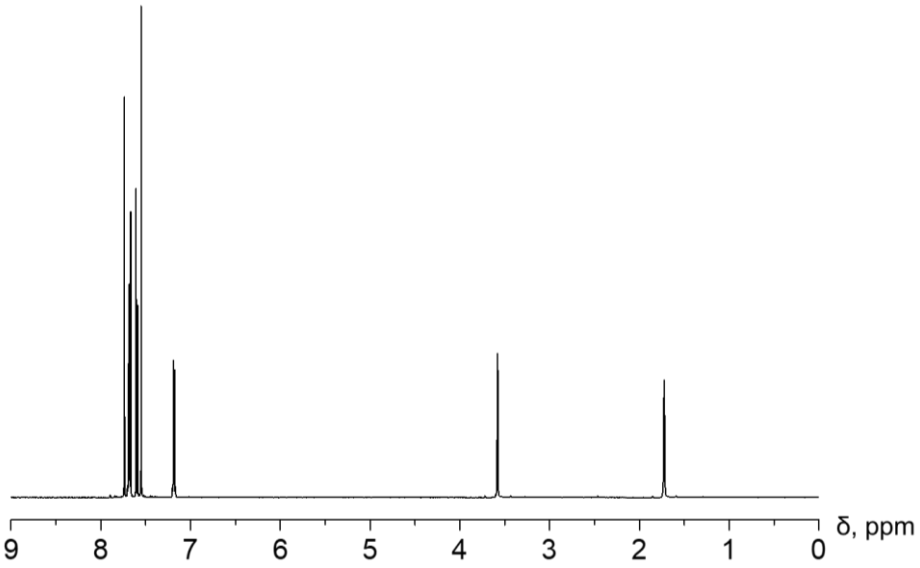


Figure S5. ^{1}H NMR spectrum of **3** in THF-d_8 at 25 ℃.

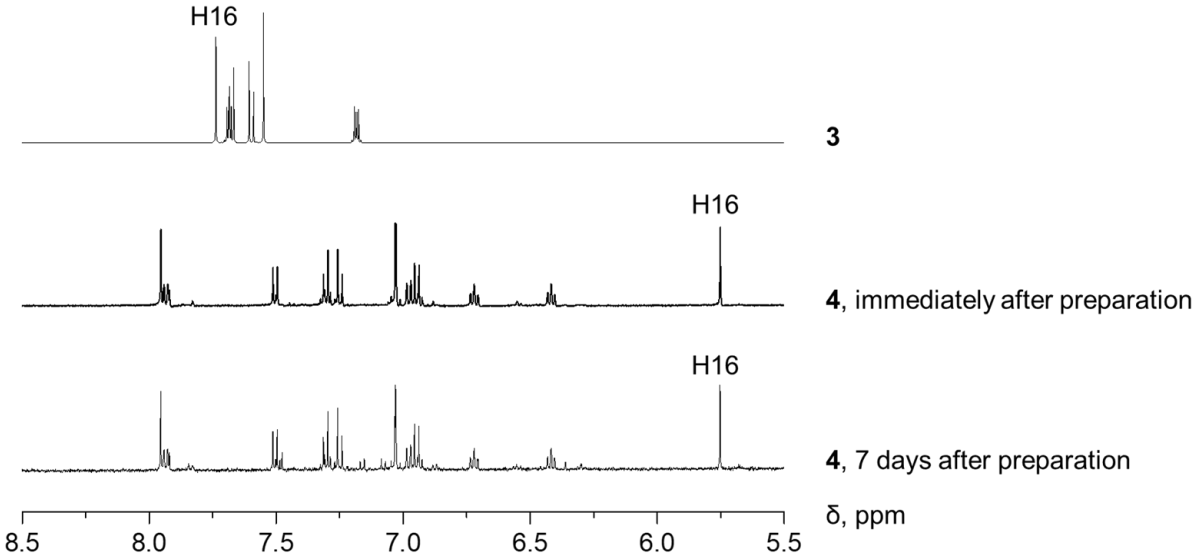


Figure S6. ^{1}H NMR spectra of **3** and **4** at different times in THF-d_8 at 25 ℃, aromatic region.

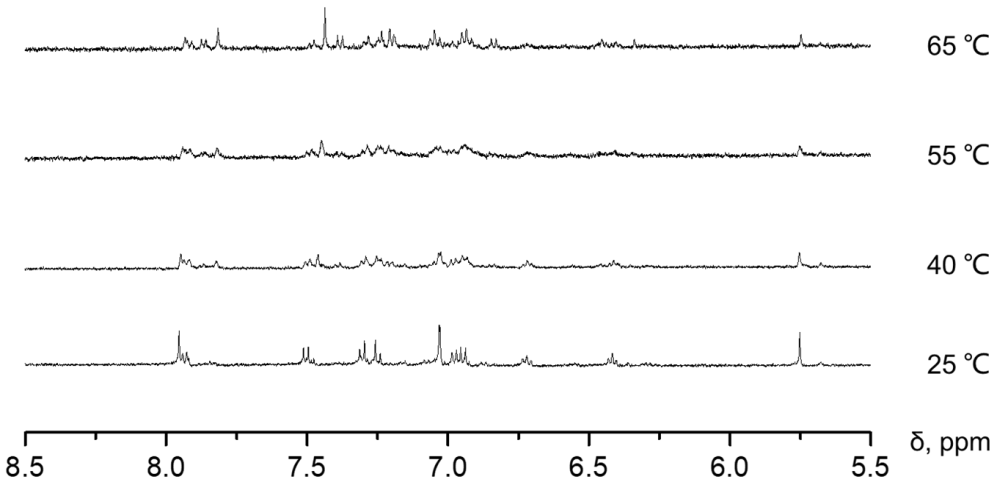


Figure S7. Variable temperature ^{1}H NMR spectra of **4** in THF-d_8, aromatic region.

Sample preparation: THF-d_8 (0.8 mL) was added to an NMR tube (O.D. 5 mm) containing crystals of **4** (5 mg, 0.003 mmol). The NMR tube with a brown solution was sealed under argon. Due to low solubility, some crystals remained at the bottom of the ampule. The solution of **4** was later exposed to air by opening the tube, and its spectrum was recorded as "quenched".

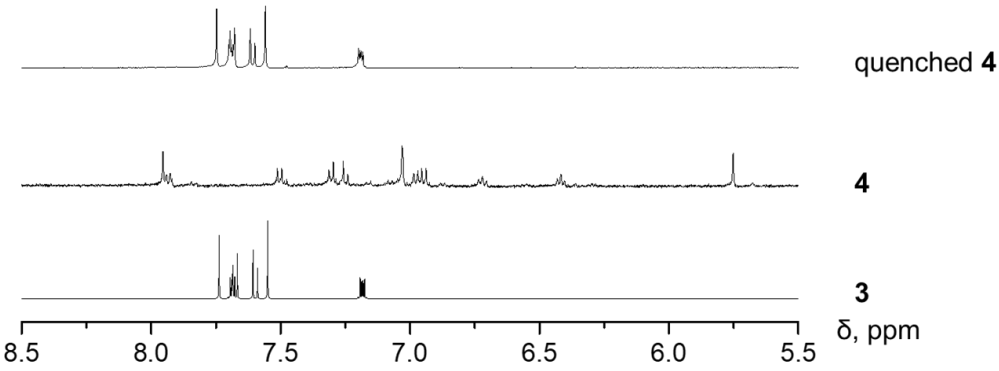


Figure S8. ^{1}H NMR spectra of **3**, **4**, and its quenched product in THF-d_8, aromatic region.

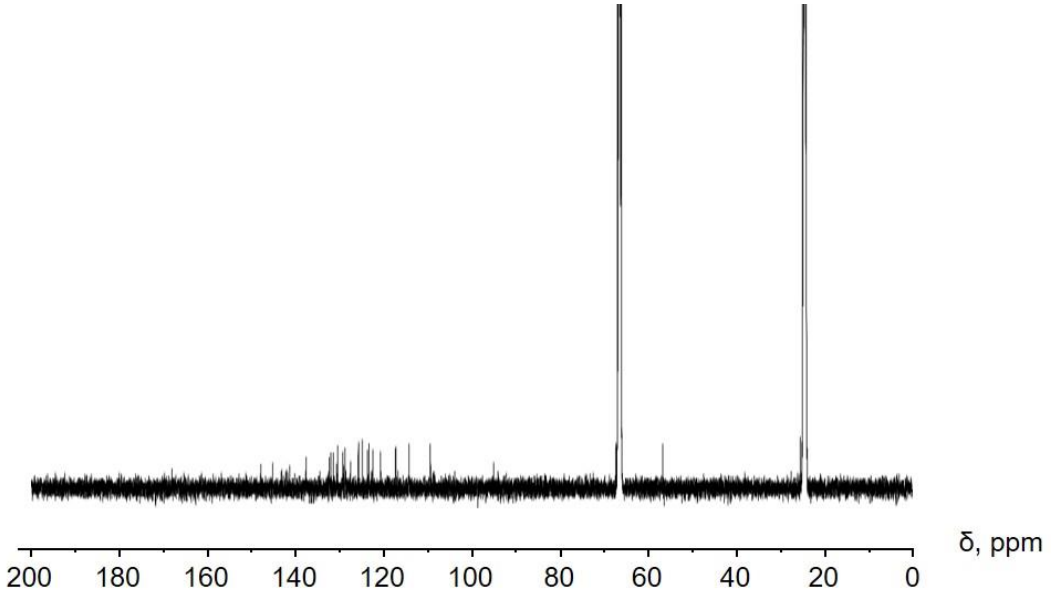


Figure S9. ^{13}C NMR spectrum of *in situ* generated $(C_{26}H_{12}–C_{26}H_{12})^{2–}$ in THF-d_8 at 25 °C.

II. Crystal Structure Solution and Refinement Details

Data collection of **4**·4THF was performed on a Bruker VENTURE system equipped with a PHOTON 100 CMOS detector and a Mo-target fine-focus X-ray source (λ = 0.71073 Å) with a graphite monochromator. The data were collected at 100(2) K crystal temperature (Oxford Cryosystems CRYOSTREAM 700), 50 kV and 30 mA with an appropriate 0.5° ω scan strategy. Data reduction and integration were performed with SAINT (version 8.38A).[3] Data were corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2).[4] The structure was solved by SHELXT (version 2018/2)[5] and refined by full-matrix least-squares procedures using the SHELXL program (version 2018/3)[6] through the OLEX2[7] graphical interface. All non-hydrogen atoms, including those in disordered parts, were refined anisotropically. All H-atoms were included at calculated positions and refined as riders, with U_{iso}(H) = 1.2 U_{eq}(C). In the asymmetric unit, one THF molecule was found to be disordered and modeled with two orientations. The geometries of the disordered parts were restrained to be similar. The anisotropic displacement parameters of the disordered molecules in the direction of the bonds were restrained to be equal with a standard uncertainty of 0.004 Å^2. They were also restrained to have the same U_{ij} components, with a standard uncertainty of 0.01 Å^2. One additional severely disordered THF molecule was removed from the asymmetric unit by the SQUEEZE routine in PLATON (version 190619).[8] The total void volume, corresponding to the squeezed THF molecules, is 1273.2 Å^3, as indicated by PLATON. This is equivalent to 16.25 % of the unit cell's total volume. Further crystal and data collection details are listed in Table S1.

Table S1. Crystallographic data for **4**·4THF.

Compound	**4**·4THF
Empirical formula	$C_{92}H_{104}Rb_2O_{16}$
Formula weight	1636.69
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
a (Å)	27.646(2)
b (Å)	14.0025(11)
c (Å)	24.309(2)
α (°)	90.00
β (°)	123.6520(10)
γ (°)	90.00
V (Å^3)	7833.3(11)
Z	4
ρ_{calcd} (g·cm^{-3})	1.388
μ (mm^{-1})	1.320
F(000)	3432
Crystal size (mm)	0.08×0.06×0.04
θ range for data collection (°)	2.91-25.42
Reflections collected	53718
Independent reflections	7199
	[R_{int} = 0.1045]
Transmission factors (min/max)	0.5486/0.6736
Data/restraints/params.	7199/206/488
*R*1,[a] *wR*2[b] (*I* > 2σ(*I*))	0.0559, 0.0996
*R*1,[a] *wR*2[b] (all data)	0.0907, 0.1112
Quality-of-fit[c]	1.013

[a]$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]$.

[c]Quality-of-fit = $[\Sigma[w(F_o^2-F_c^2)^2]/(N_{obs}-N_{params})]^{½}$, based on all data.

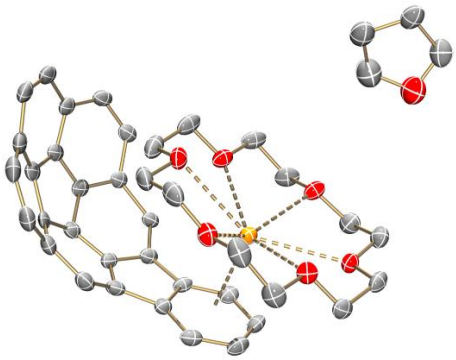


Figure S10. ORTEP drawing of the asymmetric unit of **4**·4THF shown at the 50% probability level. All hydrogen atoms are removed for clarity. Color key: C gray, O red, Rb orange.

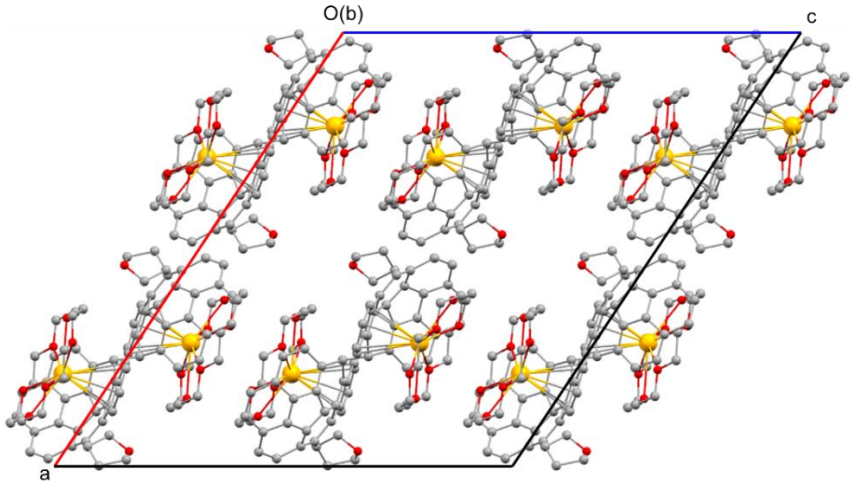
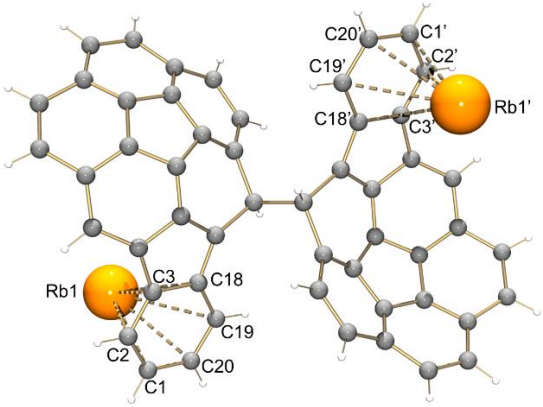


Figure S11. Solid state packing of **4**·4THF in a unit cell, ball-and-stick model. All hydrogen atoms are removed for clarity.



Bond	Distance (Å)
Rb1–C1	3.272(4)
Rb1–C2	3.301(4)
Rb1–C3	3.426(4)
Rb1–C18	3.561(4)
Rb1–C19	3.529(4)
Rb1–C20	3.370(4)

Figure S12. Metal coordination in **4**, ball-and-stick model.

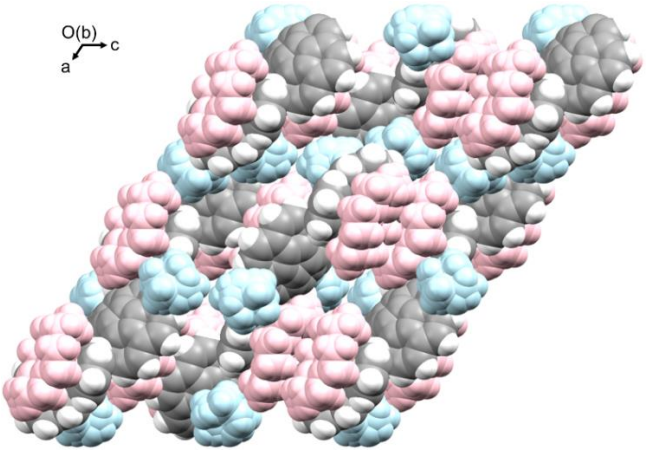
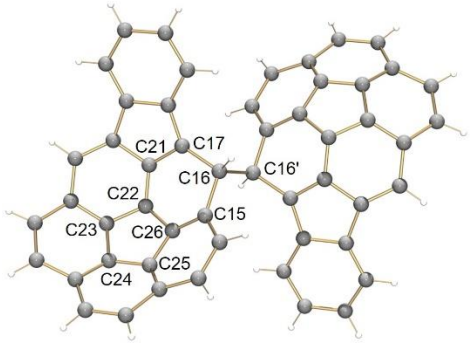


Figure S13. Solid state packing of **4**·4THF, space-filling model. Cationic {Rb^{+}(18-crown-6)} moieties are light pink and THF molecules are light blue.

Table S2. Average p-orbital axis vector (POAV) angles (°)* in $C_{26}H_{12}$ and $[\sigma\text{-}(C_{26}H_{12})_2]^{2-}$.



POAV	$C_{26}H_{12}$[2]	$[\sigma\text{-}(C_{26}H_{12})_2]^{2-}$	POAV	$C_{26}H_{12}$[2]	$[\sigma\text{-}(C_{26}H_{12})_2]^{2-}$
C1	0.361	0.000	C14	1.347	0.000
C2	0.000	0.000	C15	4.696	2.290
C3	0.203	1.142	C16	3.440	18.310
C4	5.002	5.891	C17	4.971	3.511
C5	3.234	0.000	C18	0.154	0.393
C6	5.241	6.352	C19	0.403	0.000
C7	0.000	0.000	C20	0.605	0.000
C8	2.352	0.000	C21	6.681	6.544
C9	4.171	3.913	C22	11.149	13.244
C10	2.246	0.000	C23	9.825	9.342
C11	2.160	0.000	C24	8.909	8.042
C12	4.250	3.974	C25	8.755	7.827
C13	2.418	0.000	C26	10.045	8.821

* POAV angles are calculated using reference.[9]

Table S3. Key distances (Å) and angles (°) in $[\sigma\text{-}(C_{20}H_{10})_2]^{2-}$, $[\sigma\text{-}(C_{28}H_{14})_2]^{2-}$, and $[\sigma\text{-}(C_{26}H_{12})_2]^{2-}$ in comparison to their neutral parents.

		$C_{20}H_{10}$[10][12]	$C_{28}H_{14}$[11][13]	$C_{26}H_{12}$[2][this work]
Bond length on C16 (ave.)	Neutral	1.413(2)	1.415(2)	1.418(4)
	Dimer	1.554(5)	1.538(8)	1.556(7)
Bond angle on C16 (ave.)	Neutral	122.0(2)	121.8(2)	120.3(4)
	Dimer	111.1(1)	110.4(1)	109.5(3)
Bowl depth	Neutral	0.875(2)	0.830(2)	1.065(4)
	Dimer	0.906(5)	0.891(9)	1.029(5)
Bowl depth difference		0.031	0.061	–0.036

* Data are taken from the corresponding references for $C_{20}H_{10}$,[10] $C_{28}H_{14}$,[11] $C_{26}H_{12}$,[2] $[\sigma\text{-}(C_{20}H_{10})_2]^{2-}$ [12] and $[\sigma\text{-}(C_{28}H_{14})_2]^{2-}$.[13]

III. Calculation Details

All geometry optimizations were performed at the density functional theory level with the help of hybrid correlation-exchange functional PBE0.[14] All light atoms (C, H, O) were described by correlation-consistent basis sets of double-ζ quality (cc-pVDZ), whereas a triple-ζ def2-TZVP one was used for rubidium (accompanied by effective core potential). No symmetry restrictions were applied. Calculated structures were found to be local minima (no imaginary frequencies) on the corresponding potential energy surfaces, as determined by calculation of the full Hessian matrix, followed by estimation of frequencies in the harmonic approximation. In order to get better description of energetics and electronic structure, all optimized geometries were then used in single-point calculations at the PBE0/cc-pVTZ(C,H,O)//def2-TZVP(Rb) level. Previously, this combination of techniques was found to provide accurate results as tested against those obtained by geometry optimization with the triple-ζ basis sets applied to all atoms. All calculations were performed using the Firefly program (version 8.2.0).[15]

Converged PBE0/cc-pVTZ(C,H,O)//def2-TZVP(Rb) wavefunctions were then used to get insights into the electronic structure of target systems in terms of natural bond orbitals (NBO).[16] Bond orders quoted are those from the Wiberg formulation[17] (Wiberg bond indices) incorporated in the NBO analysis. All computations were performed with the NBO[18] (version 6.0) program.

Fully relaxed potential energy surface (PES) scans were performed using two-step procedure similar to what was used for geometry optimization. All geometrical changes/optimizations were done at the PBE0/SVP/ZORA level of theory. These geometry configurations were then used in a series of single-point calculations with help of the PBE0/TZVP/ZORA method. PES scans were performed for the C–C′ bond breaking process for the range of bond distances from 1.50 Å to 3.50 Å with step of 0.02 Å. Both spin-states, singlet and triplet, were considered. Chain-of-sphere approximation[19] (RIJCOSX in ORCA terminology) was used to accelerate computations. These calculations were carried out with help of the ORCA program suit.[20]

Energy Decomposition Analysis (EDA)

The nature of the bonding between two indenocorannulene fragments, with and without counterions, was investigated with help of the energy decomposition analysis (EDA) developed by Morokuma and by Ziegler and Rauk.[21] Single-point calculations were performed by the ADF program package[22] with the same functional (PBE0). All atoms were described by full-electron uncontracted Slater-type orbitals (STOs) with TZ2P quality as basis set functions. An auxiliary set of s, p, d, and f STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle. Scalar relativistic effects have been taken into account by applying ZORA approximation.[23] Further details on the EDA can be found in literature.[24]

Throughout our papers we use bond dissociation energy, D_e, as an indicator of stability (PAH = polycyclic aromatic hydrocarbon):

$$-D_e = E((PAH)_2^{2-}) - 2\times E(PAH^-)$$

or, in presence of counterion:

$$-D_e = E([(Rb^+)_2\cdot\{(PAH)_2^{2-}\}]) - 2\times E([(Rb^+)\cdot(PAH^-)]).$$

D_e is a positive quantity, when the target dimeric system is more stable than the fragments.

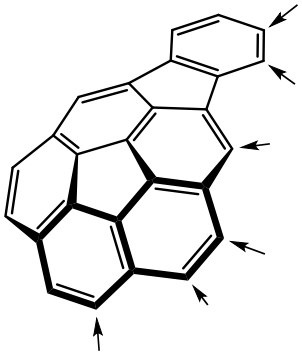


Figure S14. All tested sites of potential C–C coupling in the indenocorannulene core.

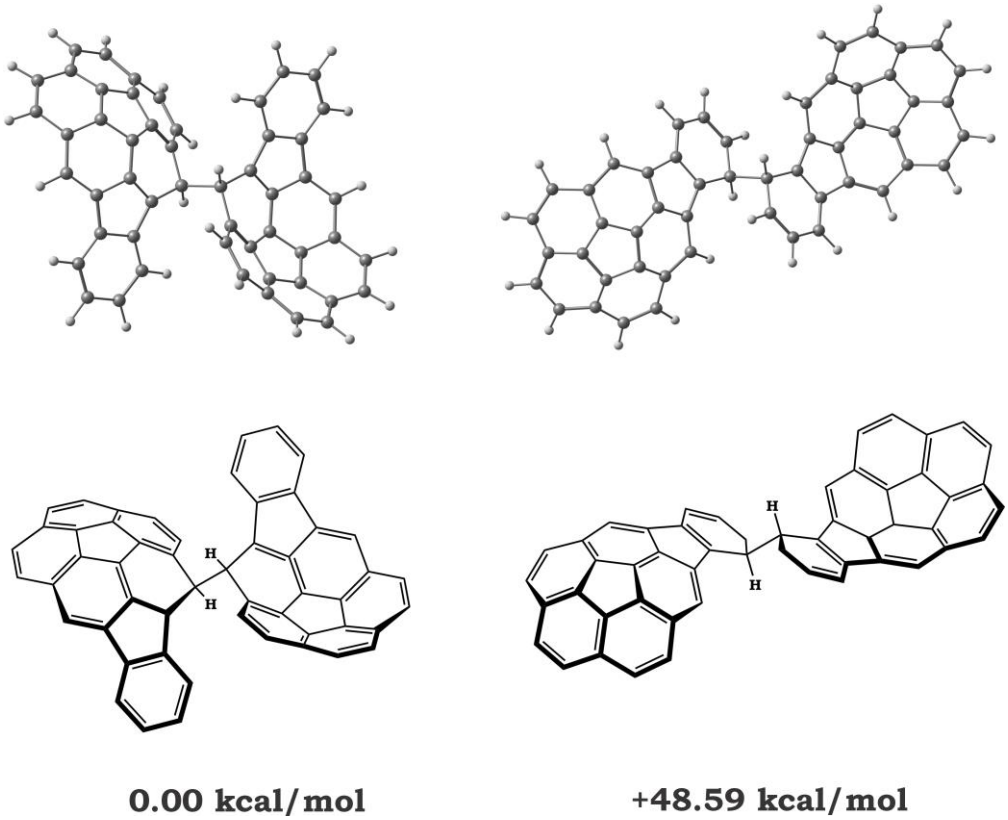


Figure S15. Two converged isomers of [σ-$(C_{26}H_{12})_2^{2-}$].

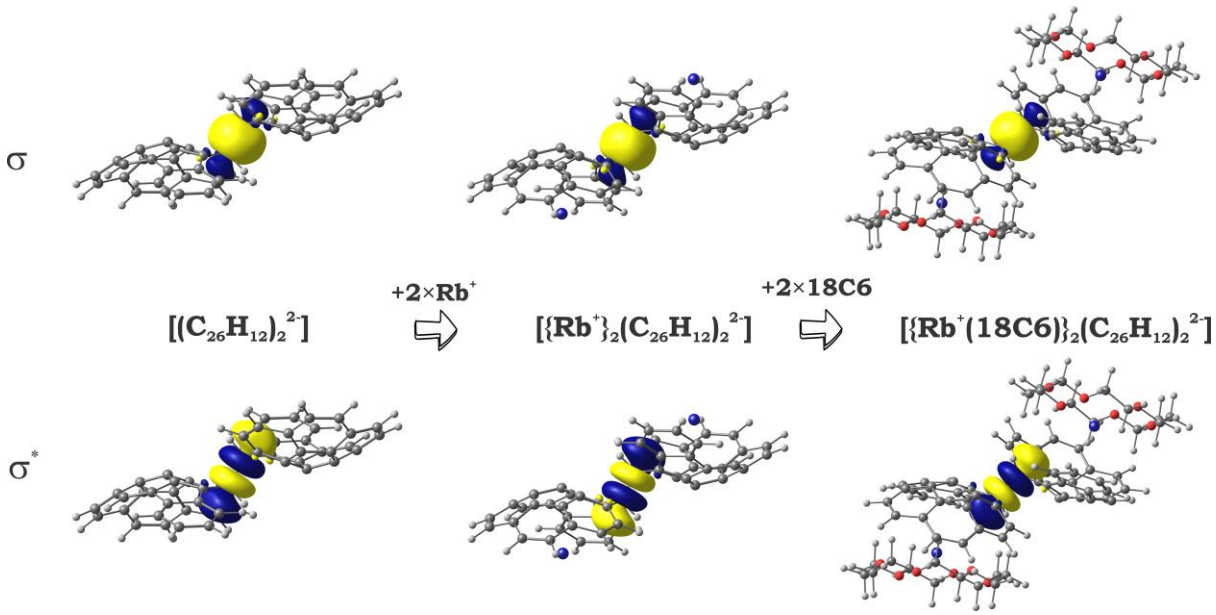


Figure S16. NBO representation of bonding between two indenocorannulene bowls in [(σ-$C_{26}H_{12})_2^{2-}$], [{Rb^+}$_2$(σ-$C_{26}H_{12})_2^{2-}$], and [{Rb^+(18C6)}$_2$(-$C_{26}H_{12})_2^{2-}$].

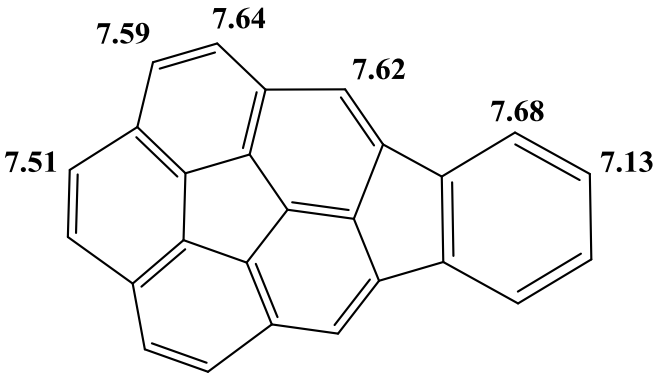


Figure S17. ^{1}H NMR spectrum of $C_{26}H_{12}$ (PBE0/TZ2P/ZORA; ppm)

Note: Due to symmetry, the chemical shifts for only unique atoms are shown.

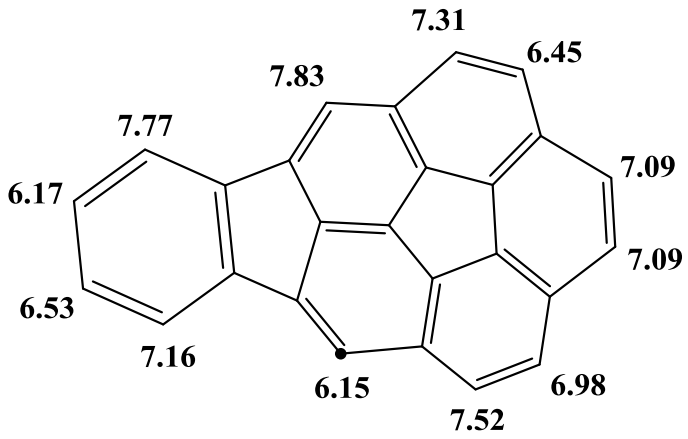


Figure S18. ^{1}H NMR spectrum of the $[C_{26}H_{12}]_2^{2-}$ anion (PBE0/TZ2P/ZORA; ppm)

Note: *Bold dot designates the carbon atom of attachment.*

TD-DFT modeling of UV-Vis spectra of $C_{26}H_{12}$ and $[C_{26}H_{12}]_2^{2-}$

Calculation details

TD-DFT calculations were performed using the same functional PBE0. All atoms were described by def2-TZVP basis sets of triple-z quality (+ECP for Rb). In order to cover an experimental range, 20 or 30 singlet excited states were considered. Solvent (THF) was accounted using CPCM (Conductor-like Polarizable Continuum Model) method. All calculations were carried out with help of ORCA program suite.

Results

Label	**λ_{max} (nm)**
Exp.	
Dissolved crystal	369, 398, 524, 763
In situ generated	367, 396, 521, 764
Calc.	
$[\{Rb^+(18\text{-crown-6})\}_2(C_{26}H_{12}–C_{26}H_{12})^{2-}]$	364, 396, 494, 581, 761
$(C_{26}H_{12}–C_{26}H_{12})^{2-}$	441, 519, 601, 799

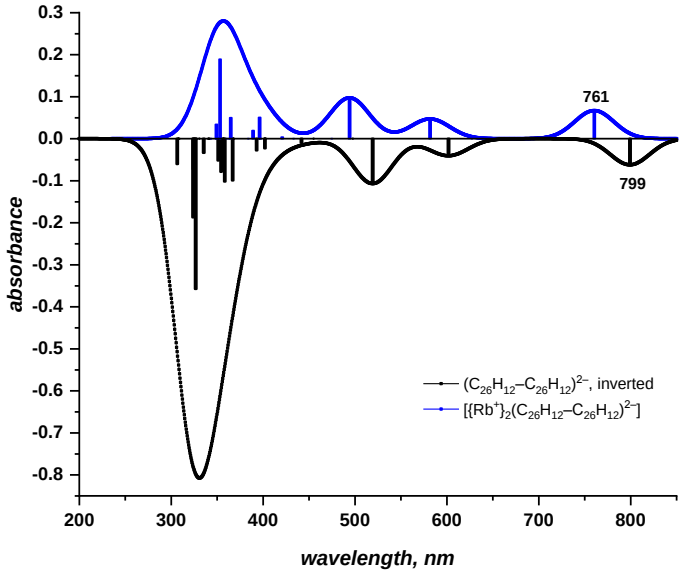


Figure S19. UV-Vis spectra calculated for $[\{Rb^+(18\text{-crown-6})\}_2(C_{26}H_{12}–C_{26}H_{12})^{2-}]$ and $(C_{26}H_{12}–C_{26}H_{12})^{2-}$ at PBE0/def2-TZVP/CPCM(THF) level of theory.

Note: the characteristic band at 761 nm can be indicative of the formation of a contact-ion pair. Coordination of Rb^+ by the indenocorannulene moiety significantly shifts this band from 799 nm to 761 nm (Fig. S20). At the same time, such band is absent in the spectrum of neutral $C_{26}H_{12}$ parent (Fig. S21). The latter can be explained when considering the nature of the transition (see below).

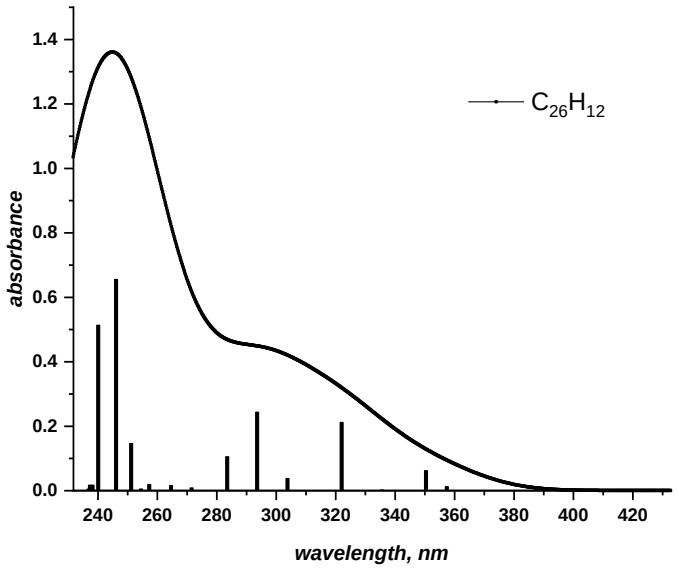


Figure S20. UV-Vis spectrum calculated for $C_{26}H_{12}$ at PBE0/def2-TZVP/CPCM(THF) level of theory.

Nature of transitions in [{Rb$^+$(18-crown-6)}$_2$($C_{26}H_{12}$–$C_{26}H_{12}$)$^{2-}$]

761 nm

HOMO → LUMO

Contributes 95%.

581 nm

HOMO-1 → LUMO+1

Contributes 95%

494 nm

HOMO → LUMO+2

Contributes 90%

HOMO-2 → LUMO+3

Contributes 5.7%

396 nm

HOMO-3 → LUMO

Contributes 44%

HOMO-2 → LUMO+1

Contributes 13%

HOMO → LUMO+6

Contributes 19%

364 nm

HOMO-3 → LUMO

Contributes 40%

HOMO-2 → LUMO+1

Contributes 36%

HOMO → LUMO+6

Contributes 20%

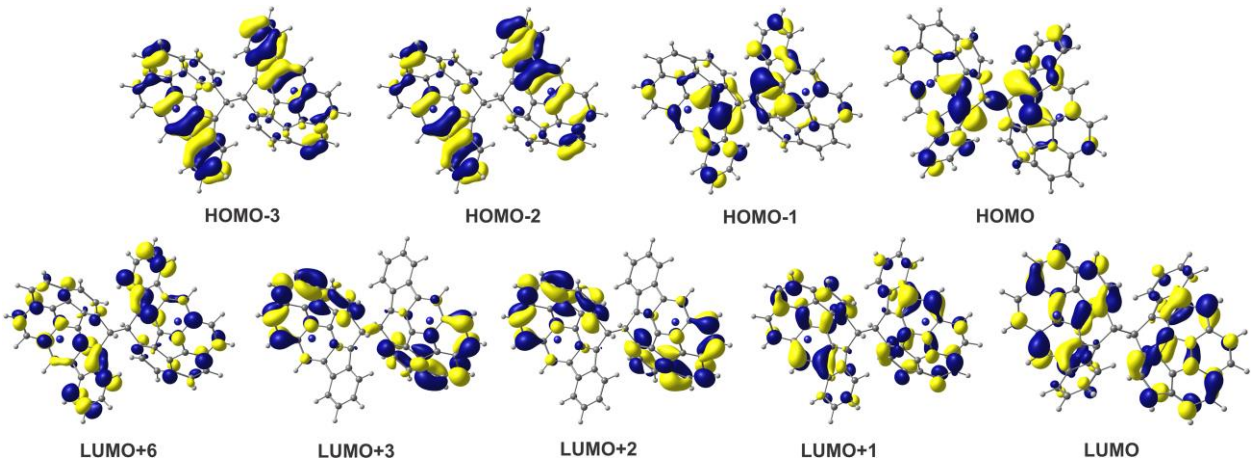


Figure S21. Active MOs in [{Rb$^+$(18-crown-6)}$_2$($C_{26}H_{12}$–$C_{26}H_{12}$)$^{2-}$] (PBE0/def2-TZVP/CPCM(THF)).

Nature of transitions in $(C_{26}H_{12}–C_{26}H_{12})^{2–}$

799 nm

HOMO → LUMO

Contributes 96%

601 nm

HOMO-1 → LUMO+1

Contributes 95%

519 nm

HOMO-1 → LUMO

Contributes 4.9%

HOMO → LUMO+2

Contributes 90%

441 nm

HOMO-1 → LUMO+3

Contributes 89%

HOMO → LUMO+2

Contributes 5.9%

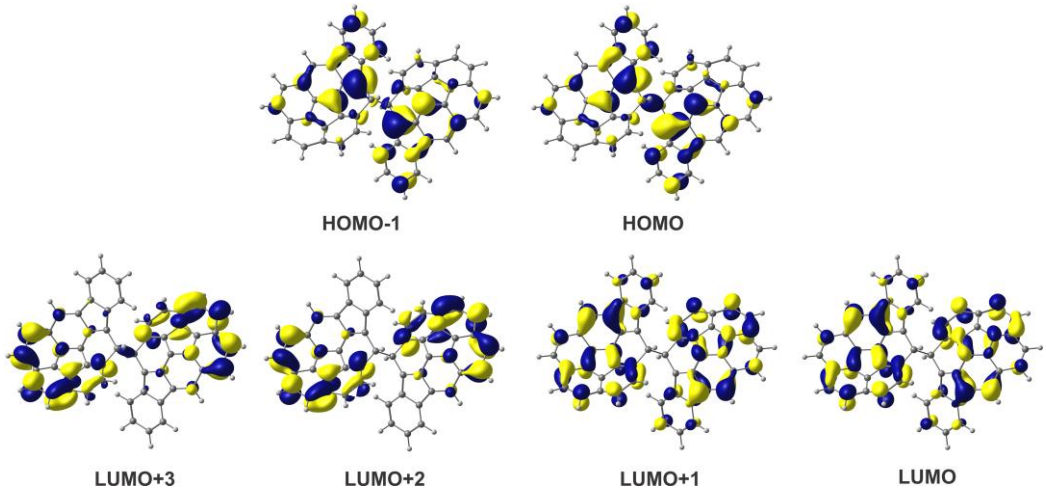


Figure S22. Active MOs in $(C_{26}H_{12}–C_{26}H_{12})^{2–}$ (PBE0/def2-TZVP/CPCM(THF)).

Nature of transitions in neutral $C_{26}H_{12}$

357 nm

HOMO-4 → LUMO

Contributes 1.7%

HOMO-3 → LUMO

Contributes 68%

HOMO-2 → LUMO+1

Contributes 26%

322 nm

HOMO-3 → LUMO+1

Contributes 13%

HOMO-2 → LUMO

Contributes 36%

HOMO → LUMO+1

Contributes 38%

350 nm

HOMO-2 → LUMO

Contributes 11%

HOMO-1 → LUMO

Contributes 76%

HOMO → LUMO+2

Contributes 4.6%

303 nm

HOMO-4 → LUMO

Contributes 31%

HOMO-2 → LUMO+1

Contributes 39%

HOMO-1 → LUMO+1

Contributes 17%

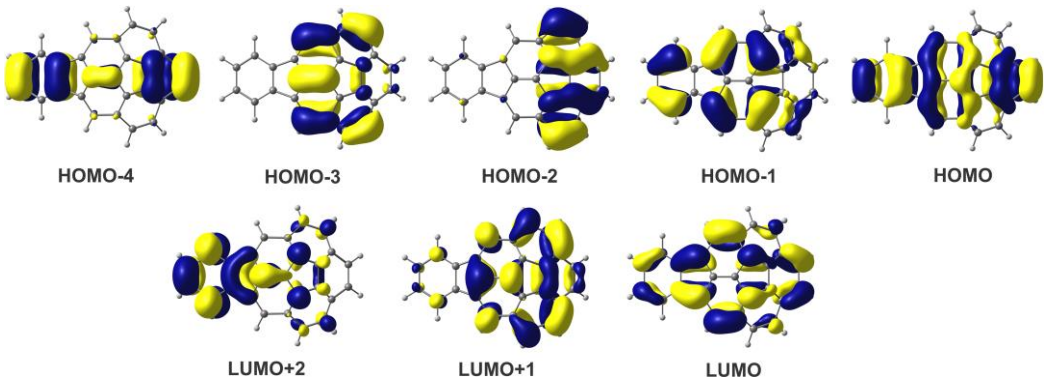


Figure S23. Active MOs in neutral $C_{26}H_{12}$ (PBE0/def2-TZVP/CPCM(THF)).

Table S4. Cartesian coordinates of $[C_{26}H_{12}]_2^{2-}$.

Symbol	X	Y	Z
C	1.713323000	-5.554363000	-1.177699000
H	1.849092000	-6.611593000	-1.422050000
C	2.658685000	-4.885285000	-0.397376000
H	3.546465000	-5.414543000	-0.034760000
C	2.478574000	-3.540546000	-0.082276000
C	3.326318000	-2.581771000	0.618393000
C	4.698087000	-2.513976000	0.852637000
H	5.320919000	-3.400323000	0.682140000
C	5.353949000	-1.245801000	1.055712000
C	6.728304000	-0.952174000	0.760897000
H	7.450727000	-1.777091000	0.746202000
C	7.165530000	0.302860000	0.347876000
H	8.211241000	0.423837000	0.046599000
C	6.231741000	1.379467000	0.134372000
C	6.349495000	2.518373000	-0.748097000
H	7.341475000	2.812579000	-1.108816000
C	5.241879000	3.171412000	-1.260895000
H	5.398057000	3.956882000	-2.008194000
C	3.895583000	2.755788000	-0.941716000
C	2.697566000	2.912506000	-1.700412000
H	2.657970000	3.644620000	-2.512966000
C	1.608484000	2.050626000	-1.522834000
H	0.758760000	2.144854000	-2.204644000
C	1.587545000	1.008440000	-0.553051000
C	0.598052000	-0.176241000	-0.480934000
H	0.149241000	-0.309272000	-1.480879000
C	1.349590000	-1.457074000	-0.087972000
C	1.302197000	-2.823038000	-0.546108000
C	0.371284000	-3.521365000	-1.339343000
H	-0.528531000	-3.012661000	-1.693469000
C	0.582551000	-4.862400000	-1.643690000
H	-0.157850000	-5.392779000	-2.250929000
C	2.521464000	-1.371624000	0.656147000
C	3.124587000	-0.168982000	1.009849000
C	4.514608000	-0.111024000	1.133052000
C	4.947669000	1.148164000	0.606938000
C	3.812028000	1.821829000	0.089587000
C	2.676908000	0.999853000	0.305876000
C	-1.713344000	5.554363000	1.177689000
H	-1.849090000	6.611588000	1.422053000
C	-2.658689000	4.885311000	0.397384000

H	-3.546447000	5.414533000	0.034768000
C	-2.478576000	3.540548000	0.082277000
C	-3.326318000	2.581764000	-0.618396000
C	-4.698090000	2.513976000	-0.852637000
H	-5.320917000	3.400325000	-0.682140000
C	-5.353953000	1.245790000	-1.055711000
C	-6.728287000	0.952198000	-0.760906000
H	-7.450729000	1.777093000	-0.746203000
C	-7.165538000	-0.302874000	-0.347872000
H	-8.211241000	-0.423834000	-0.046604000
C	-6.231724000	-1.379464000	-0.134381000
C	-6.349498000	-2.518375000	0.748096000
H	-7.341476000	-2.812577000	1.108811000
C	-5.241882000	-3.171400000	1.260879000
H	-5.398061000	-3.956889000	2.008197000
C	-3.895592000	-2.755796000	0.941720000
C	-2.697552000	-2.912505000	1.700418000
H	-2.657975000	-3.644618000	2.512959000
C	-1.608503000	-2.050632000	1.522827000
H	-0.758757000	-2.144857000	2.204649000
C	-1.587545000	-1.008445000	0.553058000
C	-0.598053000	0.176244000	0.480932000
H	-0.149243000	0.309269000	1.480883000
C	-1.349596000	1.457068000	0.087967000
C	-1.302173000	2.823043000	0.546126000
C	-0.371292000	3.521358000	1.339339000
H	0.528529000	3.012660000	1.693472000
C	-0.582541000	4.862382000	1.643694000
H	0.157856000	5.392779000	2.250938000
C	-2.521453000	1.371639000	-0.656138000
C	-3.124601000	0.168965000	-1.009850000
C	-4.514593000	0.111048000	-1.133057000
C	-4.947698000	-1.148170000	-0.606932000
C	-3.812018000	-1.821825000	-0.089593000
C	-2.676908000	-0.999846000	-0.305880000

Table S5. Cartesian coordinates of $[(Rb)_2(C_{26}H_{12})_2]$.

Symbol	X	Y	Z
Rb	-4.312714173	0.426889798	1.097545867
C	-3.920275066	-4.375705383	-0.849700635
H	-4.504310580	-5.288460171	-0.982578596
C	-4.290232987	-3.208016104	-1.514278878
H	-5.167984557	-3.201861556	-2.166716278

C	-3.531307209	-2.047705783	-1.348863074
C	-3.728769310	-0.677073348	-1.819231766
C	-4.873275361	0.028984495	-2.190219960
H	-5.791565707	-0.516291131	-2.434871827
C	-4.954536457	1.457350749	-2.000471254
C	-6.173794400	2.190835184	-1.783408104
H	-7.109782258	1.786221317	-2.182059441
C	-6.238737364	3.321191348	-0.977850885
H	-7.212797640	3.779071992	-0.787070841
C	-5.076491397	3.789545925	-0.268730718
C	-5.029897008	4.542739904	0.965138540
H	-5.914670120	5.103064010	1.281059089
C	-3.945211015	4.481158384	1.819637687
H	-4.006173629	4.992621468	2.784493579
C	-2.790530514	3.661550052	1.522947993
C	-1.875047339	3.056247912	2.434956446
H	-1.815907861	3.413944135	3.466462644
C	-1.133321886	1.923395391	2.071610508
H	-0.524686295	1.436582258	2.839055202
C	-1.193038602	1.339473256	0.774386028
C	-0.690078558	-0.058109710	0.364531822
H	-0.505700184	-0.650274387	1.277138560
C	-1.757985441	-0.734556625	-0.494991523
C	-2.353371166	-2.054213020	-0.506254207
C	-2.008866769	-3.244633220	0.158879357
H	-1.118586829	-3.280216744	0.791435920
C	-2.789337152	-4.383056358	-0.017416712
H	-2.506535339	-5.307598291	0.492039747
C	-2.552797382	0.037497177	-1.339591952
C	-2.572164403	1.436405406	-1.300921487
C	-3.778710382	2.106967932	-1.557509533
C	-3.871227945	3.211998570	-0.648645873
C	-2.750137479	3.157148003	0.221761148
C	-1.944910549	2.049533534	-0.160169288
C	3.921644250	4.375401827	0.850933830
H	4.505884828	5.287977417	0.984089520
C	4.291110819	3.207489546	1.515299769
H	5.168762672	3.200942792	2.167924934
C	3.531932717	2.047414796	1.349526685
C	3.728896200	0.676636906	1.819576666
C	4.873267566	-0.029833946	2.190533516
H	5.791615108	0.515135750	2.435416978
C	4.954089820	-1.458185043	2.000395218
C	6.173229233	-2.191874158	1.783251765

H	7.109278143	-1.787616840	2.182016055
C	6.237920573	-3.322115506	0.977376764
H	7.211877980	-3.780142122	0.786555359
C	5.075609897	-3.789986355	0.268137526
C	5.028868539	-4.542934486	-0.965910719
H	5.913520100	-5.103428261	-1.281884932
C	3.944254905	-4.480903595	-1.820451396
H	4.005129352	-4.992205786	-2.785395452
C	2.789788588	-3.661040629	-1.523675052
C	1.874520489	-3.055281942	-2.435622606
H	1.815326378	-3.412790498	-3.467192831
C	1.133135747	-1.922292197	-2.072106000
H	0.524673970	-1.435142537	-2.839490458
C	1.192933277	-1.338638419	-0.774765094
C	0.690289523	0.058966871	-0.364603873
H	0.506025306	0.651374638	-1.277068719
C	1.758323910	0.734945877	0.495130069
C	2.354080770	2.054459098	0.506719114
C	2.010089033	3.245073754	-0.158229672
H	1.119927865	3.281047608	-0.790977700
C	2.790830790	4.383239587	0.018387942
H	2.508431974	5.307956798	-0.490947468
C	2.552839343	-0.037494499	1.339650643
C	2.571813688	-1.436423236	1.300641234
C	3.778210488	-2.107351774	1.557215709
C	3.870452335	-3.212227230	0.648074783
C	2.749448894	-3.156871090	-0.222384941
C	1.944521755	-2.049120014	0.159709265
Rb	4.312906796	-0.426808161	-1.097384581

Table S6. Cartesian coordinates of $[(Rb)_2(18C6)_2(C_{26}H_{12})_2]$.

Symbol	X	Y	Z
Rb	5.360655666	-0.698878646	-0.251085695
O	7.812796411	0.799793955	0.496459984
O	8.069445966	-2.027395872	0.273188764
O	5.946094217	-3.593734688	-0.782606148
O	4.228605594	-2.293385409	-2.611688715
O	3.884955050	0.493908645	-2.442548335
O	6.000991751	2.012965926	-1.313128006
C	4.818024911	-1.806104378	2.992044400
H	5.591735186	-2.362723501	3.526391508
C	4.711582658	-0.419985131	3.152534335
H	5.421905600	0.113249851	3.791794586

C	3.693814224	0.284921976	2.511771355
C	3.382063393	1.708194342	2.452268641
C	4.129078004	2.877671503	2.636440631
H	5.116656574	2.822226281	3.108644488
C	3.727379730	4.113789264	2.018778039
C	4.589046620	5.207768156	1.647478710
H	5.538862620	5.337317508	2.177877171
C	4.333067243	6.033279249	0.560038314
H	5.075649453	6.788622716	0.287268109
C	3.189410437	5.816713046	-0.294260790
C	3.004093703	6.185528488	-1.679923127
H	3.641772408	6.960602783	-2.115968154
C	2.122308440	5.514682292	-2.510857298
H	2.096634836	5.784733923	-3.570924262
C	1.334512150	4.397252059	-2.041382131
C	0.792720421	3.295817423	-2.773641308
H	0.680432552	3.363769739	-3.859904627
C	0.523974179	2.070820971	-2.149212533
H	0.210469479	1.231299851	-2.776190605
C	0.707175466	1.850774347	-0.751732373
C	0.762450177	0.488754570	-0.020751615
H	1.080262535	-0.271628107	-0.756229625
C	1.785410986	0.528392987	1.125543101
C	2.721350482	-0.413546911	1.669347628
C	2.859022653	-1.814563195	1.529106177
H	2.129948553	-2.375998692	0.939893951
C	3.885522869	-2.487584736	2.186048244
H	3.957730882	-3.573822875	2.083112314
C	2.154892975	1.753402467	1.685880725
C	1.676723731	2.973954079	1.242987975
C	2.483526433	4.107268995	1.352698222
C	2.263218080	4.906465148	0.188065342
C	1.361962305	4.214241710	-0.661564147
C	1.016104963	2.991981158	-0.031588411
C	9.015629020	0.107004317	0.722022193
H	9.649151840	0.651197057	1.450443382
H	9.588843922	0.008688128	-0.221193199
C	8.710038077	-1.262401010	1.269970487
H	9.659761358	-1.745078993	1.575758391
H	8.065828395	-1.174970940	2.166710069
C	7.801535235	-3.348864427	0.687626789
H	7.099108872	-3.350709081	1.543433359
H	8.736843455	-3.850238292	1.007267060
C	7.210963283	-4.119721066	-0.463611975

H	7.886722145	-4.056789935	-1.339508149
H	7.127916134	-5.186001069	-0.172890857
C	5.337307717	-4.256486291	-1.868014733
H	5.172927696	-5.325172040	-1.626708276
H	5.989720079	-4.203098858	-2.761615132
C	4.009766842	-3.613590742	-2.170531035
H	3.499755047	-4.208009344	-2.954221209
H	3.366996487	-3.624269961	-1.269058616
C	3.036957667	-1.652335318	-3.023388352
H	2.312021406	-1.607607882	-2.188564765
H	2.561620281	-2.216916324	-3.849209618
C	3.363950669	-0.264087680	-3.507235887
H	4.100754162	-0.320211154	-4.333771107
H	2.440218596	0.201237144	-3.900651747
C	4.161469756	1.832383160	-2.807827351
H	3.233578235	2.340372493	-3.124717248
H	4.887540901	1.851086325	-3.645062755
C	4.732294732	2.567316572	-1.627574694
H	4.829526099	3.637923747	-1.887341726
H	4.047243105	2.497393767	-0.761228464
C	6.676600956	2.734102826	-0.308391872
H	6.080242075	2.761866432	0.622955008
H	6.841544142	3.782549208	-0.625017352
C	8.011214474	2.084157392	-0.057407752
H	8.574342643	2.003803741	-1.007969550
H	8.598786093	2.716172289	0.637150921
C	-4.743156181	2.003512938	-2.833506695
H	-5.521507439	2.495681614	-3.421515086
C	-4.445749836	0.653107843	-3.051432445
H	-5.011671605	0.080672265	-3.792886771
C	-3.421871875	0.035597212	-2.334698738
C	-2.937294840	-1.341079449	-2.309089675
C	-3.496792963	-2.583375920	-2.630397664
H	-4.426502976	-2.628753232	-3.209465964
C	-2.998930328	-3.793536101	-2.027245337
C	-3.741262701	-5.008532303	-1.801872035
H	-4.599273234	-5.233121860	-2.444807951
C	-3.498808422	-5.852401364	-0.725017606
H	-4.158577376	-6.711357134	-0.572633337
C	-2.498123968	-5.534922816	0.266007415
C	-2.424769292	-5.941172087	1.652253557
H	-3.001758070	-6.809370226	1.985617028
C	-1.739109938	-5.203019177	2.602908606
H	-1.801719469	-5.515305487	3.649698052

C	-1.053051477	-3.975479040	2.266316656
C	-0.742174742	-2.850004713	3.090917214
H	-0.744430029	-2.954149792	4.180007703
C	-0.551102110	-1.574529971	2.541046921
H	-0.405886921	-0.735367418	3.227704370
C	-0.595116087	-1.316747789	1.140867502
C	-0.678940887	0.047153256	0.420117311
H	-1.031914528	0.808615948	1.136796198
C	-1.643436178	-0.052643721	-0.770984959
C	-2.635573998	0.796087859	-1.360638069
C	-2.961342981	2.158403341	-1.166686238
H	-2.366812377	2.765854492	-0.479134880
C	-3.994080996	2.741298998	-1.895890323
H	-4.214480731	3.802375305	-1.750834924
C	-1.795623821	-1.278041400	-1.421525082
C	-1.202764836	-2.451602711	-0.985940570
C	-1.843990622	-3.668650254	-1.226773050
C	-1.652310741	-4.491952530	-0.073338604
C	-0.949132182	-3.734543812	0.898920854
C	-0.688916915	-2.453354575	0.354745593
Rb	-5.538647913	0.560000753	0.191740764
O	-7.687124812	-1.144981462	-0.972578950
O	-8.324890097	1.594745282	-0.570106935
O	-6.570858931	3.293553795	0.880303158
O	-4.900573828	2.039955994	2.789371250
O	-4.213250486	-0.661959736	2.458717742
O	-5.975829126	-2.301208975	0.974856936
C	-8.925433249	-0.577793994	-1.323653996
H	-9.374125165	-1.119410515	-2.180161800
H	-9.633476542	-0.639277400	-0.473529603
C	-8.726385390	0.865068384	-1.708559816
H	-9.681389591	1.263134130	-2.105828346
H	-7.964457544	0.942880695	-2.508857354
C	-8.203499659	2.977537003	-0.820335531
H	-7.419126106	3.167417411	-1.578370588
H	-9.159557990	3.385760895	-1.204043914
C	-7.856242350	3.684987830	0.463230947
H	-8.606496410	3.437558352	1.240183844
H	-7.894161158	4.778740125	0.288656591
C	-6.171517556	3.915039544	2.081314140
H	-6.126352060	5.014291903	1.951096033
H	-6.899071150	3.693509005	2.886797663
C	-4.809157879	3.411014600	2.479025781
H	-4.460719417	3.987976271	3.358397988

H	-4.086918956	3.579781302	1.656464515
C	-3.684071792	1.505154311	3.272544206
H	-2.888483404	1.602047991	2.508979072
H	-3.355248101	2.052093564	4.177789194
C	-3.886668391	0.054969960	3.623568874
H	-4.697287832	-0.039662407	4.373945442
H	-2.953829413	-0.336027961	4.071825959
C	-4.345512408	-2.051094701	2.688356210
H	-3.394482452	-2.467264297	3.065561978
H	-5.141873453	-2.234118982	3.437382230
C	-4.693630694	-2.739230017	1.398422883
H	-4.691807561	-3.832176912	1.565931301
H	-3.931594139	-2.521265972	0.626457231
C	-6.440396122	-3.003990601	-0.154606067
H	-5.737683483	-2.891216217	-1.001272258
H	-6.519380044	-4.086560100	0.066025406
C	-7.800781975	-2.482232288	-0.531641798
H	-8.479162912	-2.536396733	0.342263637
H	-8.223637651	-3.118201533	-1.334370526

Table S7. Cartesian coordinates of $[C_{26}H_{12}]^{-}$.

Symbol	X	Y	Z
C	-5.240879728	0.723052984	-0.875625400
H	-6.123574149	1.271043469	-1.216216786
C	-4.126816578	1.422874749	-0.417472943
H	-4.135413651	2.516710139	-0.403234168
C	-2.996164564	0.730797046	0.028817750
C	-1.697707058	1.194978015	0.503080860
C	-0.927417467	2.374141302	0.329938161
H	-1.389725072	3.266091129	-0.105833338
C	0.493242776	2.339347548	0.476944349
C	1.464958245	3.224343949	-0.138120805
H	1.144303552	4.219663772	-0.464972705
C	2.749611335	2.820407281	-0.455910214
H	3.387685865	3.516099289	-1.011224425
C	3.219896794	1.467648477	-0.218233978
C	4.234150739	0.727034110	-0.901763222
H	4.962570416	1.258513961	-1.522441641
C	4.234802479	-0.674144317	-0.929652642
H	4.963647708	-1.179791844	-1.571069871
C	3.221304989	-1.442330159	-0.276060744
C	2.752334543	-2.785012404	-0.567338557
H	3.390915019	-3.457232558	-1.150279723

C	1.468272883	-3.202735476	-0.265457324
H	1.148532972	-4.184513944	-0.631752116
C	0.495807329	-2.343983762	0.384634822
C	-0.924814493	-2.374553310	0.236506869
H	-1.386256330	-3.249041366	-0.234165874
C	-1.696415061	-1.204062217	0.456091545
C	-2.995432299	-0.723062234	0.000463724
C	-4.125461001	-1.398377086	-0.472242119
H	-4.133103023	-2.491953062	-0.500400969
C	-5.240232766	-0.682364087	-0.902864059
H	-6.122438181	-1.217579012	-1.264362504
C	-1.023973570	-0.011769600	0.867449552
C	0.307145014	-0.017012642	1.171064630
C	1.078162794	1.150488707	0.965072704
C	2.363989908	0.711242906	0.579022012
C	2.364788341	-0.719019408	0.550699636
C	1.079529026	-1.174601732	0.919199543

Table S8. Cartesian coordinates of [(Rb)($C_{26}H_{12}$)].

Symbol	X	Y	Z
Rb	-0.552626115	-0.268394982	1.335616828
C	4.598741781	-0.301027736	-1.084962747
H	5.555677268	-0.827142646	-1.069710493
C	3.436305622	-0.994470323	-1.409677094
H	3.481253667	-2.060498088	-1.646641477
C	2.212362644	-0.317943184	-1.445992089
C	0.850597783	-0.792637405	-1.683729470
C	0.203948806	-2.047823766	-1.534361563
H	0.800910402	-2.958392644	-1.422832909
C	-1.202960860	-2.113541933	-1.298201520
C	-1.915713848	-3.179489996	-0.613887957
H	-1.484363815	-4.185409828	-0.605697187
C	-3.057374859	-2.952169548	0.131843911
H	-3.487722139	-3.788451998	0.690732229
C	-3.618234906	-1.621748375	0.303010759
C	-4.390989551	-1.111540329	1.390410194
H	-4.881544865	-1.807658533	2.076581813
C	-4.432519606	0.259164846	1.687425286
H	-4.953720436	0.579580621	2.593854759
C	-3.703877942	1.217064570	0.918155290
C	-3.223401372	2.528884478	1.320449994
H	-3.694482325	3.031984907	2.170052099
C	-2.106707641	3.110284221	0.749824540

H	-1.734119062	4.045804211	1.178762278
C	-1.342483964	2.466276042	-0.305246063
C	0.062524727	2.586388157	-0.530081287
H	0.606829900	3.402358775	-0.044473105
C	0.779052767	1.545096784	-1.176790154
C	2.169037208	1.094877685	-1.139544340
C	3.351189592	1.766432530	-0.810623071
H	3.330334333	2.835507064	-0.584193367
C	4.556457466	1.070635082	-0.787150531
H	5.480867504	1.598407869	-0.542958609
C	0.057565860	0.399177335	-1.642768566
C	-1.311559034	0.341485017	-1.569435690
C	-1.949540336	-0.912088804	-1.378636765
C	-3.078008350	-0.664235178	-0.559051640
C	-3.120455100	0.734684629	-0.255884589
C	-2.018575514	1.364389250	-0.885006661

Table S9. Cartesian coordinates of [(Rb)(18C6)($C_{26}H_{12}$)].

Symbol	X	Y	Z
Rb	-1.794994120	0.087284918	0.146859749
O	-1.818382353	3.034949391	0.524187110
O	-4.345841879	1.767073007	0.361657708
O	-4.570079331	-1.051331411	0.467275693
O	-2.454462427	-2.437094557	1.755363231
O	0.090785437	-1.272328367	1.872664411
O	0.239781223	1.535910879	1.796540082
C	-2.644845177	0.037822867	-3.259061142
H	-3.559823386	0.530082536	-3.598479712
C	-1.455188922	0.763189966	-3.185198128
H	-1.446005594	1.824323422	-3.450425699
C	-0.266177739	0.133674472	-2.791865740
C	1.079574026	0.644240527	-2.575136350
C	1.654590833	1.915768030	-2.292783115
H	1.057141761	2.825275477	-2.414982578
C	2.929076107	2.004028598	-1.645615119
C	3.443422077	3.091959292	-0.829584399
H	3.041221636	4.100933626	-0.969525943
C	4.338661283	2.889096064	0.206776588
H	4.607261254	3.746579812	0.831747161
C	4.831086660	1.570610960	0.563095363
C	5.306444110	1.078888824	1.822568993
H	5.612436116	1.787322188	2.598154257
C	5.277392410	-0.283003543	2.143520517

H	5.561527686	-0.582781851	3.156628762
C	4.771723346	-1.265537858	1.231012618
C	4.226566955	-2.585857657	1.494394915
H	4.469333296	-3.085908414	2.437348568
C	3.312139399	-3.192550903	0.649153919
H	2.871064510	-4.143169286	0.967512110
C	2.837045128	-2.564756281	-0.572130133
C	1.567988047	-2.730868283	-1.210414444
H	0.938532139	-3.578713790	-0.921248228
C	1.038353513	-1.699905949	-2.033818309
C	-0.290459119	-1.293185672	-2.463506810
C	-1.502305447	-1.992714068	-2.550300846
H	-1.528002348	-3.063883769	-2.328537420
C	-2.668598266	-1.336261504	-2.942345535
H	-3.603907990	-1.894730995	-3.024850503
C	1.827782132	-0.529583595	-2.253708783
C	3.110466637	-0.446849554	-1.796826940
C	3.658548509	0.812812318	-1.468480826
C	4.529669068	0.592073550	-0.377331430
C	4.500466872	-0.797517844	-0.049848750
C	3.612963057	-1.447832882	-0.936991492
C	-3.037044101	3.735254676	0.575486519
H	-2.915363960	4.762282029	0.177495795
H	-3.393148004	3.815035700	1.621528261
C	-4.067250535	3.008266360	-0.248449348
H	-4.984423198	3.627319174	-0.302477860
H	-3.693611831	2.860441721	-1.280826575
C	-5.385108661	1.057411118	-0.273612268
H	-5.097983434	0.787866022	-1.308760127
H	-6.303795074	1.675189849	-0.321568077
C	-5.680998050	-0.187945373	0.519905775
H	-5.905927864	0.086608432	1.569215542
H	-6.577992151	-0.680885967	0.095417521
C	-4.758492462	-2.227296408	1.220646536
H	-5.629460301	-2.796478594	0.839690005
H	-4.950833927	-1.976281403	2.282154333
C	-3.528335226	-3.090041435	1.120849836
H	-3.736910494	-4.062554933	1.609482200
H	-3.293282708	-3.288152308	0.056200967
C	-1.272478311	-3.211519678	1.767400636
H	-0.928474812	-3.404619297	0.732981497
H	-1.457197031	-4.188683578	2.255709963
C	-0.202423981	-2.477045636	2.531496592
H	-0.549270374	-2.278649781	3.565626457

H	0.697184200	-3.119848749	2.587601294
C	1.143593562	-0.552048177	2.486923456
H	2.069330454	-1.154931916	2.489843471
H	0.869063523	-0.308779660	3.532622577
C	1.394904944	0.713745837	1.717439275
H	2.272493015	1.226185465	2.152720980
H	1.638510934	0.482950232	0.663389962
C	0.447743463	2.811879508	1.233055044
H	0.755164218	2.724778215	0.174227949
H	1.255921628	3.346667323	1.768656373
C	-0.821038500	3.612665978	1.343263763
H	-1.164178425	3.635630645	2.396113918
H	-0.619369331	4.654027844	1.024392761

Table S10. Cartesian coordinates of $C_{26}H_{12}$.

Symbol	X	Y	Z
C	-5.251667156	0.717087753	-0.853900192
H	-6.138561963	1.263753687	-1.180268212
C	-4.128767660	1.423413718	-0.410124157
H	-4.136781748	2.515459939	-0.393971205
C	-3.009309285	0.720036241	0.015541579
C	-1.683093188	1.187324631	0.485579610
C	-0.934995274	2.345002542	0.307407918
H	-1.393189153	3.234937934	-0.133105386
C	0.508625731	2.315789372	0.466393186
C	1.455835147	3.199463767	-0.170156864
H	1.120737083	4.179337266	-0.521032940
C	2.745462870	2.796431594	-0.477825607
H	3.379181706	3.477662225	-1.051932947
C	3.214464067	1.462470829	-0.198797975
C	4.252181889	0.717006563	-0.871620756
H	5.000260258	1.252545321	-1.462169949
C	4.252962289	-0.665409237	-0.898947404
H	5.001569765	-1.176327838	-1.510218127
C	3.216115715	-1.437964019	-0.256066043
C	2.748521990	-2.760396252	-0.587608524
H	3.383012356	-3.417634614	-1.188246444
C	1.459447377	-3.176786763	-0.296060372
H	1.125488023	-4.142392814	-0.685423969
C	0.511325088	-2.320040232	0.374952545
C	-0.932286270	-2.344522573	0.214776124
H	-1.389448514	-3.216848305	-0.260656717
C	-1.681709674	-1.195690324	0.438495383

C	-3.008481053	-0.711728364	-0.012778767
C	-4.127150245	-1.398959133	-0.465963694
H	-4.134034615	-2.490788829	-0.493086086
C	-5.250858511	-0.676844417	-0.881498284
H	-6.137137251	-1.211184135	-1.229282990
C	-1.019960355	-0.012094856	0.880890477
C	0.304361609	-0.017436501	1.191307991
C	1.077207720	1.145430921	0.969638688
C	2.380516102	0.708251282	0.611075217
C	2.381359939	-0.717251972	0.582999156
C	1.078622925	-1.169765796	0.923975766

IV. References

[1] N. V. Kozhemyakina, J. Nuss, M. Jansen, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1355-1361.

[2] B. D. Steinberg, E. A. Jackson, A. S. Filatov, A. Wakamiya, M. A. Petrukhina, L. T. Scott, *J. Am. Chem. Soc.* **2009**, *131*, 10537-10545.

[3] SAINT; part of Bruker APEX3 software package (version 2017.3-0): Bruker AXS, **2017**.

[4] SADABS; part of Bruker APEX3 software package (version 2017.3-0): Bruker AXS, **2017**.

[5] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3-8.

[6] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3-8.

[7] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339-341.

[8] A. L. Spek, *Acta Crystallogr C* **2015**, *71*, 9-18.

[9] a) R. C. Haddon, *J. Am. Chem. Soc.* **1987**, *109*, 1676-1685; b) T. Amaya, Y. Takahashi, T. Moriuchi, T. Hirao, *J. Am. Chem. Soc.* **2014**, *136*, 12794-12798.

[10] M. A. Petrukhina, K. W. Andreini, J. Mack, L. T. Scott, *J. Org. Chem.* **2005**, *70*, 5713-5716.

[11] M. A. Petrukhina, K. W. Andreini, V. M. Tsefrikas, L. T. Scott, *Organometallics* **2005**, *24*, 1394-1397.

[12] A. Y. Rogachev, M. Alkan, J. Li, S. Liu, S. N. Spisak, A. S. Filatov, M. A. Petrukhina, *Chem. Eur. J.* **2019**, *25*, 14140-14147.

[13] S. N. Spisak, A. V. Zabula, M. Alkan, A. S. Filatov, A. Yu. Rogachev, M. A. Petrukhina, *Angew. Chem. Int. Ed.* **2018**, *57*, 6171-6175.

[14] (a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, **1997**, *78*, 1396. (b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, **1996**, *77*, 3865.

[15] A. A. Granovsky, *Firefly version 8.2.0*, http://classic.chem.msu.su/gran/firefly/index.html

[16] (a) F. Weinhold, C. A. Landis, *Valency and Bonding: A Natural Bond Orbital Donor − Acceptor Perspective*. Cambridge University Press: Cambridge, **2005**. (b) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.*, **1988**, *88*, 899.

[17] K. Wiberg, *Tetrahedron*, **1968**, *24*, 1083.

[18] (a) E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, *NBO 6.0*, **2013**, University of Wisconsin, Madison. (b) E. D. Glendening, C. R. Landis, F. Weinhold, *J. Comp. Chem.*, **2013**, *34*, 1429.

[19] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.*, **2009**, *356*, 98.

[20] (a) F. Neese, ORCA, **2009**, University of Bonn, Bonn, Germany. (b) F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, **2012**, *2*, 73.

[21] (a) Morokuma, K. *J. Chem. Phys.*, **1971**, *55*, 1236. (b) Ziegler, T.; Rauk, A. *Inorg. Chem.*, **1979**, *18*, 1558. (c) Ziegler, T.; Rauk, A. *Inorg. Chem.*, **1979**, *18*, 1755.

[22] (a) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.*, **1998**, *99*, 391. (b) *ADF2008.01*, SCM, Vrije Universiteit, Amsterdam, Netherlands, http://www.scm.com. (c) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.*, **2001**, *22*, 931.

[23] J. Krijn, E. J. Baerends, *Fit Functions in the HFS-Method*, **1984**, Internal Report (In Dutch), Vrije Universiteit, Amsterdam, Netherlands.

[24] (a) Lein, M.; Frenking, G. in *Theory and Application of Computational Chemistry*, ed. Dekstra, C. **2005**. (b) von Hopffgarten, M.; Frenking, G. in *Computational Inorganic and Bioinorganic Chemistry*, ed. E. Solomon, **2009**, pp. 3-15. (c) Lein, M.; Szabo, A.; Kovac, A.; Frenking, G. *Faraday Discuss.*, **2003**, *124*, 365. (d) Frenking, G.; Wichmann, K.; Frohlich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Rayon, V. M. *Coord. Chem. Rev.*, **2003**, *238-239*, 55-82. (e) Krapp, A.; Bickelhaupt, F. M.; Frenking, G. *Chem. Eur. J.*, **2006**, *12*, 9196-9216. (f) Krapp, A.; Frenking, G. *J. Comput. Chem.*, **2007**, *28*, 15-24. (g) von Hopffgarten, M.; Frenking, G. *WIREs Comput. Mol. Sci.*, **2012**, *2*, 9196.