Electronic Supplementary Information

Axially and Helically Chiral Cationic Radical Bicarbazoles: SOMO-HOMO Level Inversion and Chirality Impact on the Stability of Mono- and Diradical Cations

Sitthichok Kasemthaveechok,[†] Laura Abella,[‡] Marion Jean,[§] Marie Cordier,[†] Thierry Roisnel,[†] Nicolas Vanthuyne,[§] Thierry Guizouarn,[†] Olivier Cador,[†] Jochen Autschbach,^{*,‡} Jeanne Crassous,[†] and Ludovic Favereau,^{*,†}

[†] Univ Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes, France.

[‡] Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14260, USA.

[§] Aix Marseille University, CNRS Centrale Marseille, iSm2, 13284 Marseille, France.

Table of Contents

A. General methods	S2
B. Synthetic procedures	S4
C. Crystal structures	S8
D. Preparative Separation of 1	S12
E. Steady-state photophysical characterizations	S15
F. Kinetic dissociation analysis of 1 ^{●+} , 3 ^{●+} , 3 ^{•+} and 3 ^{2●2+}	S24
G. NMR spectra	S28
H. Computational part	S40

A. General method

¹H and ¹³C NMR spectra were recorded at room temperature on an *AVANCE III 400 BRUKER* at Centre Régional de Measures Physiques de l'Ouest (CRMPO), Université de Rennes 1. Chemical shifts δ are given in ppm and coupling constants *J* in Hz. Chemical shifts for ¹H NMR spectra are referenced relative to residual protium in the deuterated solvent (¹H δ = 7.26 ppm, CDCl₃, δ = 5.32 ppm, CD₂Cl₂). ¹³C shifts are referenced to deuterated solvent (δ = 77.2 ppm for CDCl₃, δ = 53.8 ppm for CD₂Cl₂).

Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh). All commercial chemicals were purchased and used as received.

High-resolution mass spectrometry (HR-MS) determinations were performed at CRMPO on a Bruker MaXis 4G by ASAP (+ or -) or ESI with CH_2Cl_2 as solvent techniques. Experimental and calculated masses are given with consideration of the mass of the electron.

Low-resolution mass spectrometry (LR-MS) determinations were performed on a Bruker Daltonics flexControl Experimental and calculated masses are given with consideration of the mass of the electron.

Electrochemical measurements were performed with a potentiostat-galvanostat AutoLab PGSTAT 302N controlled by resident GPES (General Purpose Electrochemical System 4.9) software using a conventional single-compartment three-electrode cell. The working and auxiliary electrodes were platinum electrodes and the reference electrode were the saturated potassium chloride calomel electrode (SCE). The supporting electrolyte was 0.1 N Bu₄NPF₆ (tetrabutylammonium hexafluorophosphate) in dichloromethane and solutions were purged with argon before the measurements. All potentials are quoted relative to SCE.

UV-Visible/NIR (UV-vis-NIR, in M⁻¹ cm⁻¹) absorption spectra were recorded on a Jasco V-770 spectrophotometer. Fluorescence spectra were measured on an FL 920 Edinburgh fluorimeter, while absolute fluorescence quantum yields Φ were recorded with a Hamamatsu C9920– 03 integrating sphere.

Spectroelectrochemical measurement were performed with potentiostat-galvanostat Princeton by using optically transparent thin-layer electrochemical (OTTLE) cell as OMNI-cell body. The optical pathlength is *ca.* 0.2 cm.

Optical rotations were measured on a Jasco P-2000 polarimeter with a sodium lamp (589 nm) in a 1 or 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder. Specific rotations are given in 10⁻¹ deg·cm²·g⁻¹, and molar rotations are given in 10⁻³ deg·cm²·mol⁻¹. Electronic circular dichroism (ECD, in M⁻¹ cm⁻¹) was measured on a Jasco J-815 Circular Dichroism Spectrometer IFR140 facility. Part of this work has been performed using the PRISM core facility (Biogenouest©, UMS Biosit, Université de Rennes 1 - Campus de Villejean-35043 Rennes Cedex, France).

The circularly polarized luminescence (CPL) measurements were performed using a home-built CPL spectrofluoropolarimeter (constructed with the help of the JASCO Company). The samples were excited using a 90° geometry with a Xenon ozone-free lamp 150 W LS. The following parameters were used: emission slit width ≈ 2 mm, integration time = 4 sec, scan speed = 50 nm/min, accumulations = 5. The concentration of all the samples was ca. 10⁻⁶ M. Excitation of the samples was performed at 350 nm.

Electron paramagnetic resonance (EPR) measurements were carried out with a Bruker 300 spectrometer (X-band, 100 kHz field modulation). Frozen solution spectra were obtained by very rapidly cooling down the solution to avoid the formation of small crystallites.

The DC and AC magnetic susceptibility measurements were performed on solid polycrystalline samples with a Quantum Design MPMS-XL SQUID magnetometer between 2 and 300 K in applied magnetic field of 0.2 T for temperatures of 2-20 K and 1T for temperatures of 20-300 K. These measurements were all corrected for the diamagnetic contribution as calculated with Pascal's constants.

B. Synthetic procedures

BICOL was synthesized by using a synthetic method from Botman and co-workers with an improvement from Hoen.^[1] All analytical data for **BICOL**, **1'** and **3'** were in accordance with references.^[2]



Scheme 1. Carbazole and BICOL derivatives synthesis.

 (\pm) -3,3'-dimethoxy-4,4'-bis-(9-methyl-9*H*-carbazole) (1)^[3]



In a pre-dried schlenk flask, 300 mg (0.82 mmol) of (\pm) -**BICOL** was dissolved in 25 mL of acetone under inert atmosphere. Sodium hydroxide (22 M aq, 0.88 mL, 20 eq) was added and the reaction mixture was stirred for 5 minutes at room temperature before heated to reflux. Then 2.75 mL of dimethylsulfate (24.6 mmoL, 30 eq) was added and the reaction mixture was further refluxed for 2 h. After cooling down to room temperature, the reaction solution was poured in 20 mL dichloromethane and washed with water (2 x 30 mL) and brine (1 x 30 mL). The organic phase was dried over MgSO₄, and the solvents evaporated under reduce pressure. The crude product was passed through a short silica plug (1:1 *n*-heptane/CH₂Cl₂ eluent system) to yield **1** (270 mg, 77 %) as off white solid.

¹**H NMR** (400 MHz, CD₂Cl₂) δ 7.58 (d, *J* = 8.8 Hz, 1H²), 7.44 (d, *J* = 8.8 Hz, 1H¹), 7.34 (d, *J* = 8.2 Hz, 1H⁸), 7.28 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H⁷), 6.66 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H⁶), 6.53 (dt, *J* = 7.9, 0.9 Hz, 1H⁵), 3.93 (s, 3H³), 3.75 (d, *J* = 4.2 Hz, 3H⁹)

¹³C NMR (101 MHz, CD₂Cl₂) δ 150.9, 141.9, 136.9, 125.4 (C-H⁷), 122.5, 122.0, 121.4 (C-H⁵), 120.0, 118.0 (C-H⁶), 112.1 (C-H¹), 108.1 (C-H⁸), 108.0 (C-H²), 57.6 (C³-OCH₃), 29.1 (N⁹-CH₃).

HR-MS Thermo-Fisher Q-Exactive, ESI (+), CH_3OH/CH_2Cl_2 (90/10); ion [M+Na]⁺, $C_{28}H_{24}N_2O_2Na$, m/z calculated 443.173, m/z experimental 443.1728 (Δ =0 ppm).

Experimental optical rotation values

(+)-1: $[\alpha]_D^{25} = +107 \pm 2\%$, $[\phi]_D^{25} = +450$ (c = 1.3 × 10⁻³, DCM). (-)-1: $[\alpha]_D^{25} = -115 \pm 2\%$, $[\phi]_D^{25} = -485$ (c = 1.2 × 10⁻³, DCM).

 (\pm) -3,3'-methylenedioxy-4,4'-bis-(9-methyl-9*H*-carbazole) (2)^[3-4]



Boron tribromide (1 M in dichloromethane, 0.6 mmol, 6 eq) was slowly added to a solution of (+)-/(-)-1 (35 mg, 0.100 mmol) in dry dichloromethane (5 mL) at room temperature and stirred for 3 h. The crude mixture was diluted and washed with water, then dried over MgSO₄, filtered and evaporated under pressure. The obtained solid was dissolved in 30 mL of acetone and transfered to a pre-dried schlenk flask under argon. Potassium carbonate 150 mg (10 eq.) was added. The reaction mixture was stirred for 5 minutes at room temperature before heated to reflux. Then, 20 µL of diiodomethane (0.300 mmoL, 3 eq) was added and further refluxed for 16 h. The reaction mixture was allowed to cool down to room temperature and the medium was diluted with EtOAc. The mixture was then extracted with water (2 x 30 mL) and brine (1 x 30 mL). The organic phase was dried over MgSO₄, and the solvents evaporated under reduce pressure. The crude mixture was passed through short silica plugs (1:1 *n*-heptane/CH₂Cl₂ eluent system) to yield (+)-**2** (34 mg, 90 %) and (-)-**2** (35 mg, 93 %) as off-white solids.

¹**H NMR** (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.6 Hz, 1H²), 7.49 (d, *J* = 8.6 Hz, 1H¹), 7.35 (d, *J* = 8.2 Hz, 1H⁸), 7.28 – 7.22 (m, 1H⁷), 6.95 (d, *J* = 8.0 Hz, 1H⁵), 6.52 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H⁶), 5.65 (s, 1H³), 3.98 (s, 3H⁹).

¹³**C NMR** (101 MHz, CD₂Cl₂) δ 146.1, 141.9, 139.0, 125.6 (C-H⁷), 125.2, 122.7 (C-H⁵), 122.1, 121.2, 118.6 (C-H¹), 117.8 (C-H⁶), 108.9 (C-H²), 108.1 (C-H⁸), 103.8 (C³-OCH₃), 29.3. (N⁹-CH₃).

HR-MS Thermo-Fisher Q-Exactive, ESI (+), CH_3OH/CH_2Cl_2 (90/10); ion [M+Na]⁺, $C_{27}H_{20}N_2O_2Na$, m/z calculated 427.1417, m/z experimental 427.1420 (Δ =1 ppm).

Experimental optical rotation values

(+)-**2**: $[\alpha]_D^{25} = +640 \pm 1\%$, $[\phi]_D^{25} = +2,570$ (c = 1.3 × 10⁻³, DCM). (-)-**2**: $[\alpha]_D^{25} = -650 \pm 2\%$, $[\phi]_D^{25} = -2,640$ (c = 1.1 × 10⁻³, DCM). (\pm) -3,3'-dimethoxy-6,6'-di(1,1-dimethylethyl)-4,4'-bis-(9-methyl-9*H*-carbazole) (3)



A stirred solution of **1** (150 mg, 0.48 mmol) and zinc chloride anhydrous (150 mg, 3 eq.) in the nitromethane (9 mL). Then, *t*-BuCl (120 μ L) was added with and stirred for 16 h under argon atmosphere. After that, water was poured to the mixture and extracted with dichloromethane (3 x 10 mL). The organic phase was washed with water, saturated NaHCO₃, and brine (1 × 10 mL). The organic phase was dried over MgSO₄, and the solvents evaporated under reduce pressure. The crude mixture was passed through short silica plugs (1:1 *n*-heptane/CH₂Cl₂ eluent system) to yield **3** (190 mg, >99 %) as off-white solid.

¹**H NMR** (400 MHz, CD₂Cl₂) δ 7.50 (d, J = 8.8 Hz, 1H²), 7.39 (d, J = 8.8 Hz, 1H¹), 7.30 (dd, J = 8.6, 2.0 Hz, 1H⁷), 7.20 (d, J = 8.5 Hz, 1H⁸), 6.52 (d, J = 2.0 Hz, 1H⁵), 3.83 (s, 3H⁹), 3.74 (s, 3H³), 0.97 (s, 9H⁶).

¹³**C NMR** (101 MHz, CD₂Cl₂) δ 150.9, 140.7, 140.2, 137.4, 123.2 (C⁷-H⁷), 122.3, 122.3, 119.9, 118.0, 111.3 (C¹-H¹), 107.8 (C²-H²), 107.4 (C⁸-H⁸), 57.4 (C³-OCH₃), 34.0, 31.3 (C⁶-CH₃), 29.1 (N⁹-CH₃).

HR-MS Thermo-Fisher Q-Exactive, ESI (+), CH_3OH/CH_2Cl_2 (90/10); ion [M+Na]+, $C_{36}H_{40}N_2O_2Na$, m/z calculated 555.2982, m/z experimental 555.2983 (Δ =0 ppm). **Experimental optical rotation values**

(+)-**3**: $[\alpha]_D^{25} = +150 \pm 4\%$, $[\phi]_D^{25} = +780$ (c = 2.0 × 10⁻³, DCM). (-)-**3**: $[\alpha]_D^{25} = -160 \pm 3\%$, $[\phi]_D^{25} = -850$ (c = 1.5 × 10⁻³, DCM).

 (\pm) -3,3'-methylenedioxy-6,6'-di(1,1-dimethylethyl)-4,4'-bis-(9-methyl-9*H*-carbazole) (4)



Boron tribromide (1 M in dichloromethane, 0.45 mmol, 6 eq) was slowly added to a solution of **3** (40 mg, 0.075 mmol) in dry dichloromethane (5 mL) at room temperature and stirred for 3 h. The crude mixture was diluted and washed with water, then dried over MgSO₄, filtered and evaporated under pressure. The obtained solid was dissolved in 30 mL of acetone and transfered to a pre-dried schlenk flask under argon. Potassium carbonate 105 mg (10 eq.) was added. The reaction mixture was stirred for 5 minutes at room temperature before heated to reflux. Then, 20 µL of diiodomethane (0.300 mmoL, 3 eq) was added and further refluxed for 16 h. The reaction mixture was then extracted with water (2 x 30 mL) and brine (1 x 30 mL). The organic phase was dried over MgSO₄, and the solvents evaporated under reduce pressure. The crude mixture was purified over silica gel column chromatography (*n*-heptane/ethyl acetate = 19:1) to give **4** as a white solid (10 mg, 25%).

¹**H NMR** (400 MHz, CD₂Cl₂) δ 7.59 (d, *J* = 8.6 Hz, 1H²), 7.50 (d, *J* = 8.6 Hz, 1H¹), 7.31 – 7.29 (m, 2H⁷⁻⁸), 6.89 – 6.72 (m, 1H⁵), 5.70 (s, 1H³), 3.96 (s, 3H⁹), 0.66 (s, 9H⁶).

¹³C NMR (101 MHz, CD₂Cl₂) δ 146.5, 141.1, 140.7, 139.7, 125.7, 124.1 (C⁷-H⁷), 122.2, 121.9, 120.6 (C⁵-H⁵), 118.7 (C¹-H¹), 109.2 (C²-H²), 107.7 (C⁸-H⁸), 104.4 (C³-OCH₃), 34.3, 31.3 (C⁶-CH₃), 29.8 (N⁹-CH₃).

HR-MS Thermo-Fisher Q-Exactive, ESI (+), CH_3OH/CH_2Cl_2 (90/10); ion [M+Na]⁺, $C_{35}H_{36}N_2O_2Na$, m/z calculated 539.2669, m/z experimental 539.2671 (Δ =0 ppm).

Experimental optical rotation values

(+)-**4**: $[\alpha]_D^{25} = +300 \pm 2\%$, $[\phi]_D^{25} = +1,530$ (c = 2.1 × 10⁻³, DCM). (-)-**4**: $[\alpha]_D^{25} = -290 \pm 4\%$, $[\phi]_D^{25} = -1,500$ (c = 1.8 × 10⁻³, DCM).

3-methoxy-9-methyl-9*H*-carbazole (1')



A stirred solution of **3-methoxy-9***H***-carbazole** (200 mg, 1.01 mmol) was dissolved by 5 mL of acetone under inert atmosphere. Sodium hydroxide (22 M aq, 0.05 mL) was added and stirred for 5 minutes at room temperature. The reaction mixture was heated to reflux temperature, then 1.5 mL of dimethylsulfate (15 mmoL, 15 eq) was added. The reaction mixture was refluxed for 2 h. After cooling down to room temperature, the reaction solution was poured in 20 mL dichloromethane and washed with water (2 x 30 mL) and brine (1 x 30 mL). The organic phase was dried over MgSO₄, and the solvents evaporated under reduce pressure. The crude product was passed through a short silica plug (1:1 *n*-heptane/CH₂Cl₂ eluent system) to yield **1'** as a white solid (200 mg, 93% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.08 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.62 (d, *J* = 2.5 Hz, 1H), 7.49 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.23 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.15 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.96 (s, 3H), 3.82 (s, 3H). NMR spectrum of **3'** was in accordance to a reference.^[2]

3-methoxy-6-(1,1-dimethylethyl)-9-methyl-9*H*-carbazole (3')



1' was mixed with zinc chloride anhydrous (50 mg, 0.35 mmol, 3 eq.) in 3 mL nitromethane. Then, *t*-BuCl (40 μ L, 0.35 mmol, 3 eq) was added with and stirred for 16 h under argon atmosphere. After that, water was poured to the mixture and extracted with dichloromethane (3 x 10 mL). The organic phase was washed with water, saturated NaHCO₃, and brine (1 × 10 mL). The organic phase was dried over MgSO₄, and the solvents evaporated under reduce pressure. The crude mixture was passed through short silica plugs (1:1 *n*-heptane/CH₂Cl₂ eluent system) to yield **3'** as off-white solid (8.5 mg, 26% yield).

¹H NMR (400 MHz, CD_2Cl_2) δ 7.53 (s, 1H₂), 7.43 (d, J = 8.8 Hz, 1H₁), 7.34 (dd, J = 8.5, 2.0 Hz, 1H₇), 7.23 (dm, J = 8.6 Hz, 1H₈), 6.56 (d, J = 1.9 Hz, 1H₅), 3.87 (s, 3H₃), 3.78 (s, 3H₉), 1.01 (s, 9H₆). NMR spectrum of **3'** was in accordance to a reference.^[2]

C. X-ray crystallographic data



Figure S1. ORTEP diagrams of compound **1** with ellipsoids at 50% probability (at 150 K).



Figure S2. ORTEP diagrams of compound **2** with ellipsoids at 50% probability (at 150 K).

Compound	1	2
Empirical formula	$C_{28}H_{24}N_2O_2$	$C_{27}H_{20}N_2O_2$
CCDC number	2016849	2017143
Formula weight (g/mol)	420.49	404.45
Temperature	150 K	150 K
Wavelength	0.71073	0.71073
Crystal system,	triclinic	monoclinic
space group	P -1	C 2/c
a (Å)	9.5316(10)	13.408(2)
b (Å)	9.9882(11)	18.225(2)
c (Å)	12.1305(13)	7.9041(11)
a (Å)	74.757(4)	90
b (Å)	77.144(4)	94.302(6)
g (Å)	74.314(4)	90
Volume (Å ³)	1058.4(2)	1926.0(4)
Z	2	4
Colour	colourless	colourless
r _{calculated} (g.cm ⁻³)	1.319	1.395
Absorption coefficient (mm ⁻¹)	0.083	0.089
F(000)	444	848
Crystal size (mm)	0.460 * 0.270 * 0.230	0.590 * 0.180 * 0.075
q range for data collection (°)	2.169 to 27.604	3.047 to 27.484
T _{min} , T _{max}	0.858, 0.981	0.578, 0.993
Limited indices	$-12 \le h \le 12$	$-17 \le h \le 17$
	$-12 \le k \le 13$	$-23 \le k \le 21$
	$-15 \le l \le 15$	$-10 \le l \le 10$
Reflections collected	19999	5867
Reflections unique	4856 [R(int) = 0.0527]	2216 [R(int) = 0.0834]
Reflections [I>2sigma(I)]	3871	1807
Data completeness	0.987	0.996
Absorption correction type	multi-scan	multi-scan
Refinement method	Full-matrix least-squares	Full-matrix least-squares
	on F ²	on F ²
Data / restraints / parameters	4856 / 0 / 296	2216/0/141
Goodness-of-fit	1.045	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 =	R1 = 0.0572, $wR2 =$
	0.1179	0.1507
R indices (all data)	R1 = 0.0619, wR2 =	R1 = 0.0697, wR2 =
	0.1269	0.1631
Largest diff. peak and hole	0.308 and -0.279 e.≈-3	$0.385 \text{ and } -0.343 \text{ e.} \approx -3$

 Table S1. X-ray crystallographic data for compound 1 and 2.





Figure S4. ORTEP diagrams of compound **4** with ellipsoids at 50% probability (at 150 K).

Compound	3	4
Empirical formula	$C_{36}H_{40}N_2O_2$	$C_{35}H_{36}N_2O_2$
CCDC number	2016850	2017144
Formula weight (g/mol)	532.70	516.66
Temperature	150 K	150 K
Wavelength	0.71073	0.71073
Crystal system,	monoclinic	monoclinic
space group	P 2 ₁ /n	P 2 ₁ /n
a (Å)	13.1390(17)	16.902(3)
b (Å)	34.437(5)	9.9528(18)
c (Å)	13.4698(19)	17.758(2)
a (Å)	90	90
b (Å)	92.046(5)	99.900(6)
g (Å)	90	90
Volume (Å ³)	6090.8(15)	2942.8(8)
Z	8	4
Colour	colourless	yellow
r _{calculated} (g.cm ⁻³)	1.162	1.166
Absorption coefficient (mm ⁻¹)	0.071	0.072
F(000)	2288	1104
Crystal size (mm)	0.540 * 0.420 * 0.300	0.660 * 0.650 * 0.200
<i>q</i> range for data collection (°)	2.208 to 27.550	2.354 to 27.519
T _{min} , T _{max}	0.835, 0.979	0.593, 0.986
Limited indices	$-15 \le h \le 17$	$-21 \le h \le 21$
	$-44 \le k \le 41$	$-11 \le k \le 12$
	$-17 \le l \le 17$	$-23 \le l \le 22$
Reflections collected	55868	23327
Reflections unique	13753 [R(int) = 0.0647]	6630 [R(int) = 0.0735]
Reflections [I>2sigma(I)]	9784	4505
Data completeness	0.979	0.981
Absorption correction type	multi-scan	multi-scan
Refinement method	Full-matrix least-squares	Full-matrix least-squares
	on F ²	on F ²
Data / restraints / parameters	13757 / 0 / 741	6630 / 52 / 383
Goodness-of-fit	0.992	1.078
Final R indices [I>2sigma(I)]	R1 = 0.0601	R1 = 0.0917
	wR2 = 0.1397	wR2 = 0.2346
R indices (all data)	R1 = 0.0920, $wR2 = 0.1577$	R1 = 0.1255, wR2 =
		0.2641
Largest diff. peak and hole	0.648 and -0.403 e.≈-3	0.507 and -0.425 e.≈-3

Table S2. X-ray crystallographic data for compound 3 and 4.

D. Preparative separation of enantiomer 1.

Analytical chiral HPLC separation for compound 1

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 230 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

Column	Mobile Phase	t1	k 1	t2	k2	α	Rs
Chiralpak IB	Heptane / isopropanol / dichloromethane (90/5/5)	7.90 (-)	1.68	9.65 (+)	2.27	1.35	3.32





RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
7.90	8004	49.19	1.68		
9.65	8267	50.81	2.27	1.35	3.32
Sum	16271	100.00			

Preparative separation for compound 1:

• Sample preparation: About 440 mg of compound **1** are dissolved in 32 mL of dichloromethane.

• Chromatographic conditions: (R,R)-Whelk-O1 (250 x 4.6 mm), hexane / dichloromethane (75/25) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• Injections (stacked): 400 times 80 µL, every 4.5 minutes.

• First fraction: 155 mg of the first eluted with ee > 95.5%



RT [min]	Area	Area%
7.81	40602	97.84
9.70	894	2.16
Sum	41497	100.00

• Second fraction: 144 mg of the second eluted enantiomer on Chiralpak IB with ee > 99.5% DAD1 C, Sig=230,4 Ref=off



RT [min]	Area	Area%
7.94	25	0.08
9.51	31809	99.92
Sum	31834	100.00

• Intermediate fraction: 130 mg

DAD1 C, Sig=230,4 Ref=off



RT [min]	Area	Area%
7.90	4900	46.99
9.64	5527	53.01
Sum	10426	100.00

Kinetic of enantiomerization of 1 in 1,2-dichlorobenzene

About 0.9 mg of the second eluted enantiomer of **1** is heated in about 15 mL of 1,2-dichlorobenzene at 180°C. 20 μ L are taken and then injected on Chiralpak IC (90:10 heptane / 2-PrOH, 1 mL/min, UV 290 nm). The percentage decrease of the second eluted enantiomer of **1** is monitored.

Time (min)	% second eluted enantiomer	ln ((%t-50%)/(%(t=0)-50%))
0	99.02	0.00000
1422	98.18	-0.01728
2940	97.22	-0.03741
7583	95.31	-0.07870
9015	93.97	-0.10872
11561	92.99	-0.13126

 $k_{enantiomerisation} = 9.40 \times 10^{\text{-8}} \, \text{s}^{\text{-1}}$ (180°C, 1,2-dichlorobenzene)

 $\Delta G^{\neq} = 173.5 \text{ kJ.mol}^{-1} (180^{\circ}\text{C}, 1,2\text{-dichlorobenzene})$

 $t_{1/2} = 43$ days (180°C, 1,2-dichlorobenzene)



E. Steady-state physical characterizations i) neutral state characterization



Figure S5. ECD spectra (solid line) and CPL spectra (dot line) of compounds **1** (black), **2** (red), **3** (green), **4** (blue) in dichloromethane (*ca.* 10⁻⁵ M) at 298 K

Electronic circular dichroism (ECD) spectra of enantiopure (+)-/(-)-1 and (+)-/(-)-2 clearly highlight the impact of the carbazoles dihedral angle on the chiroptical properties (Figure S5). Indeed, although a qualitatively similar ECD signature was obtained for (+)-1 and (+)-2, with a positive exciton couplet around 250 nm, a positive band at *ca*. 310 nm and a low-energy negative broad band between 340 and 400 nm, (+)-2 showed a much higher overall ECD intensity in the long-wavelength region than (+)-1. This is notably illustrated by the signals at 250 and 320 nm, respectively associated to $\Delta e = +190$ and + 150 M⁻¹ cm⁻¹ for (+)-2, and $\Delta e = +110$ and +40 M⁻¹ cm⁻¹ for (+)-1. Further computational details have been performed and are detail below (Figure S54 and table S7-8).

Corresponding mirror-image CPL spectra were also obtained for both pairs of enantiomers, enabling us to determine promising g_{lum} factors of 0.6×10^{-3} and 1.5×10^{-3} for 1 and 2, respectively (Figure S5).



Figure S6. UV-vis spectra (solid line) and fluorescence spectra (dash line) of compound **1** (black), **2** (red), **3** (green), **4** (blue), **1'** (violet) and **3'** (orange) in dichloromethane (*ca.* 10⁻⁵ M) at 298 K.

Table S3: Fluorescence quantum yield (Φ) of **1-4**.

Compound	Ф
1	22
2	15
3	24
4	17

Table S4. Oxidation po	otential (E_{0x} in V) of 1-4 , 1' and 3 '	versus saturated calomel electrode	(SCE)).
------------------------	--------------------------	--	------------------------------------	-------	----

Compound	E_{Ox}^1	E_{Ox}^2	E_{Ox}^3
1	+0.92	+1.11	+1.63
2	+1.14	+1.40	-
3 (DCM)	+0.87	+1.10	-
3 (MeCN)	+0.79	+0.98	-
4	+1.06	+1.37	-
1'	+0.95	+1.60	-
3'	+0.87	+1.63	-



Figure S7. Cyclic voltammograms of 4 versus saturated calomel electrode (SCE) as the reference and $0.2 \text{ M Bu}_4\text{NPF}_6$ in CH₂Cl₂ with ferrocene as internal standard.



Figure S8. UV-vis-NIR absorption spectra during the electrochemical oxidation of 1. The spectra were measured in CH_2Cl_2 with 0.2 M *n*-Bu₄NPF₆ at 298 K.



Figure S9. UV-vis-NIR absorption spectra during the electrochemical oxidation of **2**. The spectra were measured in CH₂Cl₂ with 0.2 M *n*-Bu₄NPF₆ at 298 K.



Figure S10. UV-vis-NIR absorption spectra during the electrochemical oxidation of **3**. The spectra were measured in CH₂Cl₂ with 0.2 M *n*-Bu₄NPF₆ at 298 K.



Figure S11. UV-vis-NIR absorption spectra during the electrochemical oxidation of **4**. The spectra were measured in CH₂Cl₂ with 0.2 M *n*-Bu₄NPF₆ at 298 K.

iii) radical state characterizations.

- Radical cations.

BICOL derivatives **1**, **3** and carbazole **3'** were dissolved in dichloromethane at room temperature under air saturated atmosphere. Then, an excess amount of silver(I)tetrafluoroborate ($E_{0x} = 1.11 \text{ V } vs \text{ SCE}$)^[5] was added and the reaction mixture was further stirred for 10 min while its color turned to green (**Scheme 2**). Those solutions were filtrated through syringe filter to separated cuvettes and recorded UV-vis-NIR spectrum.







Figure S12. UV-vis-NIR absorption spectra of **1** (black) and **1**⁺ **BF**⁺ (red) in dichloromethane at 298 K.



Figure S13. UV-vis-NIR absorption spectra of **3** (black) and **3**^{•+} **BF**⁴⁻ (red) in dichloromethane at 298 K.



Figure S14. UV-vis-NIR absorption spectra of **3'** (black) and **3'**+ **BF**₄- (red) in dichloromethane at 298 K.



Figure S15. ECD spectra of compound **3**^{•+} in dichloromethane (*ca.* 10⁻⁵ M) at 298 K. Inset: Vis-NIR ECD spectra of compound **3**^{•+} in dichloromethane (*ca.* 10⁻³ M) at 298 K.



Simulated EPR spectra of monoradicals 1*. (left) and 3*. (right) suggesting te presence of an organic radical with a ½ spin.

Figure S16. Top: EPR spectra of monoradical (1^{\bullet +} (black), 3^{\bullet +} (green) and 3'^{\bullet +} (dark yellow)) with AgBF₄ in CH₂Cl₂ and 4^{\bullet +} (blue) with 1.0 equivalent of magic blue in CH₂Cl₂ at 298 K. Bottom: Simulated EPR spectra of 1^{\bullet +} (left) and 3^{\bullet +} (right).

UV-vis titration studies

Oxidation process in dichloromethane were studied by UV-vis-NIR spectroscopy at 298 K. Solution of each molecule (10⁻⁵ M) was prepared using dry-dichloromethane as a solvent. Increasing number of $(4\text{-BrPh})_3\text{NSbCl}_6$ (so-called *magic blue*, $E_{0x} = 1.16 \text{ V } vs \text{ SCE})^{[5]}$ equivalents were added to the separate vials under argon (3.0 mL in a 1 cm-pathlength quartz cell). The BICOL's derivatives concentration was kept constant.



Figure S17. UV-vis titration studies of 1 by magic blue in dichloromethane (c = 7×10^{-5} M) at 298 K.



Figure S18. UV-vis titration studies of **2** by magic blue dichloromethane (c = 7×10^{-5} M) at 298 K.



Figure S19. UV-vis titration studies of 3 by magic blue in dichloromethane (c = 7×10^{-5} M) at 298 K. * denotes an excess of magic blue oxidant.

- Diradical dications.



Figure S20. Schematic illustration of the electronic configurations that can be obtained upon oxidation of a radical exhibiting a SOMO/HOMO inversion.

To a dry and degassed acetonitrile solution of **3**, 2 equivalents of *magic blue* oxidant (E_{0x} = 1.05 V *vs* SCE in acetonitrile) were added and the resulting solution was further stirred at room temperature for 5 min while its color turned to dark green (**Scheme 3**). This solution was then

transferred to a dedicated cuvette for UV-vis-NIR and ECD analysis. The same procedure was performed for both enantiomers of **3**.

For SQUID experiment, 16 mg (2 eq.) of *magic blue* were added into an acetonitrile solution contained 5 mg (1×10^{-4} mmol) of **3** under argon atmosphere. Then, the solution was allowed to stir and controlled by UV-vis-NIR. After full conversion to **3**²⁺², the solution was dried under vacuum. 6.0 mg of this solid was loaded to capsules and mounted in the colorless plastic straws. After background SQUID run, magnetization for the background, M_{bck}, was point-by-point subtracted from magnetization for the sample, M_{sample}, to provide corrected magnetization, M_{radical}, accounting for diamagnetism of sample holder. Thus, M_{radical} corresponded to mass of 3.3 mg.

$$3 \xrightarrow[Na_2S_2O_3]{(4-BrPh)_3NSbCl_6} 3^{2\bullet 2+} 2SbCl_6^{-}$$

Scheme 3. 3²⁰²⁺ radical's generation and deactivation process.

Recovery analysis of 3^{2●2+}

To a solution of BICOL derivatives **3** (5 mg, 9.39 μ M) in 10 mL acetonitrile (MeCN) under argon atmosphere, 16.2 mg of magic blue (2.1 equivalent) were added and the solution stirred for 10 minutes under argon atmosphere to ensure full conversion. Then, the solution was quenched by addition of Na₂S₂O₃ (sat'd, aq). The color changed from dark green to yellow. The solution was evaporated under reduced pressure and purified by column chromatography (SiO₂, pentane/DCM, 1:1) to obtain a white powder of **3** (4.0 mg, 80% recovery), which was confirmed by ¹H NMR spectrum (400 MHz, CD₂Cl₂) as depicted in **Figure S21**. Since the nmr of the crude reaction shows only starting material **3** and reduced magic blue oxidant, and no presence of other side products, it is reasonable to say that the loss of 1 mg occurred during the purification step (and not from a possible degradation of **3²e²⁺**).



Figure S21. ECD spectra of compound **3**●+ and **3**²●²+ in acetonitrile form NIR-ECD recorded in range from 400 to 1100 nm (*ca.* 10⁻³ M) at 298 K.



Figure S22. Variable temperature EPR spectra of diradical **3**²•²+ (left) and half-field region showing no forbidden transition after 100 scans (right).



Figure S23. ¹H NMR spectrum (400 MHz, CD₂Cl₂, 298 K) of sample obtained after quench of diradical dication $3^{2\bullet 2+}$ 2SbCl₆- in acetonitrile, before (top, * denotes the presence of (*p*-BrPh)₃N spectator) and after (bottom) purification by column chromatography.

Kinetic analysis of 1^{●+}, 3^{●+}, 3^{•+} and 3^{2●2+} dissociation

All radical species in this analysis was prepared according to the described procedure (*vide supra*) and added directly to the separated cuvettes under argon or air atmosphere. After measurement of monoradical, sample was reduced by $Na_2S_2O_3$ (sat'd, aq) and analyzed by low-resolution mass spectrometry (LR-MS) using dithranol as matrix carrier. For 3^{202+} , specific procedure will be described in its corresponding section.



Figure S24. UV-vis-NIR absorption spectra of **1**•+ in dichloromethane at 298 K under argon atmosphere (left) and air atmosphere (right).



Figure S25. First-order fitting plot of $\ln(A/A_0)$ of **1**•+ as a function of time at 782 nm under argon atmosphere (black) and air atmosphere (red).

Table S5. Linear fitting from	first-order fitting equation	with half-life calculation
-------------------------------	------------------------------	----------------------------

Environment	A	В	r ²	half-life (min)
Air	-0.00306	-0.00439	0.9944	158 <u>+</u> 29
Ar	0.00795	-8.34031×10-4	0.9927	831 <u>+</u> 48



Figure S26. LRMS spectrum (dithranol, CH₂Cl₂) of the sample obtained after quench of monoradical cation **1**^{•+} under argon atmosphere. The spectrum suggests that an oligomerization process occurred as one of degradation pathway of **1**^{•+}.



Artiker Deliconica frexcontrol

Display Screenshot - Generated On 2020-09-21 16b27m26s

Figure S27. LRMS spectrum (dithranol, CH₂Cl₂) of the sample obtained after quench of monoradical cation **1**^{•+} under air atmosphere. The spectrum suggests that an oligomerization process occurred as one of degradation pathway of **1**^{•+}.

Compound $3^{\bullet+}$ and $3^{\prime+}$



Figure S28. UV-vis-NIR absorption spectra of **3**•+ in dichloromethane (5 \times 10⁻⁵ M) under argon atmosphere at 298 K.



Figure S29. UV-vis-NIR absorption spectra of **3**^{•+} (left) and **3**^{•+} (right) in dichloromethane (5 \times 10⁻⁵ M) under air atmosphere at 298 K.



Figure S30. Left: Zeroth-order fitting plot of absorption of **3**^{•+} as a function of time under argon atmosphere. Right: Zeroth-order fitting plot of absorption of **3**^{•+} (black) and **3**^{•+} (red) as a function of time under air atmosphere (black).

Table S6. Linear fitting from optical density as a function of time in several kinetic order withhalf-life calculation

Compound	Environment	А	В	r ²	half-life (hours)
3•+	Air	0.243	-0.00125	0.9565	97 ± 0.2
	Ar	0.634	-0.00342	0.9932	93 ± 0.2
3'•+	Air	0.133	-0.000798	0.9438	84 ± 0.2



Display Screenshot - Generated On 2020-09-25 13h53m39m

Figure S31. LRMS spectrum (dithranol, CH₂Cl₂) of the sample obtained after quench of monoradical cation **3**^{•+} after 96 h. The spectrum suggested that **3**^{•+} is stable.

Compound 3^{2^{\bullet}2^{+}} (solid state)

To a solution of BICOL derivatives **3** (5 mg, 9.39 μ M) in 10 mL acetonitrile (MeCN) under argon atmosphere, 16.2 mg of magic blue (2.1 equivalent) were added and stirred for 10 minutes under argon atmosphere. Then, 0.5 mL was taken in to 6 separated vials, evaporated under reduced pressure and store at -20 °C. Every 24 hours, each vial was refilled with degassed MeCN and recorded UV-vis-NIR spectrum (**Figure S32**).



Figure S32. UV-vis-NIR absorption spectra of $3^{2 \oplus 2+}$ in acetonitrile under argon atmosphere at 298 K.

G. NMR Spectra



Figure S33. ¹H NMR spectrum of **1** in CD₂Cl₂ at 298 K (400 MHz). * denote traces of water.



Figure S35. ¹³C NMR spectrum of **1** in CD₂Cl₂ at 298 K (100 MHz).









Figure S39. 13 C NMR spectrum of 2 in CD₂Cl₂ at 298 K (100 MHz).







Figure S43. ¹³C NMR spectrum of **3** in CD₂Cl₂ at 298 K (100 MHz).






80 70 F1 (ppm) -1 Figure S47. ¹³C NMR spectrum of 4 in CD₂Cl₂ at 298 K (100 MHz).



H Computational Part

Kohn-Sham Density functional theory (DFT) as implemented in the Gaussian (G16) package [6] was used for all computations, employing the PBE0 functional [7] and the def2-SV(P) basis [8,9]. For neutral and oxidized species, solvent effects were considered by means of the polarizable continuum model (PCM) [10] for dichloromethane and acetonitrile, respectively, to match the experimental conditions. 'D3' dispersion corrections were included in the calculations [11]. Excited state energies, transition moments, excited state structures and their vibrational normal modes were obtained from time-dependent DFT (TD-DFT) response theory. For the absorption and electronic circular dichroism (ECD) spectra we calculated the 200 lowest-energy vertical spin-allowed electronic excitations. The transitions were subsequently Gaussian-broadened with $\sigma = 0.20$ eV to simulate the spectral envelopes. For overviews of the theoretical approach to model natural optical activity by quantum chemical calculations, in particular via TD-DFT, see, for example, References [12,13]. Different functionals and solvent effects were tested for

these compounds; see Figures S73-S76.

For neutral compounds, we calculated the electronic emission and circularly polarized luminescence (CPL) spectra using the first electronic transition in the excited state optimization in gas phase, and followed by Gaussian broadening with $\sigma = 0.2$ eV for the transition. Test calculations including the state-specific solvation correction were performed. The Franck-Condon-Herzberg-Teller (FCHT) approximation [14] was employed for the vibronic intensities, with the optimized structures and harmonic force fields of the ground state and first excited state used as input.

RESULTS

The optimized structures of the carbazole derivatives are shown in **Figure S49**. The dihedral angle between the carbazole units are 76.9° (Expt. 87.1°) for **1**, 52.2° (Expt. 52.4°) for **2** and, 65.5° and 106.6° (Expt. 98-102°) for **3**. Two conformers were found for bicarbazole **3** (see **Figure S50**). The most stable conformer is the one with the smaller dihedral angle (65°). The conformer with a dihedral angle of 106.6° is predicted to be 1.84 kcal·mol⁻¹ higher in energy (Boltzmann population of 4% at 298 K). Therefore, carbazole **3** does not crystallize in its lowest-energy conformer, which is very likely due to a more effective crystal packing favoring the slightly less stable conformer in the solid. When the calculated spectra for the two conformers are compared (*vide infra*), there is a much better match for the 65° conformer, thereby lending strong support for the higher abundance of this conformer in solution.



Figure S49. Optimized structures of carbazole compounds **1**, **2** and **3**. The dihedral angle between the carbazole units are 76.9^o (Expt. 87.1°) for **1**, 52.2° (Expt. 52.4°) for **2** and, 65.5° (Expt. 98-102°) for **3**.



Figure S50. Conformers of **3** with a different dihedral angle; 65.5° (blue) and 106.6° (red).



Figure S51. Experimental (Expt.) and calculated (Calc.) absorption spectra for (+)-**1** (black) and (+)-**2** (red). Selected transitions and oscillator strengths indicated as 'stick spectra'. Predominant excitations are numbered according to **Tables S7-S8**.

	/ /				Â.	9	
Excitation	E [eV]	λ [nm]	f	R [10 ⁻⁴⁰ cgs]	occ. no.	unocc no.	%
#1	3.788	327	0.144	-23.02	111(H)	112(L)	93
#5	4.355	285	0.117	271.87	109	112	91
#6	4.426	280	0.110	-142.64	108	112	88
#9	5.024	247	0.410	694.34	111	114	78
#10	5.062	245	0.243	-374.12	110	114	82
#11	5.146	241	0.300	363.52	110 107	115 112	39 30
#12	5.148	241	0.498	-538.15	111	115	63
#14	5.371	231	0.073	-234.47	106	112	81
#15	5.379	230	0.129	30.08	109	114	58
#17	5.489	226	0.079	-187.98	107	113	79

Table S7. Selected excitations and occupied (occ)-unoccupied (unocc) MO pair contributions (greater than 10%) for (+)-**1**. H and L indicate the HOMO and LUMO, respectively.

Excitation	E [eV]	λ [nm]	f	R [10 ⁻⁴⁰ cgs]	occ. no.	unocc no.	%
#1	3.492	355	0.199	-49.15	106(H)	107(L)	97
#2	3.645	340	0.020	-54.73	105	107	95
#3	4.058	306	0.096	372.62	104	107	94
#5	4.281	290	0.141	-66.46	106	108	75
#7	4.749	261	0.053	104.60	102 106	107 109	61 19
#10	4.978	249	0.104	180.38	103 106 105	108 109 110	38 34 19
#11	4.998	248	0.111	4.45	101 105	107 109	44 43
#13	5.156	240	0.179	615.07	105 103 104	110 108 109	52 19 17
#14	5.202	238	0.742	-805.41	106 104	110 108	56 28
#16	5.440	228	0.169	130.09	104	109	64
#17	5.546	224	0.178	-279.34	102	108	73

Table S8. Selected excitations and occupied (occ)-unoccupied (unocc) MO pair contributions (greater than 10%) for (+)-**2**. H and L indicate the HOMO and LUMO, respectively.



Figure S52. Isosurfaces (± 0.030 au) of Molecular Orbitals (MOs) involved in the selected transitions for (+)-1. Values listed in parentheses are the corresponding orbitals energies in eV.



Figure S53. Isosurfaces (± 0.030 au) of Molecular Orbitals (MOs) involved in the selected transitions for (+)-**2**. Values listed in parentheses are the corresponding orbitals energies in eV.



Figure S54. Experimental (Expt.) and calculated (Calc.) electronic circular dichroism (ECD) spectra for (+)-1 (solid black line) and (+)-2 (solid red line). Corresponding (-)-enantiomers are represented in dashed lines. Selected transitions and rotatory strengths indicated as 'stick spectra'. Predominant excitations are numbered according to **Tables S7-S8**.

Emission and CPL Spectroscopy. The computed normalized emission and circularly polarized luminescence (CPL) spectra of **1** and **2** are displayed in **Figure S55**. The excited state geometries of **1** and **2** show significant differences in the helical carbazoles respect to the ground state geometries (**Figure S56**). For this reason, reasonable Franck-Condon factors could not be obtained. Therefore, the first electronic transition in the excited state optimization in gas phase has been used to plot both simulated spectra, which appears in the following order in the simulated emission and CPL spectra; (+)-1 at 24019 cm⁻¹ and (+)-2 at 23479 cm⁻¹, indicating that the emission of **2** is red shifted from **1**. Experiments also reproduce this order. The calculated spacing between the band maxima of **1** and **2** is 0.067 eV, while for experiments it is 0.106 eV for the emission and 0.136 eV for the CPL, respectively. Thus, calculations in gas phase reasonably agree with experiments (**Figure S56** and **Table S9**). In this case, calculations including the state-specific solvation correction do not match very well with the experimental data.



Figure S55. Calculated emission (left) and circularly polarized luminescence (right) spectra using the first electronic transition in the excited state optimization in gas phase. The intensities are plotted based on Gaussian broadening with $\sigma = 0.2 \ eV$. Corresponding experimental data is indicated in dashed lines.



Figure S56. Overlay of the optimized equilibrium ground state, S_0 , (red) and excited state, S_1 , (blue) structures of carbazoles **1** and **2**.

Table S9. Experimental (Expt.) and calculated emission spectroscopy data for **1** and **2** (in eV). First electronic transition in the excited state optimization in gas phase and vertical emission energy from the first excited state to ground state emission including the state-specific (SS-PCM) solvation correction.

Carbazole	Expt. ν̃	S_0-S_1	S_0-S_1 (SS-PCM)
1	3.073	2.978	2.794
2	2.967	2.911	2.860

Electrochemistry and radical 1++



Figure S57. Orbital energies (in eV) and isosurfaces of frontier molecular orbitals computed for the neutral (+)-1 (left) and the monoradical (+)- 1^{+} (right). Isosurfaces of ± 0.030 au for the neutral and the monoradical.

The total spin S² expectation value before annihilation is 0.761 for **1**•+ and 0.764 for **2**•+, with 0.750 being the correct number for a doublet. Although some spin contamination exists, it is not large for either compound.



Figure S58. Orbital energies (in eV) and isosurfaces of frontier molecular orbitals computed for neutral (+)-2 (left) and the monoradical (+)- 2^{+} (right). Isosurfaces of ± 0.030 au for the neutral and the monoradical.



Figure S59. Experimental (Expt.) and calculated (Calc.) absorption spectra for (+)-1 in neutral (black) and monoradical (red) forms. Selected transitions and oscillator strengths indicated as 'stick spectra'. Predominant transitions for the monoradical are numbered according to **Table S10**.

Excitation	E [eV]	λ [nm]	f	R [10 ⁻⁴⁰ cgs]	occ. no.	unocc no.	%
#4	1.694	732	0.047	-24.68	107β	$111\beta(L)$	93
#5	1.889	657	0.090	17.76	106β	111β	90
#10	3.138	395	0.048	7.33	102 <i>β</i>	111β	73
#15	3.692	336	0.021	-21.62	109α(S)	112α	55
#18	3.770	329	0.070	-10.91	110β 111α	113β 113α	48 33
#22	4.050	306	0.024	13.73	108β	112 <i>β</i>	13
#24	4.225	293	0.031	34.67	109β	112 <i>β</i>	66
#30	4.456	278	0.066	32.75	109β 110α	113β 113α	41 24
#39	4.764	260	0.503	168.87	108β 108α	112β 112α	26 21
#45	4.962	250	0.586	-68.42	110β 111α	115β 115α	32 22

Table S10. Selected excitations and occupied (occ)-unoccupied (unocc) MO pair contributions (greater than 10%) for (+)-**1**•+. S and L indicate the SOMO and LUMO, respectively.



Figure S60. Experimental (Expt.) and calculated (Calc.) ECD spectra for (+)-1 in neutral (black) and monoradical (red) forms. Selected transitions and rotatory strengths for the monoradical are indicated as 'stick spectra'. Predominant transitions for the monoradical are numbered according to **Table S10**. *M*-enantiomers are represented in dashed lines.



Figure S62. Isosurfaces (± 0.030 au) of Molecular Orbitals (MOs) involved in the selected transitions for (+)-**2**^{•+}. Values listed in parentheses are the corresponding orbitals energies in eV.

Diradical 3²⁺ and related characterization

Two conformers with different dihedral angle between the carbazole fragments were found in the calculations for bicarbazole **3** and its corresponding radicals **3**^{•+} and **3**^{2•2+} (see **Scheme S50** and **Table S11**). All these species of **Table S11** were characterized as minima. For **3**, **3**^{•+} and **3**^{2•2+}, the most stable conformer is the one with the smaller dihedral angle of about 60-65° (**Table S11**).

For **3**•+, the loss of one electron reduces the torsion angle from 65° to 60° . This conformer is 3.0 kcal·mol⁻¹ lower in energy than the other conformer with a dihedral of 118°. The calculated Boltzmann population at 298 K for the latter conformer is therefore low, around 0.6%. In the case of **3**²•²+, the spin-triplet conformer with a dihedral angle of 64° is predicted to be the lowest in energy, followed by the spin-triplet conformer with a dihedral of 112° at 2.63 kcal·mol⁻¹ (Boltzmann population at 298 K of 1.2%). Both conformers with a spin-singlet electronic configuration are higher in energy with a negligible Boltzmann population at 298 K (see **Table S11**).

Table S11. Dihedral angle (in degrees) between the carbazole segments, relative energies (in kcal·mol⁻¹) and Boltzmann population ratio at 298 K (in %) for the different systems of (+)-**3** in neutral, monoradical and diradical forms. For (+)-**3²⁻²⁺**, the spin multiplicity state is also indicated.

Carbazole	Dihedral angle (°)	Erel (kcal·mol-1)	Boltzmann population at 298 K (%)
(+)-3			
	65	0.00	95.7
	106	1.84	4.3
(+)-3+			
	60	0.00	99.4
	118	3.00	0.6
(+)-32+			
Singlet	55	8.87	3.1.10-5
Triplet	64	0.00	98.8
Singlet	131	12.74	4.5·10 ⁻⁸
Triplet	112	2.63	1.2

Figures S63-S64 show the isosurfaces of the frontier molecular orbitals and their energies for **3**, **3**⁺⁺ and **3**²•²⁺. Like **1** and **2**, neutral carbazole **3** is a closed-shell system with a small energetic splitting (0.191 eV) between HOMO and HOMO-1 from in-phase and out-of-phase FFO linear combinations. The HOMO and HOMO-1 present π -orbitals of the conjugated carbazole system, including some contributions on the nitrogen and oxygen atoms. As seen in **Figure S64**, molecular orbitals of **3** are expanded over the two carbazolyl moieties.

As for **1**^{•+} and **2**^{•+}, the calculated spin densities of **3**^{•+} are also represented by spin-polarized KS systems where the α -spin HOMO has a matching occupied β -spin HOMO, with both having very similar orbital energies. The 'non-Aufbau' SOMO-HOMO inversion is also observed in **3**^{•+}, along with a degree of localization of the MOs on the fragments upon ionization (**Figure S63**). The LUMO density corresponds closely to the calculated spin density (**Figure S65**). Therefore, the LUMO represents the β -spin 'electron hole' in the system. The spin contamination of **3**^{•+} is somewhat more pronounced, with an S² expectation value of 0.766, but still acceptable.



Figure S63. Orbital energies (in eV) and isosurfaces of frontier molecular orbitals computed for the neutral (+)-**3** (left) and monoradical (+)-**3**•+ (right). Isosurfaces of ± 0.030 au for the neutral and the radical.



Figure S64. Orbital energies (in eV) and isosurfaces (± 0.030 au) of frontier molecular orbitals computed for the diradical (+)-**3²**·**2**+.



Figure S65. (Left) DFT-optimized structure of (+)-**3**⁺. (Right) Calculated spin density for (+)-**3**⁺ and (+)-**3**²²⁺. Isosurfaces of ± 0.002 au.

Absorption Spectroscopy. The experimental and simulated absorption spectra for **3**, **3**⁺ and **3**²²+ are shown in **Figure S66**. The calculations were performed using the lowest-energy conformer in each case. Calculations agree reasonably well with the experiments, after accounting for blue shifts of 0.1-0.4 eV.

As in **1** and **2**, three spectral bands are observed for **3**. The assigned transitions for the two lowestenergy bands are qualitatively the same for **1** and **3**, thus only the main differences are for the strong absorption band at 240-250 nm. **Figure S67** shows the corresponding molecular orbitals of **3** associated to the most intense excitations (**Table S12**). With the exception of the HOMO-2 and HOMO-3, the isosurfaces of the molecular orbitals are delocalized over the two carbazole moieties. The lowest-energy excitation at 367 nm corresponds to the HOMO-LUMO transition, where the HOMO is localized on the π -conjugated system including the nitrogen and oxygen atoms and the LUMO only on the π -conjugated system excluding the nitrogen and oxygen atoms. The second lowest-energy band at 295 nm is due to transitions #5 and #6 corresponding to HOMO-2 to LUMO and HOMO-3 to LUMO transitions, respectively. HOMO-2 and HOMO-3 are near-degenerate in energy, with a very small energetic splitting of 0.060 eV, resulting as in-phase and out-of-phase FFO combinations. A combination of several excitations, in particular #13 and #14 showing the highest oscillator strengths, creates the strong absorption band at 250 nm, involving different $\pi \rightarrow \pi^*$ electronic transitions between the carbazolyl units. Note that similar simulated absorption spectra are observed for the two conformers of **3** with different dihedral angle (**Figure S68**).



Figure S66. Experimental (Expt.) and calculated (Calc.) absorption spectra for (+)-**3** in neutral (black), monoradical (red) and diradical (blue) forms. Selected transitions and oscillator strengths indicated as 'stick spectra'. Predominant transitions are numbered according to **Tables S12-S14**.

For **3**⁺, the calculated absorption spectra appear significantly modified. Excitations #1 and #4 cause two low-energy bands at 3179 (not observed) and 812 nm, respectively, in the simulated UV/Vis spectra of **3**⁺ due to $\pi \rightarrow \pi^*$ electronic transitions to the β 'electron hole' LUMO (**Figure**

S67 and **Table S13**). The third band of **3**•+ at 397 nm corresponds to the first lowest-energy band of **3** at 367 nm, which remains unchanged but notably red shifted by 0.260 eV. In **3**•+, we also observe a wide absorption band at 250 nm caused by several transitions, but predominantly for excitation #53 which again is attributed to a transition to the β 'electron hole' LUMO. Furthermore, this band presents a slight decrease in intensity and the broadness includes the corresponding peak at 290 nm of the neutral.

For **3^{2•2+}**, the absorption spectra seem to be also slightly changed, but showing similar features as **3•+**. Two low-energy bands at 1200 nm and 700 nm appear, caused by excitations to the LUMO and LUMO+1 (**Figure S68** and **Table S14**). These two first excitations are blue shifted by 0.641 and 0.252 eV, respectively, for **3^{2•2+}** compared to **3•+**. The band at 375 nm also remains unchanged in **3^{2•2+}**, whereas the band at 260 nm is slightly weaker and wider due to excitations #41 and #55, which overlaps the absorption band at 250 and 290 nm of the neutral compound **3**.



Figure S67. Isosurfaces (± 0.030 au) of Molecular Orbitals (MOs) involved in the selected transitions for (+)-**3**. Values listed in parentheses are the corresponding orbitals energies in eV.



Figure S68. Calculated absorption spectra for the two conformers with different dihedral angles of (+)-3.



Figure S69. Isosurfaces (± 0.030 au) of Molecular Orbitals (MOs) involved in the selected transitions for (+)-**3**•+. Values listed in parentheses are the corresponding orbitals energies in eV.



Figure S70. Isosurfaces (± 0.030 au) of Molecular Orbitals (MOs) involved in the selected transitions for (+)-**3²⁻²⁺**. Values listed in parentheses are the corresponding orbitals energies in eV.

Excitation	E [eV]	λ [nm]	f	R [10 ⁻⁴⁰ cgs]	occ. no.	unocc no.	%
#1	3.381	367	0.144	-36.23	143(H)	144(L)	98
#5	4.166	298	0.100	271.50	141	144	88
#6	4.231	293	0.145	-120.64	140	144	86
#10	4.846	256	0.167	475.04	143 140	146 145	35 32
#11	4.871	255	0.183	-25.64	138 142	144 146	42 40
#12	4.911	252	0.153	-95.38	143	147	62
#13	4.992	248	0.436	-307.56	138 142 140	144 147 145	25 18 17
#14	5.013	247	0.368	86.73	142	147	65
#15	5.262	236	0.146	-273.85	139	145	79

Table S12. Selected excitations and occupied (occ)-unoccupied (unocc) MO pair contributions (greater than 15%) for (+)-**3**. H and L indicate the HOMO and LUMO, respectively.

Table S13. Selected excitations and occupied (occ)-unoccupied (unocc) MO pair contributions (greater than 15%) for (+)-**3**•+. S and L indicate the SOMO and LUMO, respectively.

Excitation	E [eV]	$\lambda \left[nm ight]$	f	R [10-40 cgs]	occ. no.	unocc no.	%
#1	0.390	3179	0.038	-41.47	142 <i>β</i>	$143\beta(L)$	100
#4	1.528	812	0.102	-72.90	139β	143 <i>β</i>	88
#5	1.746	710	0.032	47.34	138β	143 <i>β</i>	96
#11	3.121	397	0.067	-10.56	143α	144α	27
#14	3.512	353	0.030	-69.46	$142\alpha(S)$	144α	59
#24	3.999	310	0.067	74.24	141lpha $141eta$	144α 144β	37 23
#32	4.280	290	0.114	98.39	140lpha $140eta$	144 lpha 144 eta	36 33
#39	4.570	271	0.039	122.69	139α 139β	144 lpha 144 eta	32 18
#46	4.828	257	0.046	179.80	138β 138α	144β 144α	24 23
#53	4.997	248	0.182	-191.36	119β	143 <i>β</i>	17
#54	5.028	247	0.048	150.91	$142eta \\ 140eta$	148β 145β	19 18

Excitation	E [eV]	λ [nm]	f	R [10 ⁻⁴⁰ cgs]	occ. no.	unocc no.	%
#1	1.031	1203	0.014	47.15	141eta $141eta$	142β(L) 143β	64 27
#2	1.102	1125	0.019	-42.52	140β 140β	142β 143β	58 29
#3	1.563	793	0.060	145.32	139β	142β	77
#6	1.780	697	0.158	-174.43	138β	142β	68
#13	3.273	379	0.061	-9.46	143α(S)	144α	15
#15	3.332	372	0.056	7.83	143α	144α	57
#41	4.254	291	0.104	148.25	141lpha $141eta$	144lpha $144eta$	37 27
#48	4.546	273	0.099	156.59	143α	146α	18
#49	4.567	272	0.091	19.81	143α	147α	11
#55	4.711	263	0.206	-95.33	141α	145α	19

Table S14. Selected excitations and occupied (occ)-unoccupied (unocc) MO pair contributions (greater than 10%) for (+)-**3²⁻²⁺**. S and L indicate the SOMO and LUMO, respectively.

ECD Spectroscopy. The experimental and calculated ECD spectra of **3** and **3**⁺ are displayed in **Figure S71**. Calculations reproduce very well the experiments, having some calculated bands blue shifted by 0.1 eV, which is usual in the TD-DFT calculations. Here we discuss the ECD for the (+) or *P* enantiomers. Test calculations on the ECD spectra were performed by the two conformers with different dihedral angle for each system (**Figure S72**). We note that the ECD spectra of the conformer with a large torsion angle show some similar peaks as experiments but some with a different sign. Thus, we proceed to analyze the calculations for the lowest-energy conformers of (+)-**3** and (+)-**3**⁺, which are the ones that better agree with experiments.

The UV/vis and ECD spectra of (+)-**3** share the same electronic transitions. Additionally, excitations #10 at 256 nm and #15 at 236 nm become actives in the ECD spectra.

The one-electron oxidation of **3** leads to few modifications of the ECD spectrum, mostly due to a wide and weaker band between 250 and 320 nm, involving several $\pi \rightarrow \pi^*$ transitions to the α -LUMO and β -LUMO+1 (**Table S13**). Once again, the new long-wavelength bands in the absorption spectra of the monoradical are negligible in the ECD spectrum.



Figure S71. Experimental (Expt.) and calculated (Calc.) ECD spectra for (+)-**3** in neutral (black) and monoradical (red) forms. Selected transitions and rotatory strengths for the radicals are indicated as 'stick spectra'. Predominant transitions are numbered according to **Tables S12** and **S13**. *M*-enantiomers are represented in dashed lines.



Figure S72. Calculated ECD spectra for the two different conformers of (+)-**3** (left) and (+)-**3**⁺ (right). Conformer with a dihedral angle of 110° is plotted in purple for both systems, while the other conformer (65°) appears in black and red for (+)-**3** and (+)-**3**⁺, respectively.



Figure S73. Experimental (Expt.) and calculated absorption spectra for **1** (red), **2** (orange) and **3** (green). Test calculations varying the functional: B3LYP, CAMB3LYP, M06-HF, PBE0 and TPSSh.



Figure S74. Calculated absorption spectra for 1, 2 and 3 derivatives. Test on functionals and solvent effects.



Figure S75. Experimental (Expt.) and calculated ECD spectra for **1** (red), **2** (orange) and **3** (green). Test calculations varying the functional: B3LYP, CAMB3LYP, M06-HF, PBE0 and TPSSh.



Figure S76. Calculated ECD spectra for 1, 2 and 3 derivatives. Test on functionals and solvent effects.



Figure S77. Orbital energies (in eV) and isosurfaces (± 0.030 au) of some molecular orbitals for **1**•+.



Figure S78. Orbital energies (in eV) and isosurfaces (± 0.030 au) of some molecular orbitals for **2**+.



Figure S79. Orbital energies (in eV) and isosurfaces (± 0.030 au) of some molecular orbitals for **3**+.

Table S15. Relative energies (in eV) for a model of (+)-**1**⁺⁺ varying the dihedral angle from 40° to 140°. The model of (+)-**1**⁺⁺ replaces the methyl groups of both methoxy groups by hydrogens. Data from single points calculations of model of (+)-**1**⁺⁺.

Dihedral angle (°)	Relative energy (eV)
40	1.18
60	0.01
73.5	0.00
80	0.02
100	0.07
120	0.43
140	6.48

Table S16. Orbital energies (in eV) for a model of (+)-**1**⁺⁺ varying the dihedral angle. The model of (+)-**1**⁺ replaces the methyl groups of both methoxy groups by hydrogens. Data from single points calculations of model (+)-**1**⁺⁺. Energies for the SOMO, HOMO, and β -LUMO, and energy differences between the SOMO/HOMO and SOMO/ β -LUMO. The corresponding MOs are displayed in **Figures S80-S86**.

Dihedral angle (°)	SOMO	HOMO	β-LUMO	SOMO/HOMO	SOMO/β-LUMO
40	-6.92	-6.16	-4.78	0.77	2.14
60	-6.86	-6.11	-4.88	0.75	1.98
73.5	-6.92	-6.04	-4.92	0.88	2.00
80	-6.95	-6.02	-4.94	0.94	2.02
100	-6.96	-6.03	-4.95	0.93	2.02
120	-6.85	-6.19	-4.90	0.66	1.95
140	-6.20	-6.67	-4.68	-0.47	1.52



Figure S80. Orbital energies (in eV) and isosurfaces (± 0.030 au) of model **1**^{•+}, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model (+)-**1**^{•+} with a dihedral angle of 73.5°, that it is the optimal in **1**^{•+} system.



Figure S81. Orbital energies (in eV) and isosurfaces (± 0.030 au) of model **1**⁺⁺, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model (+)-**1**⁺⁺ with a dihedral angle of 40°.



Figure S82. Orbital energies (in eV) and isosurfaces (± 0.030 au) of model 1^{•+}, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model (+)-1^{•+} with a dihedral angle of 60°.



Figure S83. Orbital energies (in eV) and isosurfaces (± 0.030 au) of model 1^{•+}, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model (+)-1^{•+} with a dihedral angle of 80°.



Figure S84. Orbital energies (in eV) and isosurfaces (± 0.030 au) of model **1**⁺⁺, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model (+)-**1**⁺⁺ with a dihedral angle of 100°.



Figure S85. Orbital energies (in eV) and isosurfaces (± 0.030 au) of model **1**⁺⁺, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model (+)-**1**⁺⁺ with a dihedral angle of 120°.



Figure S86. Orbital energies (in eV) and isosurfaces (± 0.030 au) of model 1^{•+}, where the methyl groups of both methoxy groups are replaced by hydrogens. Data from a single point calculation of model (+)-1^{•+} with a dihedral angle of 140°.

Table S17. Relative energies (in eV) for a model of (+)-1+ varying the dihedral angle. The model
of (+)-1+ replaces the methyl groups of both methoxy groups by hydrogens. Data from partial
optimizations of the geometry (i.e. constraining the dihedral angle).

	0
Dihedral angle (°)	Relative energy (eV)
40	0.02
60	0.00
73.5	0.01
80	0.03
100	0.04
120	0.01
140	0.06

Table S18. Orbital energies (in eV) for a model of (+)-**1**⁺⁺ varying the dihedral angle. The model of (+)-**1**⁺ replaces the methyl groups of both methoxy groups by hydrogens. Data from partial optimizations of the geometry (i.e. constraining the dihedral angle). Energies for the SOMO, HOMO, and β -LUMO, and energy differences between the SOMO/HOMO and SOMO/ β -LUMO. The corresponding MOs are displayed in **Figures S87**.

Dihedral angle (°)	SOMO	HOMO	β-LUMO	SOMO/HOMO	SOMO/β-LUMO
40	-6.86	-6.20	-4.82	0.66	2.04
60	-6.86	-6.10	-4.85	0.75	2.00
73.5	-6.88	-6.06	-4.87	0.82	2.01
80	-6.90	-6.04	-4.88	0.86	2.02
100	-6.92	-6.01	-4.89	0.91	2.03
120	-6.92	-6.10	-4.86	0.82	2.06
140	-6.73	-6.19	-4.81	0.54	1.91



Figure S87. Orbital energies (in eV) and isosurfaces (± 0.030 au) of model **1**°+, which the methyl groups of both methoxy groups are replaced by hydrogens. Data from partial optimizations of the geometry (i.e. constraining the dihedral angle). Dihedral angles of a) 40°, b) 60°, c) 73.6°, d) 80°, e) 100°, f) 120°, and g) 140°.



Figure S88. Orbital energies (in eV) and isosurfaces (± 0.030 au) of **1**⁺⁺. Test on different functionals and solvent effects; a) PBE0/PCM, b) PBE0/gas phase, c) PBE/PCM, d) HF/PCM, e) B3LYP/PCM, and f) CAMB3LYP/PCM.

Figure S89. Orbital energies (in eV) and isosurfaces (± 0.030 au) of **2**⁺. Test on different functionals; a) PBE0, b) B3LYP, and c) CAMB3LYP.

REFERENCES

- a) Peter N. M. Botman, M. Postma, J. Fraanje, K. Goubitz, H. Schenk, Jan H. v. Maarseveen, H. Hiemstra, *Eur. J. Org. Chem.* 2002, *2002*, 1952-1955.; b) R. Hoen, University of Groningen (Wöhrmann Print Service, Zutphen, the Netherlands), 2006.
- [2] S. Lin, X. He, J. Meng, H. Gu, P. Zhang, J. Wu, Eur. J. Org. Chem. 2017, 2017, 443-447.
- [3] S. K. Ku, J. H. Lee, Y. O, W. Lee, G. Y. Song, J. S. Bae, *Bioorg. Med. Chem. Lett.* **2015**, *25*, 4304-4307.
- [4] Y. Li, A. Urbas, Q. Li, J. Am. Chem. Soc. 2012, 134, 9573-9576.
- [5] N. G. Connelly, W. E. Geiger, *Chem. Rev.* 1996, *96*, 877-910.
- [6] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al. "Gaussian 16, Revision B.01", Gaussian, Inc.,
- Wallingford CT, 2016. URL: www.gaussian.com.
- [7] C. Adamo, V. Barone, J. Chem. Phys., 1999, 110, 6158-69.
- [8] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, 7, 3297-305.
- [9] F. Weigend, Phys. Chem. Chem. Phys., 2006, 8, 1057-65.
- [10] G. Scalmani, M. J. Frisch, J. Chem. Phys., 2010, 132, 114110.
- [11] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.
- [12] M. Srebro-Hooper, J. Autschbach, Annu. Rev. Phys. Chem., 2017, 68, 399–420.
- [13] J. Autschbach, L. Nitsch-Velasquez, M. Rudolph, Top. Curr. Chem., 2011, 298, 1–98.
- [14] F. Santoro, A. Lami, R. Improta, J. Bloino, V. Barone, J. Chem. Phys., 2008, 128, 224311.

V W7	coord	lina	toc
худ	COOLD	una	tes

(+)-1			
C	-3.045292	1.191358	-1.919390
н С	-3.967738	1.212//1	-2.504146
Н	5.474879	-0.137294	1.339214
Н	5.597007	-1.544892	0.260001
Н	4.873614	-1.735655	1.889651
N	3.684059	-0.738149	0.451240
C	3 51 5703	-2.504270	-0.578205
H	4.484655	-2.968937	-1.128105
С	2.689194	-2.990568	-2.335176
H	3.024953	-3.843921	-2.932648
н	1.434954	-2.412587	-2.598650
C	0.979105	-1.333297	-1.848137
Н	0.001581	-0.888254	-2.049353
С	1.790216	-0.824039	-0.824787
C	1.649548	0.250758	0.131475
C	0.838093	2.110918	1.416074
Č	2.020309	2.100923	2.176056
Н	2.124383	2.845606	2.970006
C	3.034543	1.180659	1.934517
H C	3.945085	1.185622	2.538054
0	-0.115963	3 049801	1 692066
č	-0.966062	-1.351427	1.830506
Н	0.010646	-0.904767	2.032235
С	-1.777587	-0.843458	0.806850
C	-1.643122	0.238720	-0.141898
C	-0.632/18	1.183837	-0.388043
C	-4.971503	-1.055298	-1.005977
H	-5.214462	-2.118482	-0.858698
Н	-4.999266	-0.852468	-2.088199
Н	-5.745958	-0.441596	-0.509497
С н	-1.098990	2.632805	2.614139
Н	-1.805079	3.469115	2.735659
Н	-0.650193	2.391725	3.597716
Ν	-3.656978	-0.781656	-0.491801
С	-3.044853	-1.437268	0.555922
С н	-3.507120	-2.516910	1.317065
C	-2.680481	-3.001627	2.326801
Ĥ	-3.021853	-3.845504	2.934465
С	-1.422829	-2.428235	2.584064
H	-0.798726	-2.833036	3.386120
с н	-2.038929	2.122942	-2.150303
C	-0.850974	2.125518	-1.399277
0	0.094066	3.077222	-1.662304
С	1.079104	2.682113	-2.591803
Н	1.635146	1.792937	-2.237944
н н	1.778856	3.525420	-2.700978
	0.050750	2.155005	5.57 6551
(+)- 2			
0	-0.330682	3.527570	-1.120543
U N	0.330682	3.52/5/0	1.120543
N	3.647669	-0.737802	0.119551
C	0.000000	4.298611	0.000000
Н	-0.849238	4.926261	0.323438
Н	0.849238	4.926261	-0.323438
C	-1.190973	2.482764	-0.888224
C	-2 499542	2.462/64	-1 380403
č	2.499542	2.556962	1.380403
Н	-2.801613	3.459406	-1.917947
Н	2.801613	3.459406	1.917947
C	-3.389061	1.504348	-1.196007
с н	3.389061	1.504348	1.196007
Н	4.408475	1.563387	1.583660
С	-2.943593	0.395044	-0.471609
С	2.943593	0.395044	0.471609
C	-1.624090	0.315174	0.052554
L C	1.024090 -0.708755	0.315174	-0.052554 -0.208520
C	0.708755	1.354355	0.208529
C	-2.844752	-1.527218	0.675480

С	2 844752	-1.527218	-0.675480
C	-3.147612	-2.740328	1.304826
C	3 1 4 7 6 1 3	-2.740328	-1.304826
Ĥ	-4.131295	-3.205394	1.204585
Н	4.131295	-3.205394	-1.204585
С	-2.157747	-3.335247	2.080307
Н	-2.372242	-4.283714	2.582564
С	-0.895530	-2.736875	2.239228
Н	-0.141134	-3.224212	2.863661
С	-0.596530	-1.532401	1.612356
С	0.596530	-1.532401	-1.612356
Н	0.383958	-1.070609	1.743226
Н	-0.383958	-1.070609	-1.743227
С	-1.569212	-0.914524	0.813472
С	1.569212	-0.914524	-0.813472
С	-5.029757	-0.981139	-0.433018
С	5.029757	-0.981139	0.433018
Н	-5.709767	-0.473645	0.276127
Н	5.709767	-0.473646	-0.276127
Н	-5.231212	-2.062217	-0.404636
Н	5.231212	-2.062218	0.404637
Н	-5.250883	-0.626531	-1.452264
Н	5.250883	-0.626530	1.452264
С	2.157747	-3.335247	-2.080307
Н	2.372242	-4.283714	-2.582564
С	0.895530	-2.736875	-2.239228
Н	0.141134	-3.224212	-2.863661
	_		
(+)-	3		
C	-3.106516	-2.832434	-0.188599
Н	-3.901657	-3.437234	-0.628046
C	-3.069791	-1.443313	-0.411133
0	-3.975415	-0.789574	-1.175342
C	-5.065485	-1.492487	-1.702344
H	-4.746744	-2.281943	-2.410385
H	-5.676863	-0.756222	-2.245750
H	-5.681953	-1.952028	-0.905721
L C	-2.045567	-0.652469	0.13996/
L C	-1.995469	0.804518	-0.132565
L C	-0.966508	1.380/39	-0.894059
C	0.200005	0.030002	1 720264
с п	0.709964	1 20 4 1 0 1	-1./20204
С	0.144494	-1.294101	-1.519219
C	2.621506	-0.005/30	2.334291
с н	2.031390	0.326570	-2.04/302
C	2 144297	1 758463	-3.343200
с u	2.144257	2 600640	2 111227
C	0.021010	1 946769	-2.073764
N	0.221203	2 1 1 0 2 0 2	1 707790
C	-0.894957	2 788646	-1.757780
c	-1.855335	2.700040	-0.507877
ц	-1.0555555	1 71 4 91 9	-0.507077
C	-2 890881	3 052809	0.227046
н	-3 641769	3 708752	0.670860
C	-2.963179	1 661537	0 423582
Č	2.488772	-2.093646	-2.441531
Ċ	2.710777	-2.627650	-1.016085
Н	3.115749	-3.656207	-1.045124
Н	1.771517	-2.648630	-0.436885
Н	3.423835	-1.989808	-0.464135
С	1.480751	-2.996711	-3.170347
Н	1.865475	-4.031097	-3.233202
Н	1.298703	-2.634544	-4.197840
Н	0.510001	-3.032978	-2.646404
С	3.820936	-2.157195	-3.193127
Н	4.604344	-1.564449	-2.689325
Н	3.723446	-1.791219	-4.230440
Н	4.173719	-3.202618	-3.238847
С	0.681835	4.445645	-2.078027
Н	-0.179245	5.087438	-2.325406
Н	1.353825	4.436646	-2.949399
Н	1.220297	4.890264	-1.219277
0	-3.923248	1.066031	1.168698
C	-4.951028	1.844037	1.715046
H	-4.567006	2.588962	2.438781
H	-5.619501	1.148402	2.244550
H	-5.529708	2.370062	0.931281
C	-2.127664	-3.4/1556	0.571708
н с	-2.165369	-4.554468	0./11567
с С	-1.109885	-2.696352	1.122354
с С	-1.066/26	-1.291069	0.919209
с С	0.133869	-0.828938	1.582622
с II	0.757505	0.420175	1.093395
н	0.262984	1.288403	1.262932

С	2.002033	0.543739	2.306396
С	2.591310	-0.620805	2.852445
Н	3.569480	-0.551388	3.338318
C H	1.989259	-1.872049	2.786333
н С	2.488770	-2./4/493	3.208740
N	-0.020931	-3.087014	1.882830
C	2.760318	1.874316	2.340060
Č	4.056681	1.723019	1.525751
Н	3.827856	1.453140	0.478921
Н	4.711647	0.938387	1.942712
Н	4.625640	2.671027	1.522744
C	1.945139	3.016224	1.724137
H	1.708943	2.825413	0.662464
п ц	2.524028	3.955454	2 262472
C	3 101654	2 251435	2.202472
H	3.660662	3.204523	3.819662
Н	3.725450	1.483618	4.278994
Н	2.182059	2.373621	4.389262
С	0.319947	-4.445330	2.201567
Н	0.956409	-4.467772	3.099145
H	0.858581	-4.942528	1.372370
н	-0.593503	-5.019826	2.424356
(+)-	1+		
È ĺ	-3.255041	0.804931	-1.901485
Н	-4.214957	0.684645	-2.405882
С	4.793080	-1.276754	0.930469
Н	5.358824	-0.366398	1.183034
H	5.394811	-1.858172	0.216305
п N	4.051575	-1.0/3529	1.040700
C	2 872005	-1.628146	-0.648227
č	3.257016	-2.803503	-1.304927
H	4.194908	-3.310014	-1.065669
С	2.401881	-3.316122	-2.274921
Н	2.682959	-4.234108	-2.800077
С	1.186667	-2.682756	-2.592637
H	0.538630	-3.111780	-3.362112
с u	0.800562	-1.519/66	-1.935204
C	1 640463	-0.982403	-0.949315
č	1.569042	0.169325	-0.080611
C	0.613638	1.177512	0.115828
С	0.858025	2.159961	1.088501
С	2.037349	2.131170	1.854413
Н	2.218029	2.893949	2.613173
C U	2.988914	1.131278	1.669607
C	2 756611	0.158940	0.695828
õ	-0.101429	3.103249	1.211180
C	-0.718987	-1.052664	2.004629
Н	0.243594	-0.544442	2.081677
С	-1.621881	-0.738844	0.989577
C	-1.632644	0.203822	-0.121239
C	-0.698302	1.126603	-0.5/2450
c	-4 924354	-1 408613	-0.475272
Н	-4.892336	-2.497772	-0.639412
Н	-5.281605	-0.919524	-1.389753
Н	-5.620626	-1.186879	0.350284
С	0.030908	4.103526	2.193179
Н	0.078051	3.666739	3.207612
H	-0.866845	4.733126	2.112663
H N	2 602202	4./2/252	2.019555
C	-2.859321	-1.419360	0.935041
Č	-3.220158	-2.402337	1.848664
Н	-4.181432	-2.917093	1.791147
С	-2.297775	-2.705689	2.855157
H	-2.545457	-3.474301	3.592322
C	-1.071063	-2.039859	2.933335
н с	-0.370370	-2.293924	3./33191
Ч	-2.558518	2.358786	-3.206717
C	-1.074006	1.910295	-1.711258
0	-0.342854	2.816615	-2.321543
С	0.937557	3.277780	-1.913752
Н	0.860851	3.787630	-0.941902
H	1.243889	3.991597	-2.690214
н	1.657816	2.447304	-1.859571

0	-0.822954	3.834022	0.944415
0	0.464891	3.727165	-1.021138
N N	-3.490987	-0.816239	0.144649
C	0.276432	4.352847	0.188789
Н	0.004651	5.399900	-0.002639
Н	1.171744	4.287471	0.831350
C	-1.378424	2.648496	0.784739
C	-2.677332	2.555506	1.358138
С	2.487624	2.546822	-1.476119
Н	-3.052316	3.435923	1.883596
п С	-3.439864	1.424696	1.231199
Č	3.292573	1.422999	-1.324158
Н	-4.436199	1.375553	1.673089
H	4.288967	1.394932	-1.769812
C	2.807027	0.366061	-0.548387
Č	-1.592247	0.418131	-0.093294
С	1.514702	0.395025	0.045750
C	-0.762047	1.516466	0.144639
C	-2.629625	-1.547304	-0.666000
Č	2.622735	-1.522567	0.632318
С	-2.856375	-2.790647	-1.250831
С ц	2.871060	-2.749062	1.263714
Н	3.809117	-3.287788	1.112814
С	-1.849849	-3.302600	-2.070888
Н	-1.990109	-4.276767	-2.547003
C	-0.674127	-2.579120	-2.301856
п С	-0.456239	-2.993400	-2.962443
Č	0.443254	-1.338810	1.705408
Н	0.465791	-0.788019	-1.901759
H	-0.485302	-0.800050	1.903863
C C	-1.435163	-0.813801	-0.855388
č	-4.806161	-1.273812	0.526161
С	4.777807	-1.181458	-0.597758
Н	-5.433916	-1.397888	-0.371543
н Н	-4 723821	-0.81//23	0.129213
Н	4.850648	-2.276923	-0.668427
Н	-5.278313	-0.546465	1.197613
H	5.009503	-0.765736	-1.589611
H	2.057568	-3.255505	2.6101122
С	0.687764	-2.553001	2.331992
Н	-0.059376	-2.970309	3.012818
(+)	-3+		
Ċ	-3.169407	-2.813474	-0.591792
H	-3.989792	-3.335417	-1.085909
0	-3.997631	-0.639059	-0.604972
Č	-5.160659	-1.211340	-1.804930
Η	-4.915575	-1.907850	-2.627126
H U	-5.751282	-0.375370	-2.205679
п С	-2.050798	-0.712300	0.030810
Č	-2.035003	0.757444	-0.020371
С	-1.016630	1.494095	-0.620914
C	0.196587	1.132200	-1.333239
н	0.794127	-0.070921	-1.693490
С	2.042373	-0.081500	-2.338320
С	2.657245	1.152272	-2.631503
H	3.626689	1.171531	-3.131635
с Н	2.074749	2.375151	-2.546215
С	0.842909	2.351237	-1.651610
Ν	0.074286	3.409471	-1.206070
C	-1.039192	2.919033	-0.581956
с Н	-2.095393	3.020845 4 711930	0.020/16
C	-3.119602	2.897382	0.605537
Н	-3.938389	3.434357	1.085302
C	-3.093995	1.485778	0.613699
C C	2.703398	-1.426562	-2.046419
Ĥ	3.495870	-3.106488	-1.498337
Η	2.091615	-2.316926	-0.727799
Н	3.683553	-1.520417	-0.688607

(+)-**2+**

С	1.748910	-2.296882	-3.480187		
Ĥ	2.222104	-3.269940	-3.702179		
Н	1.503949	-1.806940	-4.439066		
Н	0.803488	-2.502060	-2.949427		
С	4.013536	-1.267985	-3.422180		
Ĥ	4.766960	-0.702953	-2.846547		
н	3 858072	-0.757221	-4.388641		
Н	4.439202	-2.263961	-3.634395		
C	0.443972	4.794458	-1.365325		
Ĥ	-0.381396	5.442544	-1.044321		
н	0.666242	5 002645	-2 424256		
н	1 336443	5 022416	-0.757826		
0	-3.991157	0.745185	1.247736		
Č	-5.124735	1.335733	1.850566		
н	-4 829359	2.010494	2 672928		
н	-5.717266	0.504216	2,255676		
н	-5.724635	1 888028	1.106464		
Ċ	-2 170984	-3 561076	0.019973		
н	-2 221585	-4 651807	0.000755		
c	-1 111845	-2 887859	0.636221		
c	-1.046669	-1 467947	0.654547		
c	0.167461	-1 132796	1 367358		
ĉ	0.808666	0.068830	1.689552		
н	0.327122	1 009708	1 433413		
C	2 061285	0.062675	2 301980		
c	2.637226	-1 187590	2.501700		
н	2.037220	-1.107570	2.030007		
C	2 015070	-2 397743	2 364728		
н	2.013070	-3 341542	2.504720		
C	0 774469	-2 363031	1 716833		
N	-0.019314	-3 406220	1 294658		
C	2 845646	1 352510	2 552118		
c	4 119764	1 319403	1 689502		
н	3 862009	1 242159	0.617640		
н	4.765899	0.462304	1 946423		
н	4.708405	2 242890	1 9390923		
C	2 043410	2.242070	2 167643		
н	1 793394	2.577457	1 092122		
н	2 641504	2.000371	2 275244		
н	1 104942	2 678033	2.373344		
C	3 226189	1 459963	4.036886		
н	3 802805	2 284011	4.217120		
н	3 848163	0.610602	4.267222		
н	2 2 2 2 2 2 1 0 3	1 488035	4.507552		
C	0 300620	-4 802177	1 429215		
с н	0.300020	-1.072527	2 408280		
н	0.794220	-5.146527	0.630086		
н	-0.62100	-5.140557	1 / 1 0 5 0 0 5 0		
11	-0.021005	-5.401041	1.410303		
(+)- 3²⁺					
c	2 200040	2 760211	0 620122		

С	3.289048	-2.768311	0.630122
Н	4.146701	-3.254332	1.095211
С	3.182782	-1.359730	0.628314
0	4.007174	-0.567457	1.269635
С	5.187677	-1.061479	1.887215
Н	4.931023	-1.754829	2.705319
Н	5.699099	-0.179663	2.293705
Н	5.831796	-1.561454	1.144991
С	2.070633	-0.689881	-0.009656
С	2.045290	0.767335	0.003288
С	1.006279	1.528697	0.527639
С	-0.222624	1.210153	1.233861
С	-0.823073	0.038105	1.673604
Н	-0.319332	-0.916272	1.522652
С	-2.085032	0.077306	2.297743
С	-2.704242	1.330650	2.492428
Н	-3.681159	1.384169	2.974033
С	-2.113712	2.524283	2.093895
Н	-2.612101	3.479938	2.268334
С	-0.868611	2.450898	1.464578
Ν	-0.082779	3.473820	0.983641
С	1.041488	2.949352	0.421475
С	2.134751	3.625361	-0.157680
Н	2.165045	4.714672	-0.218392
С	3.181297	2.885064	-0.664551
Н	4.024519	3.397630	-1.127468
С	3.136848	1.471959	-0.633075
С	-2.756201	-1.236800	2.689141
С	-3.054863	-2.023838	1.398137
Н	-3.560964	-2.974380	1.644123
Н	-2.132181	-2.264098	0.844100
Н	-3.711137	-1.445581	0.724200
С	-1.813016	-2.057521	3.584713
Н	-2.298371	-3.009276	3.863491

Н	-1.572734	-1.508892	4.512118
Н	-0.865419	-2.306538	3.077511
С	-4.072069	-1.019682	3.440596
Н	-4.819346	-0.495073	2.820773
Н	-3.922092	-0.444575	4.370895
Н	-4.501765	-1.997526	3.717233
С	-0.440134	4.870815	1.079778
Н	0.363556	5.494886	0.671130
Н	-0.604650	5.140374	2.135174
Н	-1.364855	5.055337	0.508654
0	4.003912	0.706900	-1.248292
С	5.170513	1.239797	-1.861289
Н	4.894482	1.897265	-2.702358
Н	5.728993	0.372226	-2.235049
Н	5.777947	1.789350	-1.123245
С	2.284147	-3.542460	0.086723
H	2.362709	-4.630643	0.121666
С	1.170162	-2.903308	-0.491769
Č	1.068991	-1.483682	-0.560343
č	-0.167384	-1 204259	-1.267378
č	-0.829095	-0.043369	-1.658301
н	-0.366521	0 924045	-1 480904
C	-2.094371	-0.121477	-2.257963
č	-2 646384	-1 400851	-2 512493
н	-3 629717	-1 478169	-2 982563
c	-1 992747	-2 576403	-2 179072
н	-2 443148	-3 548112	-2 390783
C	-0 749637	-2 464567	-1 544048
N	0.078806	-3 462998	-1.087060
C	-2 907502	1 1 2 9 7 0 2	-2 577680
c	-4 173505	1.120703	-1 700147
ч	-3 906054	1 102502	-0.628176
н	-4.802403	0.227369	-0.020170
н	-4.702403	2 011656	-1.902300
C II	2 125607	2.011030	2 277050
с u	1 005405	2.417403	1 205060
11	-1.003403	2.301011	2 527474
п	1 202024	3.269301	-2.55/4/4
п	-1.202924	2.467000	-2.003123
L H	-3.301230	1.131827	-4.064061
п u	-3.898918	2.032042 0.251000	-4.291346 4 22E427
11	-3.900310	0.431988	-4.33342/
п с	-2.404452	1.142202	-4./U/982
с П	-0.212413	-4.8/152/	-1.224035
п	-0.410693	-5.10/182	-2.282064
п	-1.100105	-5.120013	-0.022239
н	0.640291	-5.468660	-0.8/9646