### 5,10-Dimesityldiindeno[1,2-a:2',1'-i]phenanthrene: A Stable Biradicaloid Derived from Chichibabin's Hydrocarbon

**Supporting Information** 

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# Experimental

**General.** Tetrahydrofuran, toluene and 1,4-dioxane were dried using a commercial solvent purification system. Dichloromethane was distilled from calcium hydride when used as a reaction solvent. All other solvents and reagents were used as received. Compounds **S1**–**S4** were prepared according to literature procedures.<sup>1</sup> <sup>1</sup>H NMR spectra were recorded on high-field spectrometers (<sup>1</sup>H frequency 500.13 or 600.13 MHz), equipped with broadband inverse gradient probeheads. Spectra were referenced to the residual solvent signals (chloroform-*d*, 7.24 ppm, dichloromethane-*d*<sub>2</sub>, 5.32 ppm, tetrahydrofuran-*d*<sub>8</sub>, 3.58 ppm or toluene-*d*<sub>8</sub>, 2.09 ppm). <sup>13</sup>C NMR spectra were recorded with <sup>1</sup>H broadband decoupling and referenced to solvent signals (<sup>13</sup>CDCl<sub>3</sub>, 77.0 ppm). Two-dimensional NMR spectra were recorded with 2048 data points in the t<sub>2</sub> domain and up to 1024 points in the t<sub>1</sub> domain, with a 1 s recovery delay. All 2D spectra were recorded with gradient selection, excluding ROESY. The ROESY spinlock time was 300 ms. High resolution mass spectra were measured on a UV-Vis-NIR spectrometer (Cary 5000). TG-DTA measurements were performed on a Setaram SETSYS 16/18 instrument in nitrogen atmosphere.

**DFT calculations.** All calculations were carried out using the Gaussian 09 program.<sup>2</sup> Open-shell singlets were optimized using the broken-symmetry formalism, with mixed initial guesses. In each case, DFT geometries were refined to meet standard convergence criteria, and the existence of a local minimum was verified by a normal mode frequency calculation. Geometry optimizations were performed using unrestricted wavefunctions with the CAM version<sup>3</sup> of the B3LYP<sup>4,5</sup> functional (UCAM-B3LYP), combined with the 6-311++G(d,p) basis set<sup>6-8</sup> (for **2**), and the 6-31G(d,p) basis set (for the oligomerization intermediates, Table S2). The dianion **2**<sup>2-</sup> was optimized using the 6-31G(d,p) basis set and the PCM solvent model using standard tetrahydrofuran parameterization. Nucleus-independent chemical shifts (NICS)<sup>9</sup> were calculated using the standard GIAO method at the level of UB3LYP/6-311++G(d,p) and UCAM-B3LYP/6-311++G(d,p). The iso-chemical shielding surface (ICSS)<sup>10,11</sup> calculations were additionally carried out to visualize aromaticity differences between the singlet and triplet state of **2**. Anisotropy of the Induced Current Density (ACID) calculations were performed using the program developed by the Herges group.<sup>12,13</sup>

**ZFS Calculations.** The zero-field splitting (ZFS) calculations were performed employing the ORCA 4.0.1 suite of programs.<sup>14,15</sup> Calculations were performed on the DFT-optimized geometry of **2** and on the geometry derived from X-Ray diffraction experiment, with the positions of all hydrogen atoms optimized at the level of B3LYP/6-31G(d,p). The ZFS describes the interaction of unpaired electrons in the phenomenological spin Hamiltonian, using parameters *D* and *E*, and is assumed to arise from two contributions: direct spin-spin dipole-dipole interaction (SS) and spin-orbit coupling (SOC).<sup>16,17</sup> However, for organic molecules with *S* > ½, the SOC contribution is negligible and thus the ZFS is determined by the SS interaction,<sup>17,18</sup> which was calculated here for **2** as proposed by Sinnecker and Neese<sup>16</sup> with the use of the B3LYP,<sup>4,5</sup> CAM-B3LYP,<sup>3</sup> PBE0,<sup>19,20</sup> and TPSSO<sup>21</sup> functionals combined with the EPR-II<sup>22</sup> and 6-311++G(d,p)<sup>6-8</sup> basis sets.

In order to confirm the conclusion that the ZFS for **2** is of minor magnitude, the parameters *D* and *E* were calculated at the DFT level with the B3LYP, CAM-B3LYP, PBEO and TPSSO functionals combined with the EPR-II and 6-311++G(d,p) basis sets. All the functionals and basis sets yielded similar results (Table S4). The parameters *D* and *E* were calculated for the fully DFT-optimized planar structure of **2** and for the distorted geometry determined by the X-Ray crystallography (with reoptimized C–H bonds). Again, the results were very similar, indicating that the distortion had a negligible effect on the ZFS. Regardless of the functional and basis set used, the predicted ZFS parameters are of a small

magnitude, namely below 0.01 cm<sup>-1</sup> and thus ESR spectra of **2** can remain unresolved due to the ZFS. This finding can be put into perspective by comparison with the significantly lager *D* parameters determined for the lowest triplet states of benzene, naphthalene, anthracene and tetracene, equal to 0.159, 0.100, 0.070 and 0.057 cm<sup>-1</sup>, respectively.<sup>22,23</sup> Although DFT methods performed generally well for calculation of ZFS for organic systems, earlier reports indicated that the parameters *D* were systematically underestimated by a factor of almost 2 in the case of aromatic hydrocarbons due to the insufficient description of static  $\pi$ -electron correlation.<sup>17</sup> However, even if the calculations presented in the present work were affected to a similar degree, the *D* parameter for **2** should remain lower than 0.02 cm<sup>-1</sup>.

**RAS(h,p)-SF calculations.** By using a high-spin reference, the spin-flip approach<sup>24</sup> provides a balanced treatment of the near-degenerate frontier orbitals, enabling accurate estimation of S–T gaps.<sup>25,26</sup> RAS(h,p)-SF requires auxiliary basis sets, as it takes advantage of the RI-MP2 approximation<sup>27</sup> to reduce the cost of computing and storing necessary two-electron integrals. As such, the correlation-consistent Dunning basis sets (cc-pvdz/pvtz) were used as opposed to the Pople series because there exist standard auxiliary basis sets for cc-pvxz (rimp2-cc-pvxz), but not for the Pople series. Importantly, there is negligible difference between the cc-pvdz/pvtz quantities, indicating that cc-pvdz provides a sufficiently accurate description. One of the strengths of RAS(h,p)-SF as opposed to other active space methodologies is that there is an obvious choice of active space, the singly occupied orbitals of the high-spin reference (i.e. the triplet, in the case of DIPh). The (2,2) active space was found sufficient, because the ST gaps and radical indexes were negligibly affected by expanding the active space to (4,4).

**X-ray crystallography.** X-ray quality crystals were grown by slow diffusion of hexane into a chloroform solution of **2**. Diffraction measurements were performed on a  $\kappa$ -geometry Ruby PX diffractometer ( $\omega$  scans) with graphite-monochromatized Mo K $_{\alpha}$  radiation. The data for **2** were collected at 100 K, corrected for Lorenz and polarization effects. Data collection, cell refinement, data reduction and analysis were carried out with the Xcalibur PX software, CRYSALIS CCD and CRYSALIS RED, respectively (Oxford Diffraction Ltd., Abignon, England, 2009). The structure was solved by direct methods with the SHELXS-2013 program and refined using SHELXL-2013 with anisotropic thermal parameters for non-H atoms. In the final refinement cycles, all H atoms were treated as riding atoms in geometrically optimized positions. CCDC 1861241 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data\_request/cif</u>.

**Magnetic susceptibility measured using the Evans method.** A solution of compound **2** (10 mg) in 0.5 mL of toluene- $d_8$  (with 0.025% v/v of *tert*-butylbenzene as internal reference) was placed in the outer NMR tube of a coaxial set. The inner tube was filled with the same solvent mixture and placed in the outer tube and the set was sealed for <sup>1</sup>H VT NMR measurements.<sup>28</sup> The variable-temperature data were corrected for the thermal changes of the solvent density and molar susceptibilities were calculated and corrected by Pascal constants. Finally, the data were fitted to the Bleaney–Bowers equation.<sup>29</sup> In each case, a temperature-independent paramagnetic term corresponding to a doublet impurity was included in the model.

**Relaxation times**  $T_1$  An inversion-recovery pulse sequence was used for the  $T_1$  relaxation time measurements at 220 K and 300 K and the single-exponential curves were fitted to  $I = f(\tau)$  data.

**ESR spectra** (X-band) were recorded on a Bruker ELEXSYS E500 spectrometer equipped with a variabletemperature equipment ER4131VT. EPR spectra were simulated using WinEPR Simfonia v.1.25 (shareware version) by Bruker. Variable-temperature experiments were carried out for the solid sample contained in a flame-sealed capillary packed under innert atmosphere of argon glove-box. The spin susceptibility (proportional to the area of the signal) was obtained by integrating the area of the signal at each temperature. The obtained variation of the spin susceptibility with temperature can be reproduced with the Bleaney-Bowers model.<sup>30</sup>

**Electrochemical measurements** were performed by means of an Autolab (Metrohm) potentiostat/galvanostat system for dichloromethane solutions with a glassy carbon, a platinum wire, and Ag/AgCl as the working, auxiliary, and reference electrodes, respectively. Tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte. The potentials were referenced with the ferrocene/ferrocenium couple used as an internal standard. Cyclic and differential pulse voltammetric methods were applied.

**TA measurements**. To obtain the time-resolved transient absorption difference signal ( $\Delta A$ ) at a specific time, the pump pulses were chopped at 500 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 2000 pulses excite the samples to obtain the fsTA spectra at each delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7°) using a Glan-laser polarizer with a half-wave retarder in order to prevent polarization dependent signals. Cross-correlation fwhm in pump–probe experiments was less than 200 fs and chirp of WLC probe pulses was measured to be 800 fs in the 400–800 nm region. To minimize chirp, all reflection optics in the probe beam path and a quartz cell of 2 mm path length were used. After fs-TA experiments, the absorption spectra of all compounds were carefully examined to detect if there were artifacts due to degradation and photo-oxidation of samples. The three-dimensional data sets of  $\Delta A$  versus time and wavelength were subjected to singular value decomposition and global fitting to obtain the kinetic time constants and their associated spectra using Surface Xplorer software (Ultrafast Systems).<sup>31</sup> Evolution associated spectra (EAS) were obtained from Glotaran program.<sup>32</sup>

# Synthesis



1,8-Diphenylphenanthrene-2,7-dicarbaldehyde (5). To a solution of S4 (400 mg, 1.02 mmol) in 1,4-(80 added phenylboronic dioxane mL) was acid (261 mg, 2.14 mmol), tetrakis(triphenylphosphine)palladium (236 mg, 0.2 mmol). The solution was purged with nitrogen for 10 min, after which 4 mL of 2 M aqueous solution of sodium carbonate was added and the mixture was stirred in 115 °C under nitrogen overnight. The resulting suspension was extracted with dichloromethane, dried over anhydrous sodium sulfate(VI) and evaporated. The residue was separated by column chromatography and the combined fractions evaporated to yield 5 as a pale-yellow solid (270 mg, 78 %). R<sub>f</sub> 0.2 (silica, dichloromethane). <sup>1</sup>H NMR (500 MHz, chloroform-d, 300 K): δ 9.91 (2H, s), 8.92 (2H, d), 8.30 (2H, d), 7.50 (8H, m), 7.37 (4H, m). <sup>13</sup>C NMR (125 MHz, chloroform-d, 300 K): δ 192.4, 145.8, 135.1, 133.3, 132.7, 131.8, 131.0, 128.5, 128.4, 125.7, 123.9, 123.7. HRMS (ESI-TOF): *m*/*z*: [M + Na]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>18</sub>O<sub>2</sub>Na: 409.1199; Found 409.1193.



**5,10-Dimesityl-5,10-dihydrodiindeno[1,2-a:2',1'-i]phenanthrene (6).** Compound **5** (135 mg, 0.34 mmol) was dissolved in a flame-dried Schlenk flask equipped with septum in tetrahydrofuran (30 mL) and purged with nitrogen for 10 min. To the vigorously stirred solution was added 2-mesitylmagnesium bromide (1.4 mL, 1 M in THF) and the reaction was kept under nitrogen overnight. The mixture was qunched with water, extracted with dichloromethane, dried over anhydrous sodium sulfate(VI) and evaporated to dryness. The residue was dissolved in freshly distilled dichloromethane (35 mL), purged with nitrogen for a few minutes and borontrifluroide diethyl etherate was added dropwise via septum. After 10 min of stirring the mixture was evaporated, the residue was separated by column chromatography and the combined fractions evaporated to yield **6** as a white solid (205 mg, 99 %, mixture of stereoisomers).  $R_f$  0.6 (silica, dichloromethane/hexane, 1:4). <sup>1</sup>H NMR (500 MHz, chloroform-*d*, 300 K):  $\delta$  8.98 (4H, bs), 8.68 (2H, d, *J* = 8.6 Hz), 8.67 (2H, d, *J* = 8.6 Hz), 8.55 (2H, bs), 8.54 (2H, bs), 7.53 (8H, m), 7.32 (8H, m), 7.06 (4H, bs), 6.65 (2H, bs), 6.64 (2H, bs), 5.62 (4H, bs), 2.74 (12H, s), 2.29 (4H, s), 2.28 (4H, s), 1.07 (6H, s), 1.04 (6H, s). <sup>13</sup>C NMR (125 MHz, chloroform-*d*, 300 K):  $\delta$  148.5, 146.6, 141.9, 138.0, 136.4, 133.6, 130.6, 128.9, 127.5, 127.1, 126.6, 124.3, 123.4, 122.8, 50.0, 21.9, 20.9, 18.5. HRMS (MALDI–TOF): m/z: [M]<sup>+</sup> Calcd for C<sub>46</sub>H<sub>38</sub>: 590.2968; Found 590.5058.



**5,10-Dimesityldiindeno[1,2-a:2',1'-i]phenanthrene (2).** In a 50 mL flame-dried Schlenk flask was dissolved **6** (205 mg, 0.35 mmol) in toluene (24 mL), the solution was purged with nitrogen for 10 min and 2,3-dichloro-5,6-dicyanobenzoquinone (2.5 equiv., 197 mg, 0.87 mmol) was added and the

mixture was stirred under nitrogen in ambient temperature overnight. Fast separation by column chromatography yielded **2** as a dark-blue, crystaline solid (203 mg, 99 %).  $R_f$  0.5 (silica, dichloromethane). <sup>1</sup>H NMR (600 MHz, chloroform-*d*, 220 K):  $\delta$  8.16 (2H, s), 7.98 (2H, d, *J* = 7.7 Hz), 7.56 (2H, d, *J* = 9.6 Hz), 7.14 (2H, t, *J* = 7.5 Hz), 7.04 (2H, t, *J* = 7.5 Hz), 7.00 (4H, s), 6.83 (2H, d, *J* = 7.7 Hz), 6.74 (2H, d, *J* = 9.6 Hz), 2.35 (6H, s), 2.11 (12H, s). <sup>13</sup>C NMR (151 MHz, chloroform-*d*, 220 K):  $\delta$  143.6, 142.2, 137.6, 137.5, 137.1, 137.0, 134.8, 132.0, 130.0, 129.8, 128.0, 127.4, 126.8, 125.4, 124.6, 123.3, 122.8, 120.9, 21.2, 20.5. HRMS (ESI–TOF): *m/z*: [M + Na]<sup>+</sup> Calcd for C<sub>46</sub>H<sub>36</sub>Na: 611.2701; Found 611.2709. **UV-vis** (dichloromethane, 300 K)  $\lambda$  [nm] ( $\epsilon$  in M<sup>-1</sup>cm<sup>-1</sup>): 230 (34 000), 278 (34 000), 306 (31 000), 324 (27 000), 451 (10 000), 600 (41 000),.753 (8 000).

**Thermal conversion to 6 and 7.** Compound **2** (19 mg) wa placed in a flame-dried pressure tube, sealed under argon atmosphere (glovebox). The setup was submerged in sand and heated for 14 h in 240 °C. The dark green residue, along the dark blue sublimed material on the tube walls, was separated by column chromatography and the combined fractions were evaporated to yield **6** (5 mg, 25 %) and **7** (11 mg, 60 %) as a dark green solid, accompanied with recovered **2** (1 mg, 5%). Some dark green residue could not be washed from the silica. R<sub>f</sub> 0.1 for **7**, 0.5 for **2** and 0.6 for **6** (silica, dichloromethane/hexane, 1:4, then dichloromethane to elute **7**, then up to 10 % MeOH in dichloromethane for attempts to elute the remaining material).

**Oxidation to 2**<sup>++</sup>. Compound **2** (3 mg) was dissolved in dichloromethane (250 mL) and 2 mL of the stock solution was transferred to a quartz spectrophotometer cell, where **2** was titrated using a dichloromethane solution of tris(4-bromophenyl)ammoniumyl hexachloroantimonate (3.5 mg, Magic Blue) in dichloromethane (10 mL) and progress of the reaction was monitored spectrophotometrically.

**Reduction to 2**<sup>2-</sup>. Compound **2** (5 mg) was placed in glovebox in a flame-dried vial and dissolved in THF $d_8$  (1 mL) from a freshly-opened ampule. The dark blue solution was stirred in room temperature with an excess of sodium metal for 24 h, after which 0.5 mL of the now-dark-orange solution was transferred to a previously flame-dried NMR tube, tightly sealed and could be transered from glovebox for subsequent NMR measurements. Exposing the solution to air lead to recovery of the dark blue color. Traces of moisture and oxygen present during the first attempt of this experiment lead to the partially reduced compound **2(-H)**<sup>-</sup>.

### **Additional Schemes**



**Scheme S1.** Synthesis of compounds **S1-S4**. Reagents and conditions: a) TiCl<sub>4</sub> (1.1 equiv.), Zn (2 equiv.), THF (85 mL); b) UV-light (150 W medium-pressure Hg lamp), I<sub>2</sub> (1.1 equiv.), toluene (700 mL); c) NBS (8 eqiv.), benzoil peroxide (0.1 equiv.), 1,2-dichloroethane (50 mL); d) AgNO<sub>3</sub> (4.5 equiv.), EtOH (20 mL), H<sub>2</sub>O (4 mL).



Scheme S2. Synthesis of compounds 5, 6 and 2. Reagents and conditions: e) phenylboronic acid (2.1 equiv.),  $Pd(PPh_3)_4$  (0.2 equiv.), 2M  $Na_2CO_3$  aq (4mL), dioxane (80 mL); g) 1. 1 M 2-MesMgBr in THF (4 equiv.), THF (30 mL), 2.  $BF_3 \cdot Et_2O$ , dichloromethane (35 mL); h) DDQ (2.5 equiv.), toluene (24 mL).



**Scheme S3.** <sup>1</sup>H and <sup>13</sup>C chemical shifts of **2** (assignment based on data obtained from COSY, ROESY, HSQC and HMBC experiments). The k-p and s-t pairs could not be distinguished with certainty.



**Scheme S4.** <sup>1</sup>H and <sup>13</sup>C chemical shifts of  $2^{2}$  (assignment based on data obtained from COSY, ROESY, HSQC and HMBC experiments). The k-p, l-q and s-t pairs could not be distinguished with certainty.

# **Additional Figures**



Figure S1. Solvent-dependent stability of 2 in solution (stored under ambient conditions).



**Figure S2.** UV-Vis spectrum showing the stability of a dichloromethane solution of **2** over time  $(2 \cdot 10^{-5} \text{ M}, \text{ in days, sealed quartz spectrophotometric cell filled under air, stored under ambient conditions). The apparent minor increase in intensity is caused by gradual loss of solvent from the cell.$ 



Figure S3. TG-DTA analysis of 2 (12 mg, nitrogen atmosphere, heating rate 10 °C/ min, 30 to 1000 °C).



**Figure S4.** <sup>1</sup>H NMR spectra of compounds from thermal conversion of **2** (500 MHz, CDCl<sub>3</sub>, 300 K): **6** (green) and two subsequent chromatography fractions of **7** (red and blue, respectively). The signal at 5.6 ppm corresponds to the indene C(sp<sup>3</sup>)-H position. Only the aromatic region is shown for clarity.



**Figure S5.** UV-Vis absorption spectra of **2** (blue), **7** (grey) with comparable concentrations (ca.  $10^{-5}$  M) and **7** five times more concentrated (orange). All spectra were recorded in dichloromethane.



Figure S6. DOSY NMR spectrum of 6 (600 MHz, CDCl<sub>3</sub>, 300 K).





**Figure S8.** ESR varying temperature spectra for **2** in the solid state (top) and doubly integrted ESR signals (bottom).



**Figure S9.** Top: ESR spectrum of **2** recorded at the initial stage of decomposition (dichloromethane solution, room temperature, black trace) and the corresponding simulated spectrum obtained (red trace, parameters as listed). Bottom: calculated <sup>1</sup>H hyperfine (hf) coupling constants (Fermi contacts) for the [**2**-H]<sup>-</sup> radical (X = H) obtained at the CAM-B3LYP/EPR-II//6-31G(d,p) level of theory, showing qualitative agreement with the experimental spectrum, i.e. the presence of three resolvable hf splittings. The observed splitting multiplicity is not compatible with the triplet state of **2**.



Figure S10. Values of relaxation time  $T_1$  for 2 measured at 220 K (in seconds, 600 MHz, CDCl<sub>3</sub>).



**Figure S11.** Values of relaxation time  $T_1$  for **2** measured at 300 K (in seconds, 600 MHz, CDCl<sub>3</sub>).



**Figure S12.** Top and center: <sup>1</sup>H NMR spectrum of  $[2-H]^-$  (600 MHz, THF- $d_8$ , 250 K). Bottom: key regions of ROESY (blue and green peaks) and COSY (red peaks). The assignment (center panel) shows key ROE contacts as purple lines.



**Figure S13.** Key regions of ROESY (top) and COSY (down) NMR spectra of  $2^{2-}$  (600 MHz, THF- $d_8$ , 250 K). The inset shows key ROE contacts as purple lines.



**Figure S14.** Key regions of HSQC (top) and HMBC (down) NMR spectra of  $2^{2-}$  (600 MHz, THF- $d_8$ , 250 K). The <sup>1</sup>H–<sup>13</sup>C HMBC correlations between the quinomethane carbon o and protons b and g are marked in red and shown as purple lines in inset.



**Figure S15.** Fitting curves for magnetic succeptibility values obtained from the Evans method (VT <sup>1</sup>H NMR, 600 MHz, tol- $d_8$  + 0.025% *t*-butylbenzene (top) and from VT EPR in the solid state (bottom).



Figure S16. ACID plots for 2 (B3LYP/6-31g(d,p)).



**Figure S17.** Calculated NICS scans for the singlet and triplet state of **2** over the individual aromatic rings using two different methods: B3LYP/6-311++G(d,p) (top) and CAM-B3LYP/6-311++G(d,p) (bottom).



Figure S18. TA decay profile and population ratio for 2.



**Figure S19.** Electronic absorption spectrum of **2** simulated at the TD-UB3LYP/6-31G(d,p) level of theory.



**Figure S20.** ESR spectra (DCM, room temperature) generated by oxidation of **2** with a Magic Blue solution.

## **Additional Tables**

 Table S1. RAS(h,p)-SF calculations on 2.

Level of theory	cc-VDZ, trip	let ref, (2,2)	cc-VTZ, trip	let ref, (2,2)
Geometry of 2 <sup>[a]</sup>	Singlet	Triplet Singlet T		Triplet
SO Energy (Ha)	-1069.717321	-1069.717939	-1069.946055	-1069.946529
T1 Energy (Ha)	-1069.713074	-1069.715252	-1069.941705	-1069.943778
diradical index $\gamma_0$	0.71		0.70	
Vertical ST gap (eV)	0.116	0.073	0.118	0.075
Adiabatic ST gap (eV)	0.056		0.062	
Adiabatic ST gap (kcal/mol)	1.30		1.4	43

[a] CAM-B3LYP/6-311++G(d,p) geometries (see the zip file for Cartesian coordinates).

Code <sup>[a]</sup>	SCF E <sup>[b,c]</sup>	<b>ZPV</b> <sup>[b,d]</sup>	lowest freq. <sup>[b,e]</sup>	<b>G</b> <sup>[b,f]</sup>	<s<sup>2&gt;<sup>[g]</sup></s<sup>
	a.u.	a.u.	cm⁻¹	a.u.	
D-2+	-1773.414542	0.680267	12.29	-1772.811231	0.76
D-m-8a+	-3547.029527	1.363452	2.85	-3545.800158	0.75
D-m-9a+	-3547.116031	1.365812	3.46	-3545.883310	0.77
D-r-8a+	-3547.034704	1.363399	5.59	-3545.800872	0.75
D-r-9a+	-3547.116064	1.365835	3.65	-3545.882539	0.77
S-10	-3546.083718	1.336805	3.56	-3544.878329	6.15
S-2	-1773.633706	0.678555	10.84	-1773.031522	0.95
S-6	-1774.880353	0.706283	11.98	-1774.249889	0.00
S-m-8	-3547.247403	1.361985	2.77	-3546.019218	0.93
S-m-9a	-3547.328243	1.364497	3.56	-3546.094446	0.90
S-m-9b	-3547.325443	1.364471	3.39	-3546.091790	0.86
S-r-8	-3547.249689	1.362040	4.37	-3546.016656	0.93
S-r-9a	-3547.328191	1.364382	3.55	-3546.095292	0.90
S-r-9b	-3547.325589	1.364585	3.43	-3546.091363	0.86
T-10	-3546.062845	1.338933	3.10	-3544.855942	2.01
T-2	-1773.629506	0.678605	10.26	-1773.028412	2.00
T-m-8	-3547.247401	1.361985	2.76	-3546.020268	2.01
T-m-9a	-3547.325830	1.364524	3.57	-3546.093029	2.01
T-m-9b	-3547.325443	1.364471	3.39	-3546.092826	2.01
T-r-8	-3547.249657	1.362044	4.38	-3546.017630	2.01
T-r-9a	-3547.325797	1.364447	3.47	-3546.093675	2.01
T-r-9b	-3547.325588	1.364587	3.43	-3546.092378	2.01
TS-m-8+	-3547.016579	1.359346	-620.83	-3545.792040	1.41
TS-S-8	-3547.223519	1.358034	-919.74	-3545.999348	4.51
TS-T-m-8	-3547.222107	1.358117	-936.87	-3545.998982	2.19

**Table S2.** Investigations of the oligomerization mechanism (Scheme 4).

[a] Structure code (see the zip file for Cartesian coordinates). [b] CAM-B3LYP/6-31G(d,p) energies and geometries. [c] SCF electronic energy. [d] Zero-point vibrational energy. [e] lowest vibrational frequency. [f] Gibbs free energy. [g] after annihilation of the first spin contaminant.

No.	Energy (cm <sup>-1</sup> )	λ (nm)	<b>f</b> <sup>[a]</sup>	Major excitations <sup>[b]</sup>	-	No.	Energy (cm <sup>-1</sup> )	λ (nm)	<b>f</b> <sup>[a]</sup>	Major excitations <sup>[b]</sup>
1	10102	989.9	0.001	HOMO(A)»LUMO(A) (47%) HOMO(B)»LUMO(B) (47%)		20	25281	395.6	0.034	H-8(A)»LUMO(A) (10%) H-7(A)»LUMO(A) (10%) H-6(A)»LUMO(A) (21%) H-8(B)»LUMO(B) (10%)
2	12184	820.8	0.159	HOMO(A)»LUMO(A) (30%) HOMO(B)»LUMO(B)		21	25601	200.0	0.001	H=7(B)×LUMO(B) (10%) H=6(B)×LUMO(B) (21%)
3	13766	726.5	0.000	(30%) H–2(A)»LUMO(A) (14%) H–1(A)»LUMO(A) (32%) H–2(B)»LUMO(B) (14%) H–1(B)»LUMO(B) (23%)		21	25601	390.6	0.001	H=8(A)»LUMO(A) (20%) H=1(A)»L+1(A) (13%) H=8(B)»LUMO(B) (20%) H=1(B)»L+1(B) (13%)
4	15502	645.1	0.081	H=1(B)×LUMO(B) (32%) H=2(A)×LUMO(A) (36%) HOMO(A)×LUMO(A) (11%)		22	26457	378.0	0.053	H–2(A)»L+1(A) (18%) HOMO(A)»L+2(A) (17%) H–2(B)»L+1(B) (18%) HOMO(B)»L+2(B) (17%)
				H–2(B)»LUMO(B) (36%) HOMO(B)»LUMO(B) (11%)		23	28171	355.0	0.008	H–9(A)»LUMO(A) (34%) H–9(B)»LUMO(B) (34%)
5	16931	590.6	0.003	H–2(A)»LUMO(A) (31%) H–1(A)»LUMO(A) (15%) H–2(B)»LUMO(B) (31%) H–1(B)»LUMO(B) (15%)		24	28175	354.9	0.001	H–9(A)»LUMO(A) (16%) HOMO(A)»L+2(A) (11%) H–9(B)»LUMO(B) (16%) HOMO(B)»L+2(B) (11%)
6	17632	567.1	0.497	H–1(A)»LUMO(A) (39%) H–1(B)»LUMO(B) (39%)		25	28778	347.5	0.022	H–9(A)»LUMO(A) (16%) H–9(B)»LUMO(B) (16%)
7	20431	489.5	0.019	H–3(A)»LUMO(A) (45%) H–3(B)»LUMO(B) (47%)		26	29300	341.3	0.001	HOMO(A)»L+2(A) (33%) HOMO(B)»L+2(B) (33%)
8	20435	489.4	0.005	H–3(A)»LUMO(A) (48%) H–3(B)»LUMO(B) (46%)		27	30091	332.3	0.001	H–2(A)»L+1(A) (25%) HOMO(A)»L+3(A) (21%) H–2(B)»L+1(B) (25%)
9	9 22041 453.7 0.001	3.7 0.001 H–5(A)»LUMO(A) (19%) HOMO(A)»L+1(A) (22%)		20	20242	220.0	0.027	HOMO(B)»L+3(B) (21%)		
10	22101	152 5	0.000	H–5(B)»LUMO(B) (20%) HOMO(B)»L+1(B) (22%)		20	30312	529.9	0.037	H–1(A)»L+1(A) (15%) HOMO(A)»L+3(A) (23%) H–1(B)»L+1(B) (15%)
10	22101	452.5	0.000	$H = 5(A) \times LUMO(B) (49\%)$ $H = 5(A) \times LUMO(B) (49\%)$		29	30994	322.6	0.289	HOMO(B)»L+3(B) (23%) H–10(A)»LUMO(A) (28%)
11	22140	451.0	0.005	HOMO(A)»L0MO(A) (30%) HOMO(A)»L+1(A) (14%) H–5(B)»LUMO(B) (30%)		30	31381	318.7	0.000	H–10(B)»LUMO(B) (28%) H–2(A)»L+2(A) (11%)
12	23069	433.5	0.122	HOMO(B)»L+1(B) (14%) HOMO(A)»L+1(A) (36%)			01001	01017		HOMO(A)»L+4(A) (10%) H–2(B)»L+2(B) (11%) HOMO(B)»L+4(B) (10%)
13	23569	424.3	0.009	HOMO(B)»L+1(B) (36%) H $-8(A)$ »LUMO(A) (20%)		31	31453	317.9	0.131	HOMO(A)»L+4(A) (16%) HOMO(B)»L+4(B) (16%)
				H–8(B)»LUMO(B) (20%)		32	31540	317.1	0.008	( ) ( ) ( - · )
				H–7(B)»LUMO(B) (20%)		33	31724	315.2	0.035	H–2(A)»L+1(A) (10%)
14	23681	422.3	0.011	H–7(A)»LUMO(A) (27%) H–1(A)»L+1(A) (10%) H–7(B)»LUMO(B) (27%)						H-1(A)»L+2(A) (20%) H-2(B)»L+1(B) (10%) H-1(B)»L+2(B) (20%)
15	24061	415.6	0.004	H–1(B)»L+1(B) (10%) H–4(A)»LUMO(A) (34%)		34	32016	312.3	0.014	H–10(A)»LUMO(A) (18%) H–10(B)»LUMO(B) (18%)
16	24204	413.2	0.018	H–4(B)»LUMO(B) (34%) H–4(A)»LUMO(A) (40%)		35	32579	307.0	1.091	H–1(A)»L+1(A) (14%) HOMO(A)»L+3(A) (14%)
17	24383	410.1	0.024	H–4(B)»LUMO(B) (40%) H–1(A)»L+1(A) (13%)						H–1(B)»L+1(B) (14%) HOMO(B)»L+3(B) (14%)
18	24982	400.3	0.045	H–1(B)»L+1(B) (13%) H–6(A)»LUMO(A) (29%)		36	33039	302.7	0.036	H–1(A)»L+2(A) (10%) HOMO(A)»L+6(A) (10%)
19	25111	398.2	0.000	H–6(B)»LUMO(B) (29%) H–6(A)»LUMO(A) (48%)						H–1(B)»L+2(B) (10%) HOMO(B)»L+6(B) (10%)
				H–6(B)»LUMO(B) (48%)		37	33228	301.0	0.001	H–11(A)»LUMO(A) (23%) H–11(B)»LUMO(B) (23%)

 Table S3.
 Electronic transitions calculated for 2 using the TD-UB3LYP/6-31G(d,p) level of theory.

No.	Energy (cm <sup>-1</sup> )	λ (nm)	<b>f</b> <sup>[a]</sup>	Major excitations <sup>[b]</sup>
47	35754	279.7	0.000	HOMO(A)»L+5(A) (36%) HOMO(B)»L+5(B) (36%)
48	35819	279.2	0.001	HOMO(A)»L+5(A) (29%) HOMO(B)»L+5(B) (29%)
49	36086	277.1	0.013	H-4(A)»L+1(A) (11%) H-3(A)»L+1(A) (10%) H-4(B)»L+1(B) (11%) H-3(B)»L+1(B) (10%)
50	36140	276.7	0.000	H-4(A)»L+1(A) (12%) H-2(A)»L+3(A) (11%) H-4(B)»L+1(B) (12%) H-2(B)»L+3(B) (11%)

[a] Oscillator strength. [b] Contributions smaller than 10% are not included. H = HOMO, L = LUMO. Orbitals are numbered consecutively regardless of possible degeneracies.

No.	Energy (cm <sup>-1</sup> )	λ (nm)	<b>f</b> <sup>[a]</sup>	Major excitations <sup>[b]</sup>
38	33354	299.8	0.000	HOMO(A)»L+4(A) (13%) HOMO(B)»L+4(B) (13%)
39	33463	298.8	0.056	HOMO(A)»L+4(A) (24%) HOMO(B)»L+4(B) (24%)
40	33731	296.5	0.023	HOMO(A)»L+4(A) (10%) HOMO(B)»L+4(B) (10%)
41	34348	291.1	0.057	H–1(A)»L+3(A) (32%) H–1(B)»L+3(B) (32%)
42	34754	287.7	0.000	H–11(A)»LUMO(A) (15%) H–11(B)»LUMO(B) (15%)
43	35041	285.4	0.002	HOMO(A)»L+7(A) (40%) HOMO(B)»L+7(B) (41%)
44	35045	285.3	0.004	HOMO(A)»L+7(A) (44%) HOMO(B)»L+7(B) (42%)
45	35356	282.8	0.019	HOMO(A)»L+5(A) (10%) HOMO(A)»L+6(A) (12%) HOMO(B)»L+5(B) (10%) HOMO(B)»L+6(B) (12%)
46	35405	282.4	0.007	H–2(A)»L+3(A) (13%) H–2(B)»L+3(B) (13%)

		EPR-II		6-311++	G(d,p)
		cm <sup>-1</sup>	Gauss	cm⁻¹	Gauss
		Optimize	d structure		
B3LYP	D	0.0065	70	0.0065	70
	Е	0.0044	50	0.0029	30
CAM-B3LYP	D	0.0049	50	0.0049	50
	Е	0.0038	40	0.0038	40
PBE0	D	0.0060	60	0.0060	60
	Е	0.0042	50	0.0042	40
TPSS0	D	0.0058	60	0.0058	60
	E	0.0041	40	0.0041	40
		X-Ray s	structure		
B3LYP	D	0.0090	100	0.0091	100
	Е	0.0062	70	0.0029	30
CAM-B3LYP	D	0.0070	70	0.0070	70
	Е	0.0055	60	0.0025	30
PBE0	D	0.0084	90	0.0084	90
	Е	0.0059	60	0.0027	30
TPSS0	D	0.0081	90	0.0081	90
	Е	0.0057	60	0.0027	30

Table S4. Calculated ZFS parameters for the triplet state of 2.

#### Table S5. Crystal data and structure refinement for $\textbf{2}{\cdot}C_{6}H_{14}.$

Identification code	MM7	
Empirical formula	$C_{46}H_{36} \cdot C_6H_{14}$	
Formula weight	674.92	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 16.156 (4) Å	<i>α</i> = 90°.
	b = 11.811 (3) Å	β= 93.63 (3)°.
	c = 20.079 (5) Å	$\gamma = 90^{\circ}$ .
Volume	3823.8 (17) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.172 Mg/m <sup>3</sup>	
Absorption coefficient	0.07 mm <sup>-1</sup>	
F(000)	1448	
Crystal size	$0.20\times0.11\times0.10\ mm^3$	
Theta range for data collection	2.8 – 57.2°.	
Index ranges	-20<=h<=17, -15<=k<=9	, -17<=l<=25
Reflections collected	14622	
Independent reflections	8330 [R(int) = 0.050]	
Completeness to theta	99.6 %	
Absorption correction	none	
Max. and min. transmission	0.993 and 0.987	
Refinement method	Full-matrix least-squares	on F <sup>2</sup>
Data / restraints / parameters	8330 / 10 / 590	
Goodness-of-fit on F <sup>2</sup>	1.03	
Final R indices [I>2sigma(I)]	R1 = 0.0825, wR2 = 0.13	67
R indices (all data)	R1 = 0.1710, wR2 = 0.17	61
Extinction coefficient	n/a	
Largest diff. peak and hole	0.294 and -0.296 e.Å <sup>-3</sup>	

# NMR Spectra



ò ppm Figure S22. <sup>13</sup>C NMR spectrum of 5 (125 MHz, chloroform-*d*, 300 K).











## Mass Spectra



Figure S29. High resolution mass spectrum of 5 (ESI, top: experimental, bottom: simulated).



Figure S30. High resolution mass spectrum of 5 (MALDI, top: experimental, bottom: simulated).



Figure S31. High resolution mass spectrum of 2 (ESI, top: experimental, bottom: simulated).



**Figure S32.** MALDI analysis of **7**. Distribution of olygomers of different length (top left inset), mixed patterns for lenghts of n = 2-6 (red spectra) and for molecular ions (black spectra).

#### References

- (1) Shimizu, M.; Tomioka, Y.; Nagao, I.; Kadowaki, T.; Hiyama, T. Palladium-Catalyzed Annulation of 1,2-Diborylalkenes and -Arenes with 1-Bromo-2-[(Z)-2-Bromoethenyl]Arenes: A Modular Approach to Multisubstituted Naphthalenes and Fused Phenanthrenes. *Chem. Asian J.* **2012**, *7* (7), 1644–1651. https://doi.org/10.1002/asia.201200132.
- (2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09 Revision E.01*; Gaussian Inc.: Wallingford CT, 2009.
- (3) Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange–Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393* (1–3), 51–57. https://doi.org/10.1016/j.cplett.2004.06.011.
- (4) Becke, A. D. Density-functional Thermochemistry. III. The Role of Exact Exchange. J. Chem. Phys. **1993**, 98 (7), 5648–5652. https://doi.org/10.1063/1.464913.
- (5) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37* (2), 785–789. https://doi.org/10.1103/PhysRevB.37.785.
- (6) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions. *J. Chem. Phys.* **1980**, *72* (1), 650–654. https://doi.org/10.1063/1.438955.
- (7) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. Efficient Diffuse Function-Augmented Basis Sets for Anion Calculations. III. The 3-21+G Basis Set for First-Row Elements, Li–F. J. Comput. Chem. 1983, 4 (3), 294–301. https://doi.org/10.1002/jcc.540040303.
- (8) Frisch, M. J.; Pople, J. A.; Binkley, J. S. Self-consistent Molecular Orbital Methods 25. Supplementary Functions for Gaussian Basis Sets. *J. Chem. Phys.* **1984**, *80* (7), 3265–3269. https://doi.org/10.1063/1.447079.
- (9) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. von R. Nucleus-Independent Chemical Shifts (NICS) as an Aromaticity Criterion. *Chem. Rev.* **2005**, *105* (10), 3842–3888. https://doi.org/10.1021/cr030088+.
- (10) Klod, S.; Kleinpeter, E. Ab Initio Calculation of the Anisotropy Effect of Multiple Bonds and the Ring Current Effect of Arenes—Application in Conformational and Configurational Analysis. J. Chem. Soc. Perkin Trans. 2 2001, 0 (10), 1893–1898. https://doi.org/10.1039/B009809O.
- (11) Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. J. Comput. Chem. **2012**, 33 (5), 580–592. https://doi.org/10.1002/jcc.22885.
- (12) Herges, R.; Geuenich, D. Delocalization of Electrons in Molecules <sup>+</sup>. *J. Phys. Chem. A* **2001**, *105* (13), 3214–3220. https://doi.org/10.1021/jp0034426.
- (13) Geuenich, D.; Hess, K.; Köhler, F.; Herges, R. Anisotropy of the Induced Current Density (ACID), a General Method To Quantify and Visualize Electronic Delocalization. *Chem. Rev.* 2005, 105 (10), 3758–3772. https://doi.org/10.1021/cr0300901.
- (14) Neese, F. The ORCA Program System. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2* (1), 73–78. https://doi.org/10.1002/wcms.81.
- (15) Neese, F. Software Update: The ORCA Program System, Version 4.0. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**, *8* (1), e1327. https://doi.org/10.1002/wcms.1327.
- (16) Neese, F. Calculation of the Zero-Field Splitting Tensor on the Basis of Hybrid Density Functional and Hartree-Fock Theory. *J. Chem. Phys.* **2007**, *127* (16), 164112. https://doi.org/10.1063/1.2772857.
- (17) Sinnecker, S.; Neese, F. Spin–Spin Contributions to the Zero-Field Splitting Tensor in Organic Triplets, Carbenes and BiradicalsA Density Functional and Ab Initio Study. J. Phys. Chem. A 2006, 110 (44), 12267–12275. https://doi.org/10.1021/jp0643303.
- (18) Adamo, C.; Barone, V. Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0 Model. J. Chem. Phys. **1999**, 110 (13), 6158–6170. https://doi.org/10.1063/1.478522.
- (19) A hybrid functional on the basis of TPSS and including 25% HF as proposed in: a) Grimme, S. Accurate Calculation of the Heats of Formation for Large Main Group Compounds with Spin-Component Scaled MP2 Methods. *J. Phys. Chem. A* **2005**, *109* (13), 3067–3077; b) Quintal, M. M.; Karton, A.; Iron, M. A.; Boese, A. D.; Martin, J. M. L. Benchmark Study of DFT Functionals for Late-Transition-Metal Reactions. J. Phys. Chem. A **2006**, *110* (2), 709–716.
- (20) Quintal, M. M.; Karton, A.; Iron, M. A.; Boese, A. D.; Martin, J. M. L. Benchmark Study of DFT Functionals for Late-Transition-Metal Reactions. J. Phys. Chem. A **2006**, 110 (2), 709–716. https://doi.org/10.1021/jp054449w.
- (21) Chong, D.; Barone, V. *Recent Advances in Density Functional Methods* | *Recent Advances in Computational Chemistry*; World Scientific: Singapore, 1995.

- (22) McGlynn, S. P.; Azumi, T.; Kinoshita, . *Molecular Spectroscopy of the Triplet State*; Prentice Hall, Inc.: Englewood Cliffs, New Jersey, 1969.
- (23) Clarke, R. H.; Frank, H. A. Triplet State Radiationless Transitions in Polycyclic Hydrocarbons. J. Chem. Phys. **1976**, 65 (1), 39–47. https://doi.org/10.1063/1.432781.
- (24) Krylov, A. I. Size-Consistent Wave Functions for Bond-Breaking: The Equation-of-Motion Spin-Flip Model. *Chem. Phys. Lett.* **2001**, *338* (4), 375–384. https://doi.org/10.1016/S0009-2614(01)00287-1.
- (25) Slipchenko, L. V.; Krylov, A. I. Singlet-Triplet Gaps in Diradicals by the Spin-Flip Approach: A Benchmark Study. J. Chem. Phys. **2002**, 117 (10), 4694–4708. https://doi.org/10.1063/1.1498819.
- (26) Shao, Y.; Head-Gordon, M.; Krylov, A. I. The Spin–Flip Approach within Time-Dependent Density Functional Theory: Theory and Applications to Diradicals. J. Chem. Phys. 2003, 118 (11), 4807–4818. https://doi.org/10.1063/1.1545679.
- (27) Feyereisen, M.; Fitzgerald, G.; Komornicki, A. Use of Approximate Integrals in Ab Initio Theory. An Application in MP2 Energy Calculations. *Chem. Phys. Lett.* **1993**, *208* (5), 359–363. https://doi.org/10.1016/0009-2614(93)87156-W.
- (28) Evans, D. F.; Jakubovic, D. A. Water-Soluble Hexadentate Schiff-Base Ligands as Sequestrating Agents for Iron(III) and Gallium(III). J. Chem. Soc. Dalton Trans. **1988**, 0 (12), 2927–2933. https://doi.org/10.1039/DT9880002927.
- (29) Gasque, L.; Ugalde-Saldívar, V. M.; Membrillo, I.; Olguín, J.; Mijangos, E.; Bernès, S.; González, I. A Dicopper Complex with Distant Metal Centers. Structure, Magnetic Properties, Electrochemistry and Catecholase Activity. J. Inorg. Biochem. 2008, 102 (5–6), 1227–1235. https://doi.org/10.1016/j.jinorgbio.2007.12.032.
- Rudebusch, G. E.; Zafra, J. L.; Jorner, K.; Fukuda, K.; Marshall, J. L.; Arrechea-Marcos, I.; Espejo, G. L.; Ponce Ortiz, R.; Gómez-García, C. J.; Zakharov, L. N.; et al. Diindeno-Fusion of an Anthracene as a Design Strategy for Stable Organic Biradicals. *Nat. Chem.* 2016, 8 (8), 753–759. https://doi.org/10.1038/nchem.2518.
- (31) Malinowski, E. R. Factor Analysis in Chemistry, 3 edition.; Wiley: New York, 2002.
- (32) Snellenburg, J. J.; Laptenok, S. P.; Seger, R.; Mullen, K. M.; Stokkum, I. H. M. van. **Glotaran** : A *Java* -Based Graphical User Interface for the *R* Package **TIMP**. *J. Stat. Softw.* **2012**, *49* (3), 1–22. https://doi.org/10.18637/jss.v049.i03.