Supporting Information for:

A Biradical Balancing Act: Redox Amphoterism in a Diindenoanthracene Derivative Results from Quinoidal Acceptor and Aromatic Donor Motifs

Gabriel E. Rudebusch,[†] Guzmán L. Espejo,[‡] José L. Zafra,[‡] Miriam Peña-Alvarez,[‡] Sarah N. Spisak,[§] Kotaro Fukuda,[∥] Zheng Wei,[§] Masayoshi Nakano,*[,∥] Marina A. Petrukhina,*[,§] Juan Casado,*[,‡] and Michael M. Haley*[,†]

[†]Department of Chemistry & Biochemistry and the Materials Science Institute, University of Oregon, Eugene, Oregon 97403-1253, United States

[‡]Department of Physical Chemistry, University of Malaga, Campus de Teatinos s/n 229071 Malaga, Spain

[§]Department of Chemistry, University at Albany, State University of New York, Albany, New York 12222-0100, United States

[∥]Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

Table of Contents **page**

Variable Temperature UV-vis Spectroscopy

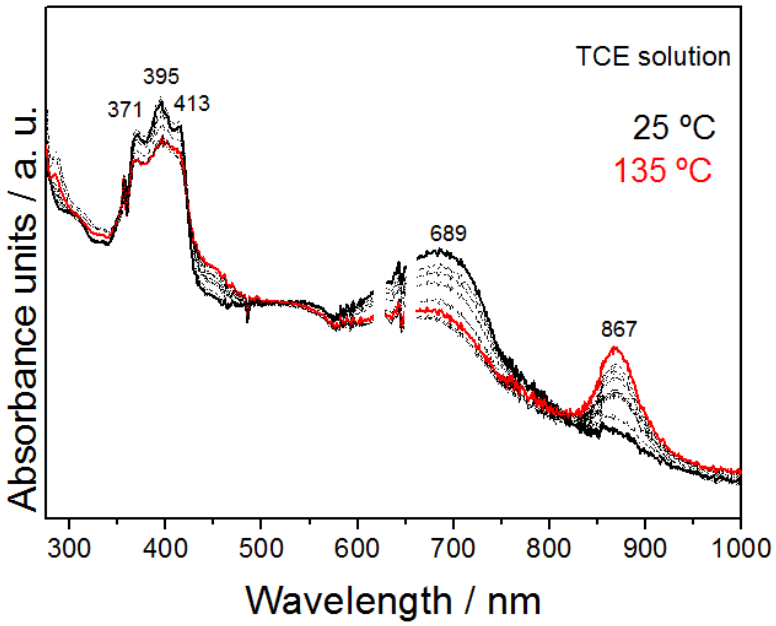

Figure S1. DIAn in tetrachloroethane from 25 to 135 °C. The 689 nm peak corresponding to neutral **DIAn** is fully recovered upon cooling to 25 °C.

Spectroelectrochemistry

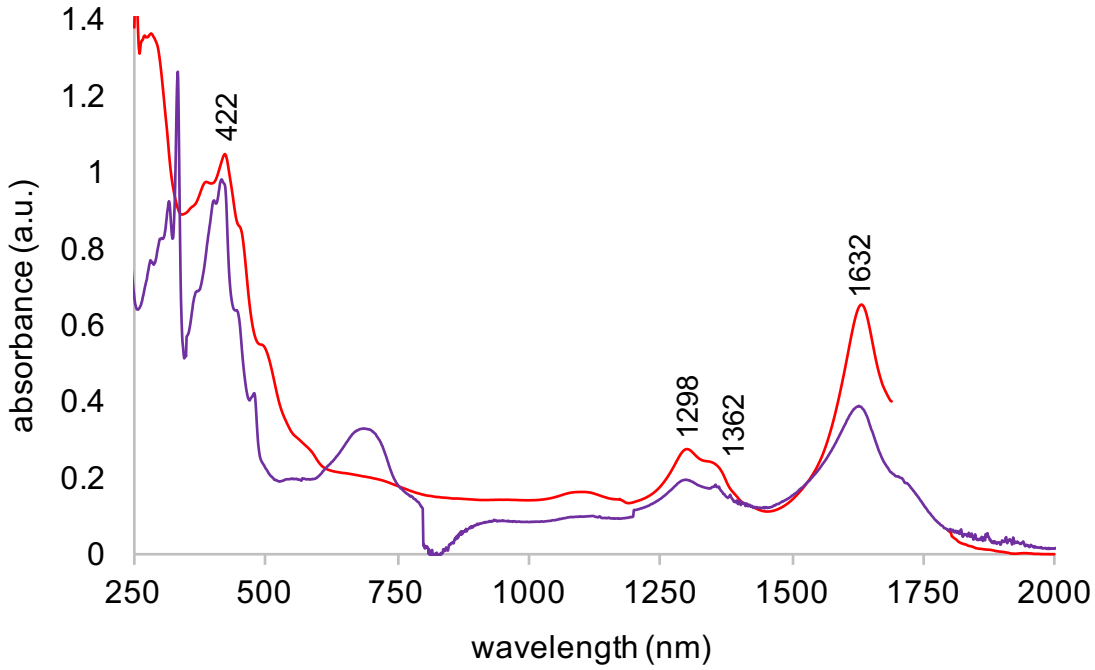

Figure S2. Comparison of **DIAn**$^{\bullet-}$ (red) generated by contact with potassium in THF and by electrolysis (violet).

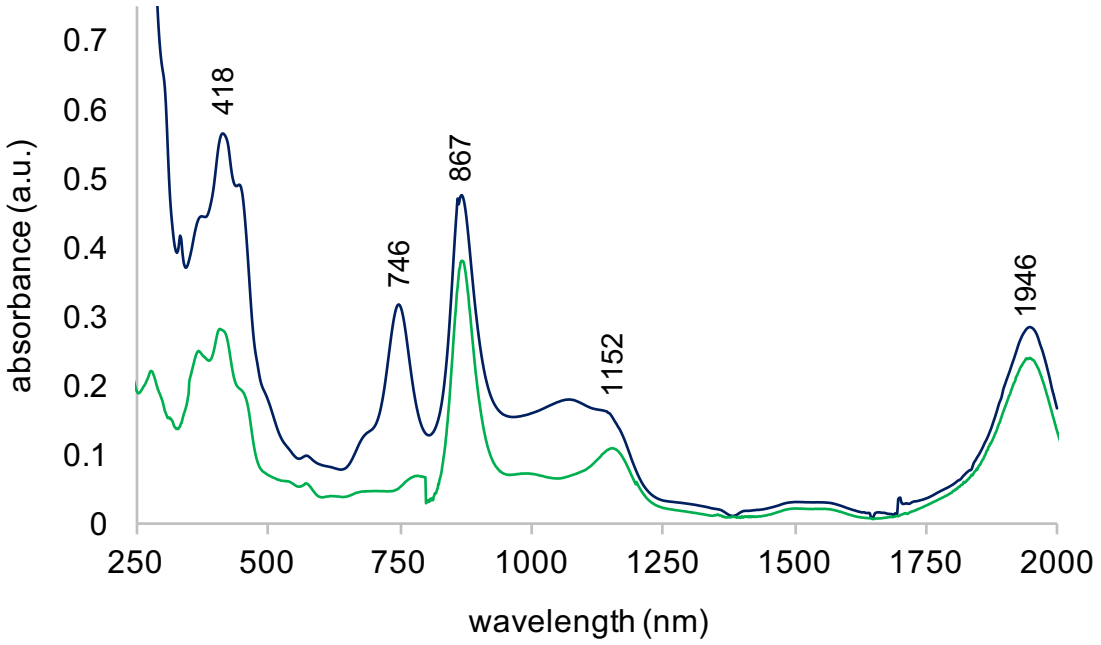

Figure S3. Comparison of **DIAn**$^{\bullet+}$ (blue) generated by $NOBF_4$ in CH_2Cl_2 and by electrolysis (green). The absorbance at 746 nm could be due to over-oxidation towards $DIAn^{2+}$.

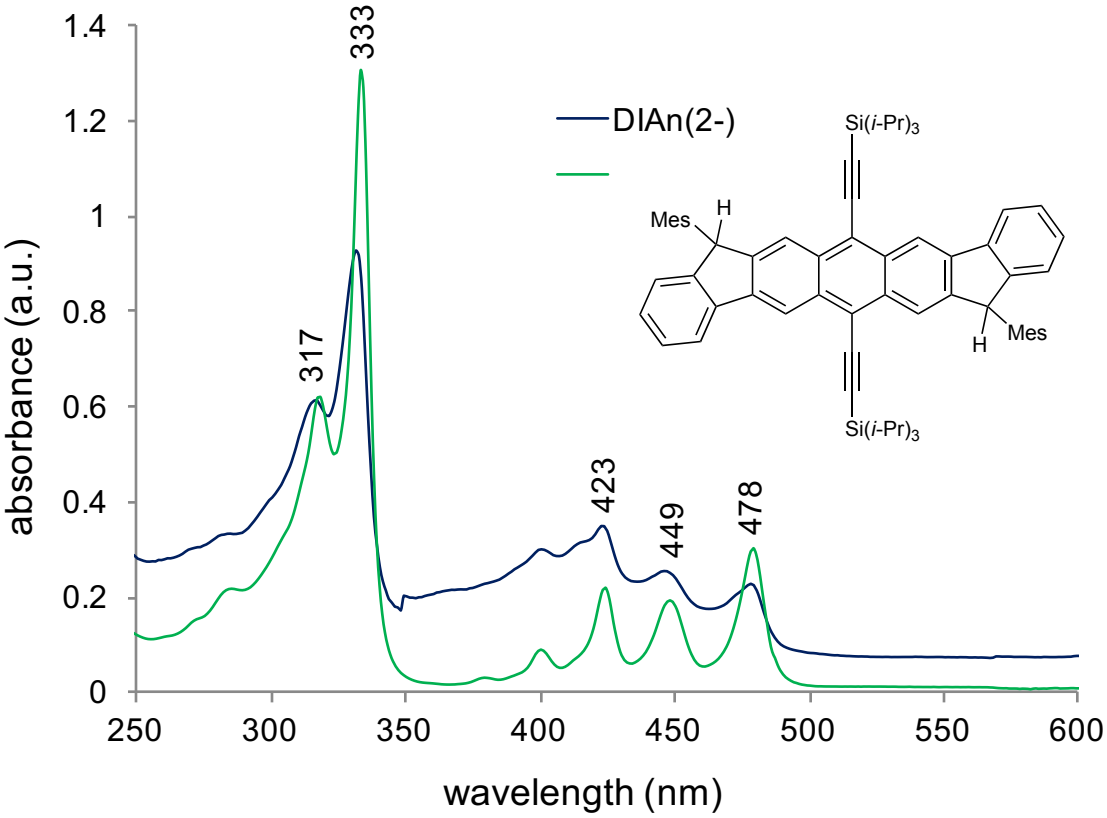

Figure S4. Comparison of **DIAn**$^{2-}$ prepared by electrolysis (navy) and the dihydro-**DIAn** precursor (green).

Experimental Details for Chemical Reduction

All manipulations were carried out using break-and-seal[1] and glove-box techniques under an atmosphere of argon. THF and hexanes were dried over Na/benzophenone and distilled prior to use. THF-d_8 and diglyme were dried over sodium-potassium alloy and distilled prior to use. Potassium was purchased from Strem Chemicals. 18-Crown-6 ether was purchased from Sigma Aldrich and dried over P_2O_5 *in vacuo* for 24 h. **DIAn** was prepared as described previously.[2]

[{K(18-crown-6)(THF)$_2$}DIAn$^{\bullet-}$] • 2THF (Compound 1)

THF (3 mL) was added to a closed system containing **DIAn** (~2 mg), excess of K metal and 18-crown-6. The initial color of the mixture was blue-green (neutral parent ligand). After stirring at room temperature for 10 min, the reaction solution turned deep green. The mixture was stirred at room temperature until brown swirls were seen coming off the K metal (indication of the dianion beginning to form). The mixture was then filtered and the green filtrate was layered with hexanes (3.1 mL) and cooled to 0 °C. After 5 d, dark brown plates of **1** were formed in moderate yield (*ca*. 40 %). Crystals were collected, washed with hexanes (3 × 2 mL) and dried before measurements.

[{K(18-crown-6)(THF)$_2$}$_2$DIAn^{2-}] • 4THF (Compound 2)

THF (3 mL) was added to a closed system containing **DIAn** (~3 mg), excess of K metal and 18-crown-6. The initial color of the mixture was blue-green. After being stirred at room temperature for 10 min, the reaction solution turned deep green. The mixture was stirred for an additional 2 h resulting in a brown suspension. After stirring at room temperature for a total of 10 h, the deep brown mixture was filtered and the orange-brown filtrate was layered with hexanes (2.7 mL) and cooled to 10 °C. Red-brown plate shaped crystals of **2** had formed in good yield (*ca*. 70 %) after 3 d. Crystals were collected, washed with hexanes (3 × 2 mL) and dried before measurements.

[{K(diglyme)(THF)}$_2$DIAn^{2-}] • 2THF (Compound 3)

THF (3 mL) was added to a closed system containing **DIAn** (~2 mg) and an excess of K metal. The initial color of the mixture was blue-green. After being stirred at room temperature for 10 min, the reaction solution turned deep green. The mixture was stirred for an additional 2 h resulting in a brown suspension. After stirring at room temperature for a total of 10 h, the deep brown mixture was filtered and the brown filtrate was layered with diglyme:hexanes (1:20, 1.4 mL). The ampoule was placed at 0 °C. After 4 d, orange-brown plate-shaped crystals of **3** had formed in moderate yield (*ca*. 35 %). Crystals were collected, washed with hexanes (3 × 2 mL) and dried before measurements.

X-ray Crystallography

Data collections for **1**, **2**, and **3** were performed on a Bruker D8 VENTURE X-ray diffractometer with PHOTON 100 CMOS detector and mirror-monochromated Cu-Kα radiation (λ= 1.54178 Å) at T = 100(2) K. Data were corrected for absorption effects using the empirical method SADABS.[3] The structures were solved by direct methods and refined using the Bruker SHELXTL (Version 6.14) software package.[4] All non-hydrogen atoms were refined anisotropically. All H-atoms were included at calculated positions and refined as riders, with $U_{iso}(H) = 1.2\ U_{eq}(C)$ and $U_{iso}(H) = 1.5\ U_{eq}(C)$ for methyl groups. In **1**, two of three isopropyl groups connected with silicon atom were found to be disordered. The disorder was modelled with two orientations having relative occupancies of 0.70:0.30 and 0.53:0.47 for the two parts, separately. The geometries of the disordered parts were restrained to be similar. The anisotropic displacement parameters of the disordered molecules in the direction of the bonds were restrained to be equal with a standard uncertainty of 0.01 Å^2. They were also restrained to have the same U_{ij} components, with a standard uncertainty of 0.04 Å^2. Two severely disordered solvent THF molecules in the unit cell were removed by the SQUEEZE routine in PLATON. In **2**, one of two THF molecules coordinated to potassium cation was found to be disordered. The disorder was modeled with two orientations having relative occupancies of 0.65:0.35 for the two parts. The geometries of the disordered parts were restrained to be similar. The anisotropic displacement parameters of the disordered molecules in the direction of the bonds were restrained to be equal with a standard uncertainty of 0.01 Å^2. They were also restrained to have the same U_{ij} components, with a standard uncertainty of 0.04 Å^2. The severely disordered solvent THF molecules were removed by the SQUEEZE routine in PLATON.[5] In **3**, the whole molecule was found to be disordered. The disorder was modeled with two orientations having relative occupancies of 0.50:0.50 for the two parts. The geometries of the disordered parts were restrained to be similar. The anisotropic displacement parameters of the disordered molecules in the direction of the bonds were restrained to be equal with a standard uncertainty of 0.01 Å^2. They were also restrained to have the same U_{ij} components, with a standard uncertainty of 0.04 Å^2. Two severely disordered solvent THF molecules in the unit cell were removed by the SQUEEZE routine in PLATON.

Table S1. Crystallographic data for **1**, **2**, and **3**.

Parameter	**1**	**2**	**3**
Empirical formula	$C_{88}H_{116}KO_8Si_2$	$C_{108}H_{156}K_2O_{20}Si_2$	$C_{88}H_{120}K_2O_8Si_2$
M_r	1397.09	1844.71	1440.22
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*-1	$P2_1/c$	*P*-1
a (Å)	11.5995 (3)	14.2971 (6)	9.1690 (4)
b (Å)	12.1738 (3)	31.7860 (15)	15.4719 (7)
c (Å)	17.0652 (4)	13.0756 (6)	17.6353 (7)
α (°)	78.478 (2)	90	66.240 (2)
β (°)	82.510 (2)	94.512 (3)	84.584 (1)
γ (°)	72.257 (1)	90	81.803 (2)
V (Å^3)	2242.66 (10)	5923.8 (5)	2264.45 (17)
Z	1	2	1
ρ_{calcd} [g·cm^{-3}]	1.034	1.034	1.056
μ [mm^{-1}]	1.15	1.33	1.55
2θ-range [deg]	5.3–147.5	6.2–149.2	5.5–150.0
Reflections collected	38215	196398	51467
no. unique data, R_{int}	8603, 0.062	12111, 0.096	9027,0.046
no. obsd data [$I \geq 2\sigma(I)$]	6086	9254	6705
R_1[a]	0.062	0.076	0.059
wR_2[b]	0.177	0.199	0.151
Data/restraints/parameters	8603/150/517	12111/151/632	9027/1528/856
Quality-of-fit[c]	1.08	1.09	1.04
peak/hole [e·Å^{-3}]	0.58/–0.62	0.50/–0.46	0.33/–0.25

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{½}$. [c] Quality-of-fit = $[\Sigma[w(F_o^2-F_c^2)^2]/(N_{obs}-N_{params})]^{½}$, based on all data.

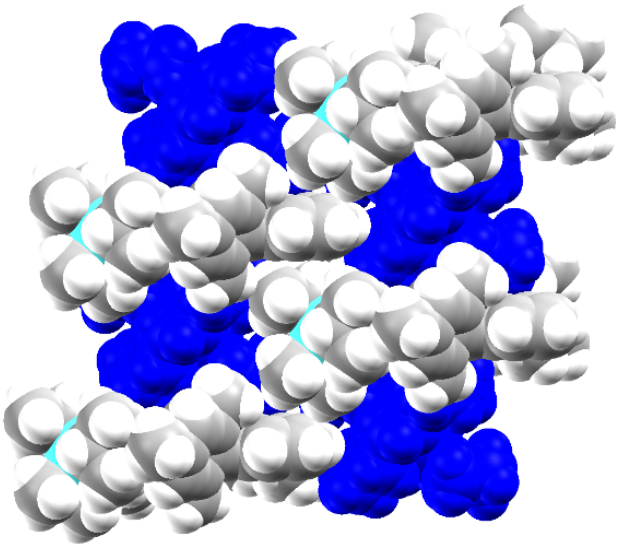

Figure S5. Solid-state packing of **1**, space-filling model. The $[\{K(18\text{-crown-6})(THF)_2\}]^+$ cations are shown in dark blue.

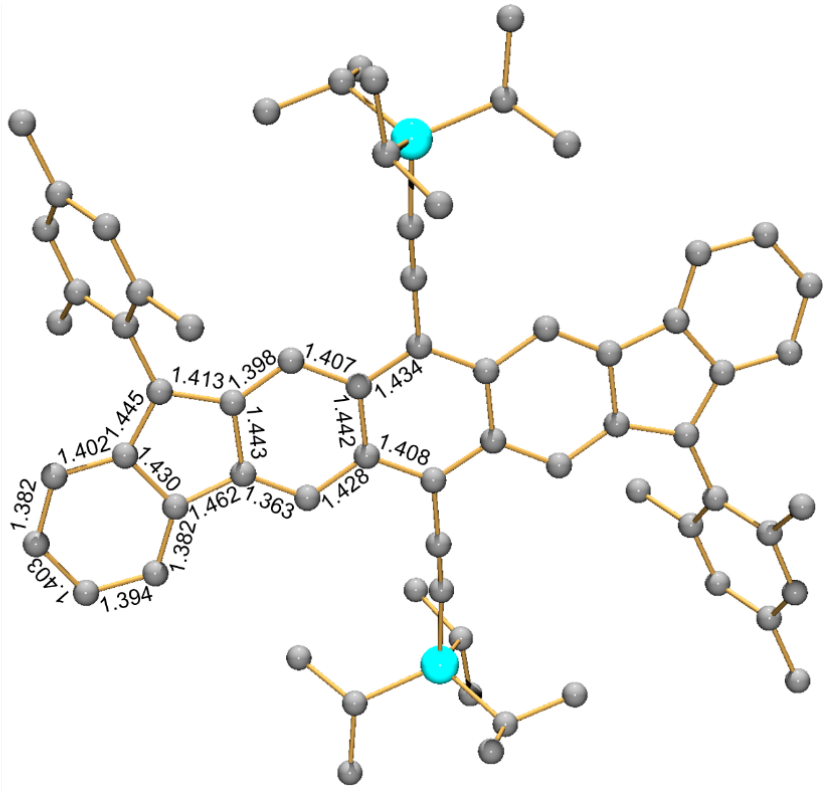

Figure S6. Key bond distances (Å) in the core of $[\{K(18\text{-crown-6})(THF)_2\}DIAn^{\bullet-}]$ (**1**).

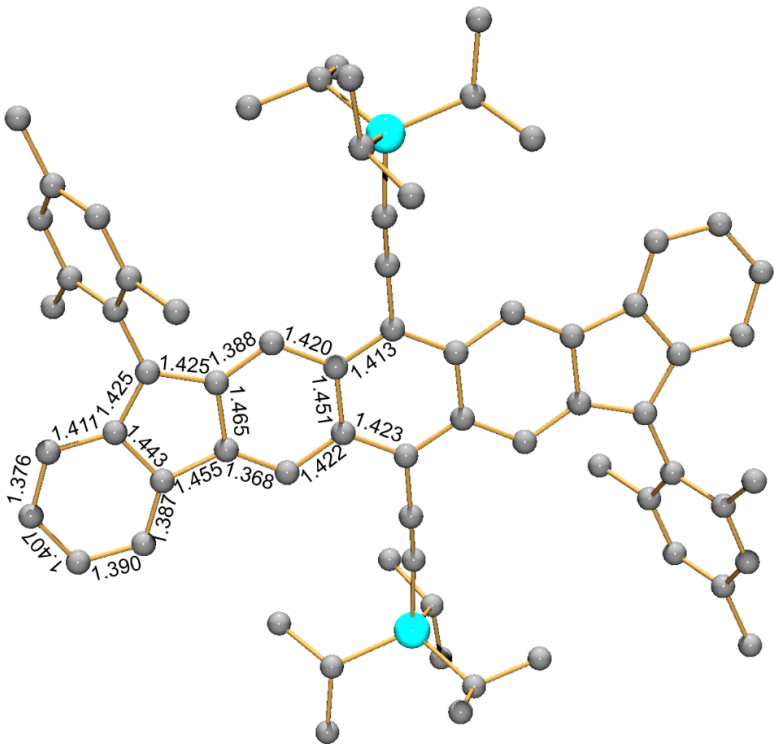

Figure S7. Key bond distances (Å) in the core of [{K(18-crown-6)(THF)$_2$}$_2$DIAn^{2-}] (**2**).

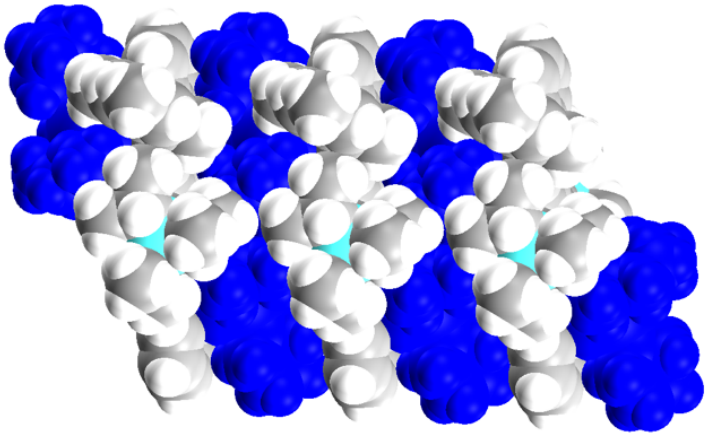

Figure S8. Solid-state packing of **3**. The [{K(diglyme)(THF)}]$^+$ cations are shown in dark blue.

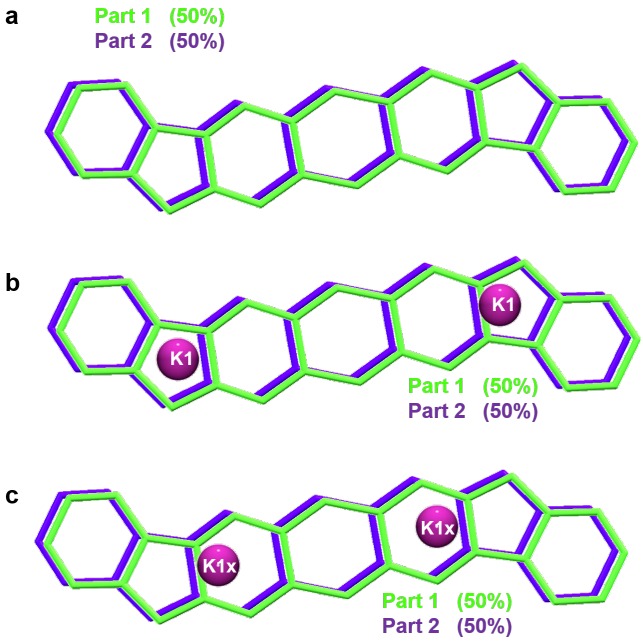

Figure S9. The anion and K ion are disordered over two orientations, which were resolved as part 1 and part 2. Disorder of the core of $C_{68}H_{76}Si_2^{2-}$ in **3** (a), and binding of K ions (b and c).

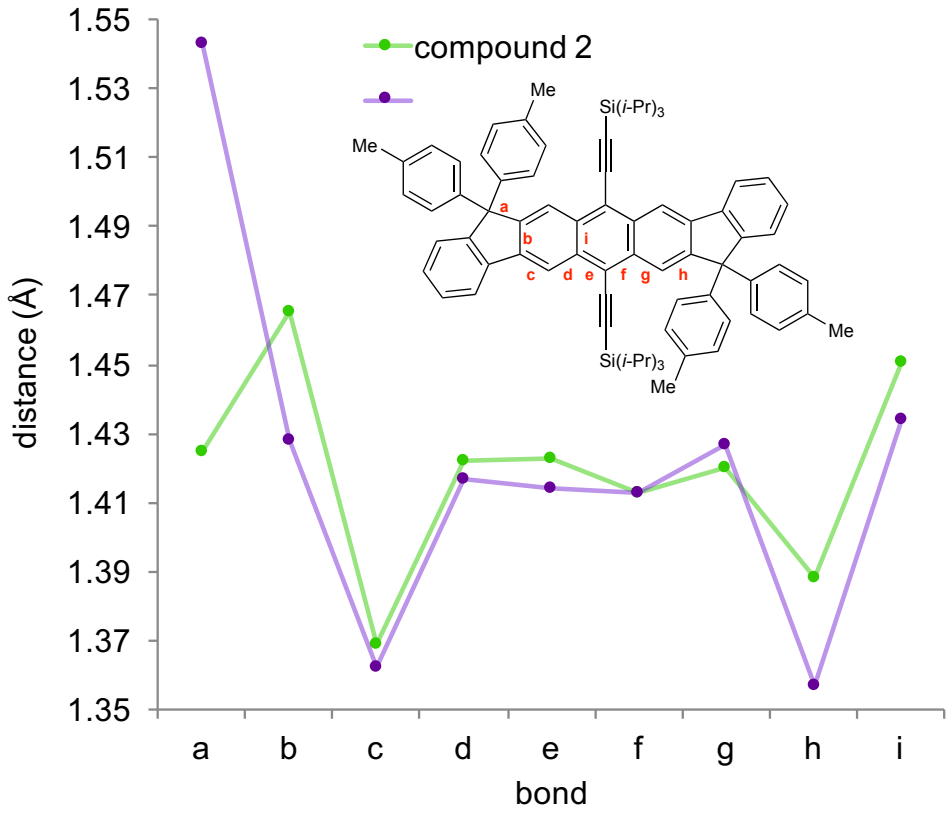

Figure S10. Comparison of the solid-state structures of the non-contact ion pair $DIAn^{2-}$ (compound **2**, green) and a tetrakis-*p*-tolyl DIAn derivative (violet). Bond lettering shown in red.

High-Pressure Raman Measurements

High pressure experiments were conducted in a sapphire anvil cell (SAC) and moissanite anvil cell[6,7] with a diameter culet of 360 μm and a gold gasket, specified in each section. No pressure transmitting medium was used and diamond chips were placed as the pressure calibrant. Raman and photoluminescence measurements were performed using an air-cooled argon ion laser, a Spectra-Physics solid state laser, operating at 532 nm. The device is equipped with a 10x Mitutoyo long working distance objective coupled to a 10x Navitar zoom system and focused onto the slit of an ISA HR460 monochromator with a grating of 600 grooves mm^{-1} and a liquid nitrogen cooled CCD detector (ISA CCD3000, 1024−256 pixels). Spectra were measured with a spectral resolution of about 2−3 cm^{-1} and calibrated with a standard neon emission lamp. The SAC is mounted on a xyz stage, which allows us to move the sample with an accuracy of 1 μm. The typical sampling area was about 1−2 μm in diameter.

Raman measurements were conducted at 633 nm with a Senterra Dispersive Raman Spectrophotometers from Bruker, which combines a dispersive Raman spectrophotometers with a confocal microscope in a single device. Detection is done through a high-sensitive CCD detector (charge couple device) with a Peltier-cooling to −70 °C (thermoelectrically cooled). A grating of 1200 grooves mm^{-1} provides a standard spectral resolution of 3 cm^{-1}. Measurements were done with 5 mW power. The calibration wavelength is continuous throughout the process of the spectral registration. *The method used* calibrates the system automatically with unmatched wavelength precision and accuracy using a Neon light as reference. Raman scattering radiation is collected in back–scattering configuration spatial resolution of 0.5 μm, and spot size of about 3 μm.

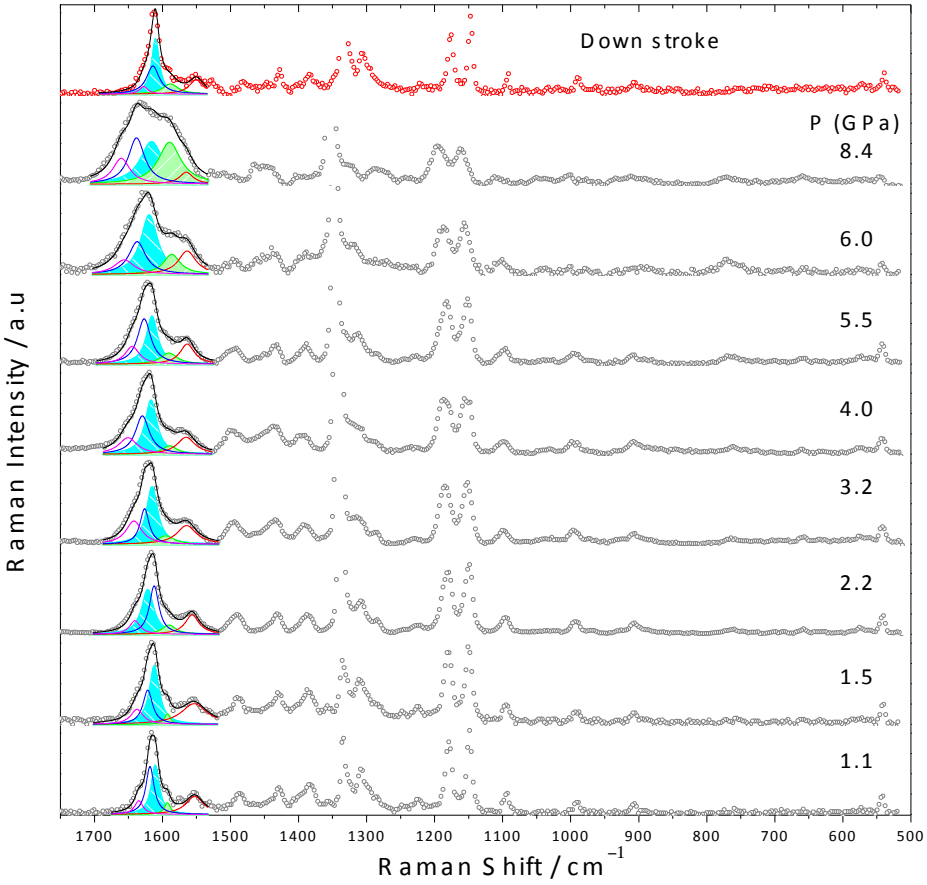

Figure S11. Raman spectrum at selected pressures measured with a laser of 532 nm in the 1750-500 cm^{-1} region. the background has been subtracted to obtain better visibility.

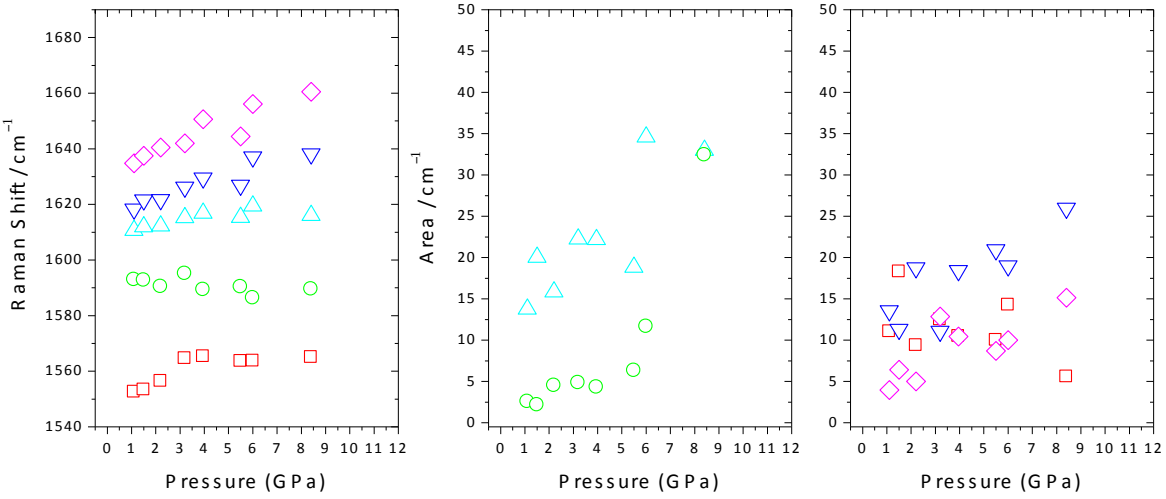

Figure S12. (left) Raman shift pressure evolution of the contributions fitted as in previous figure from experimental Raman spectra taken with 532 nm as excitation line; each color corresponds to the fitted contribution. (middle) Area obtained for the 1610 and 1589 cm^{-1} contributions (cyan and green). (right) Area obtained for the 1637, 1620 and 1555 cm^{-1} contributions (pink, dark blue and red, respectively).

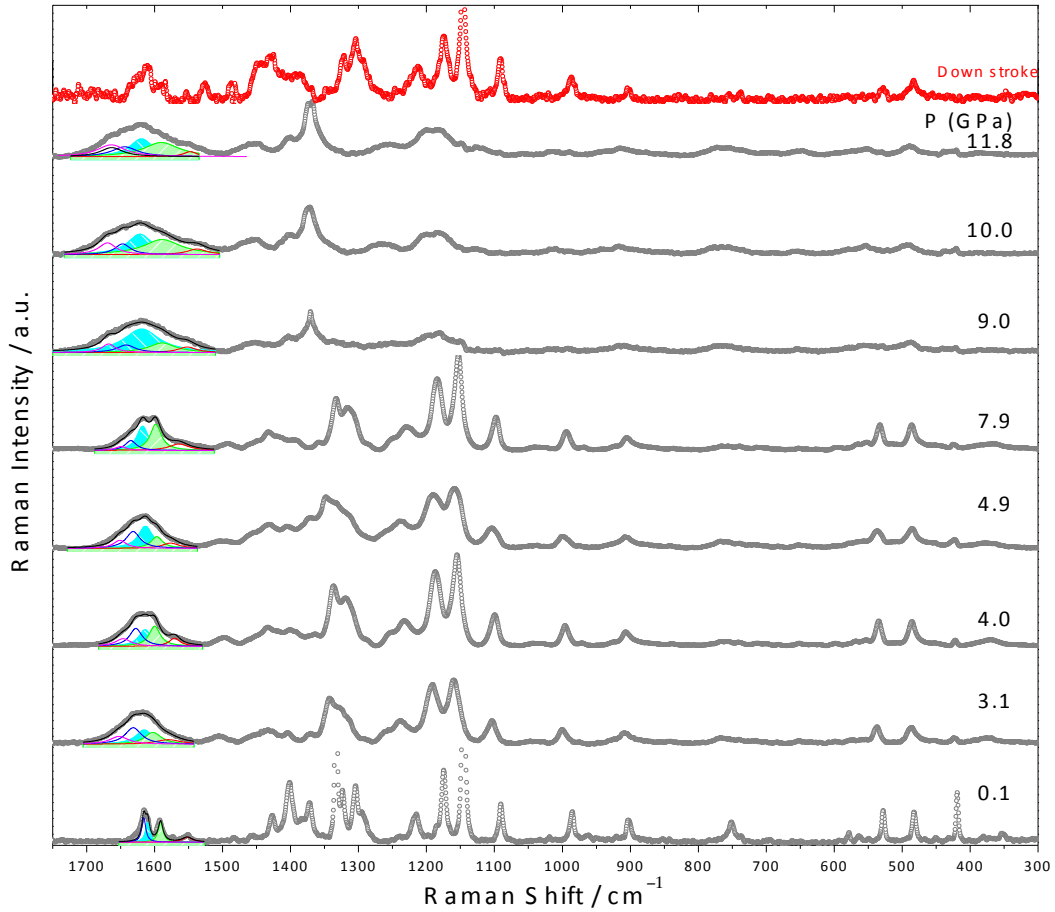

Figure S13. Raman spectrum at selected pressures measured with a laser of 633 nm in the 1750-300 cm^{-1} region. The background has been subtracted to obtain better visibility.

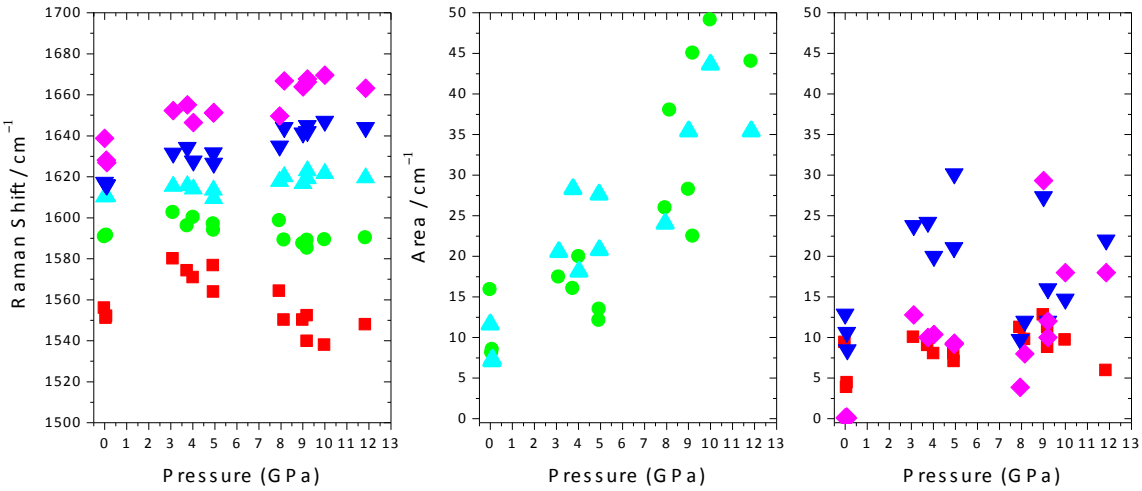

Figure S14. (left) Raman shift pressure evolution of the contributions fitted as in previous figure from experimental Raman spectra taken with 633 nm as excitation line, each color corresponds to the fitted contribution. (middle) Area obtained for the 1610 and 1589 cm^{-1} contributions (cyan and green) (right) Area obtained for the 1637, 1620 and 1555 cm^{-1} contributions (pink, dark blue, and red, respectively) .

In both spectra sets (532 nm and 633 nm), it is seen how with increasing pressure induces the intensity growth of the 1610 and 1591 cm^{-1} bands, which could indicate that pressure leads towards the aromatization of the core.

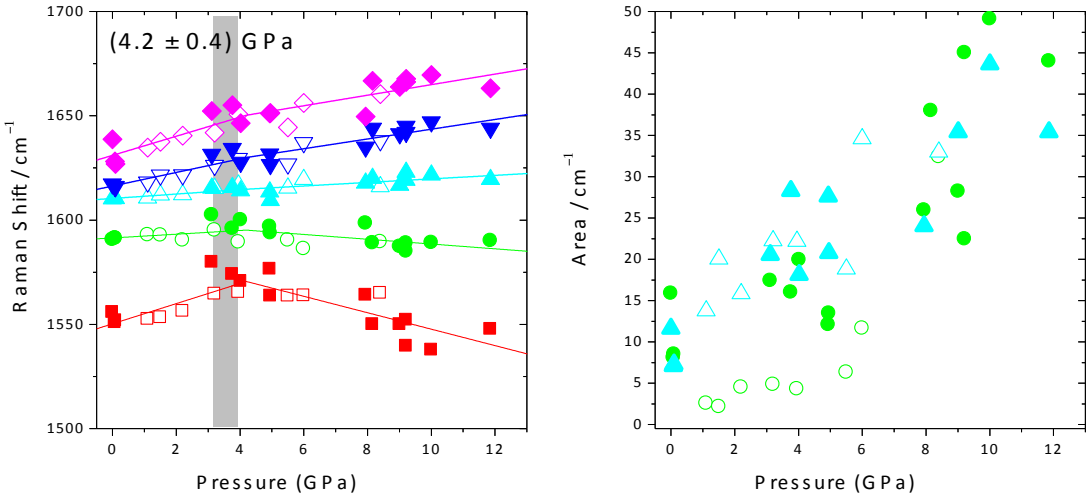

Figure S15. (left) Raman shift pressure evolution of the contributions fitted as in previous figure from experimental Raman spectra taken with 633 and 532 nm, filled and empty symbols respectively; each color corresponds to the fitted contribution. (right) Area obtained for the 1610 and 1589 cm^{-1} contributions (cyan and green)

Table S2. Experimental interceptions and pressure coefficients of the Raman bands

ω_0 (cm^{-1})	1637	1616	1610	1591	1551
S_1(cm^{-1}/GPa)	4.6 ± 0.7	3.3 ± 0.7	1.1 ± 0.7	0.9 ± 0.7	4.8 ± 0.9
S_2(cm^{-1}/GPa)	2.5 ± 0.5	2.3 ± 0.5	0.8 ± 0.5	–1.1 ± 0.5	–3.9 ± 0.6

The observed shifts of all the contributions with pressure show a two regime stage where the different Raman bands shift with different slope with increasing pressure. We have conducted a fitting of all the bands with a shared pressure transition, with the data obtained from the fittings of the 633 nm and 532 nm spectra. We obtain a pressure transition of (4.2 ± 0.4) GPa, from this the slopes of any contribution are smaller than in the previous stage. In the literature of PAHs changes in slopes are related with phase transition within the crystal phase group;[8-10] however, those changes in slopes described for anthracene for instance are softer than the ones obtained for DIAn. Additionally, it should be mentioned that the 1600 and 1591 cm^{-1} show slopes below those observed for other PAHs, and lower than the other DIAn contribution. On the other hand, at pressures above pressure transition not only the slopes of these two contributions, 1600 and 1591 cm^{-1} bands are lower, but in the case of the 1591 cm^{-1} this is negative. These results corroborate that at pressures above 4.2 GPa the aromatic core is favored, explaining the intensity increase of the corresponding features and the lower slopes of the C-C contributions.

Computational Details

Geometry Optimization

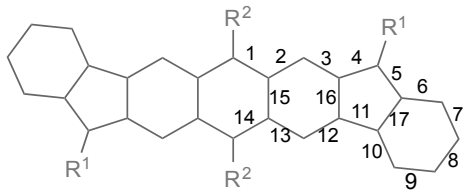

Figure S16. Bond numbering scheme for geometry optimization.

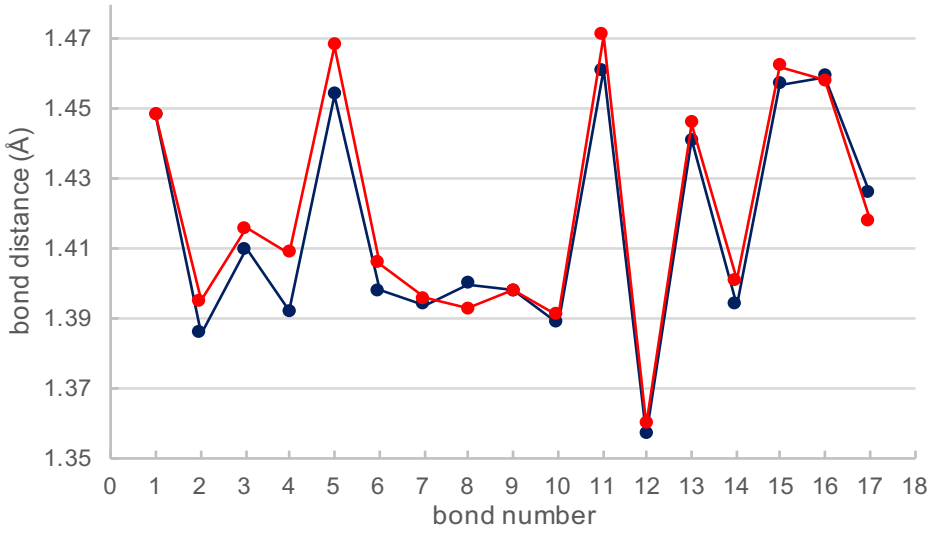

Figure S17. Bond distances from the solid-state structure of **DIAn** (navy) and DFT optimized geometry (red) of model **DIAn**. RMS deviation = 0.008 Å.

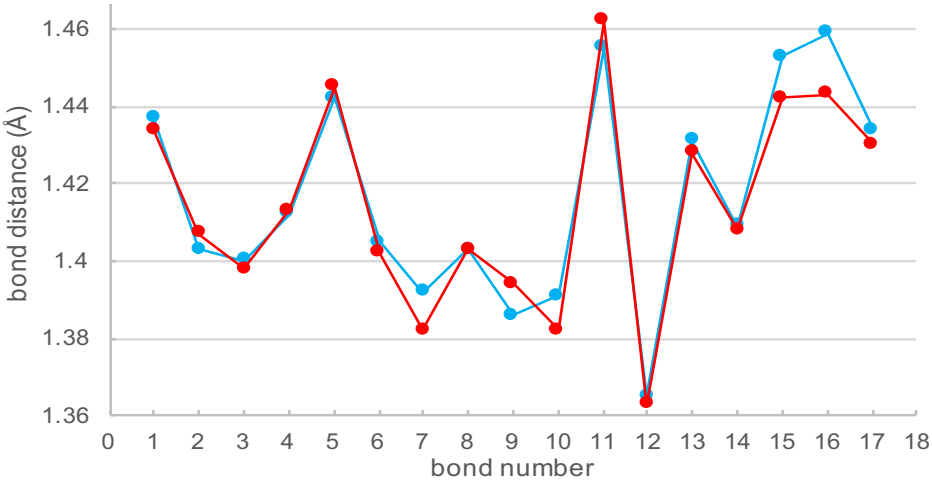

Figure S18. Bond distances from the solid-state structure of radical anion **1** (red) and DFT optimized geometry (blue) of model **DIAn**$^{\bullet-}$. RMS deviation = 0.007 Å.

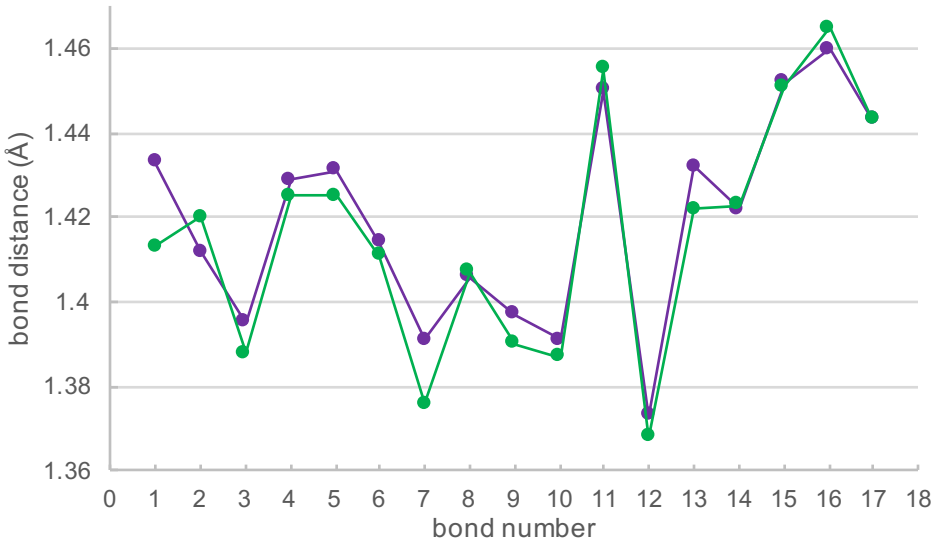

Figure S19. Bond distances from the solid-state structure of dianion **2** (green) and DFT optimized geometry (violet) of model **DIAn** $^{2-}$. RMS deviation = 0.008 Å.

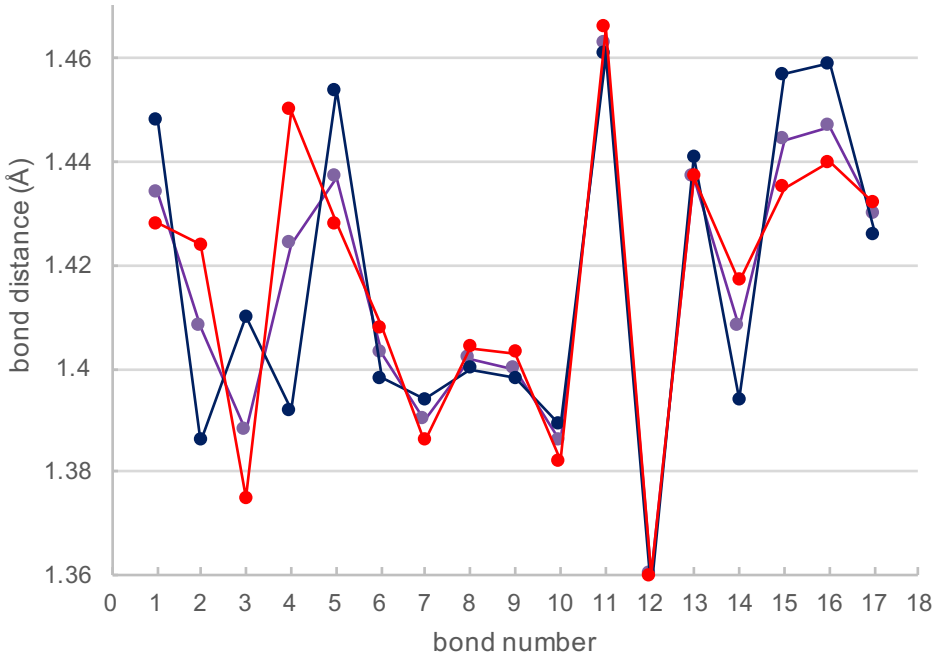

Figure S20. Bond distances from the DFT optimized geometries of the computationally simplified models for **DIAn** (navy), **DIAn**$^{\bullet+}$ (purple), and **DIAn**$^{2+}$ (red).

Cartesian Coordinates

Table S3. Optimized geometry of **DIAn** calculated at RB3LYP/6-311G* level of theory.

Zero-point correction = 0.837187 (Hartree/Particle)
Thermal correction to Energy = 0.893461
Thermal correction to Enthalpy = 0.894405
Thermal correction to Gibbs Free Energy = 0.738425
Sum of electronic and zero-point Energies = –2665.313495
Sum of electronic and thermal Energies = –2665.257222
Sum of electronic and thermal Enthalpies = –2665.256277
Sum of electronic and thermal Free Energies = –2665.412257
NImag = 0

	x	*y*	*z*
C	1.198133	0.785288	0.100175
C	2.377084	1.608252	0.198490
H	3.341749	1.114431	0.231178
C	2.274909	2.960386	0.247085
C	3.269581	4.026014	0.343470
C	4.655646	4.012597	0.424720
H	5.206309	3.076690	0.420415
C	5.340055	5.228112	0.514378
H	6.423301	5.231145	0.578123
C	4.643307	6.441923	0.524961
H	5.195506	7.373549	0.597842
C	3.251935	6.470616	0.445213
H	2.716862	7.414896	0.458185
C	2.556757	5.261053	0.351022
C	1.131548	4.989137	0.262524
C	0.968246	3.607671	0.200980
C	-0.193186	2.814132	0.099815
H	-1.166251	3.289455	0.057640
C	-0.106375	1.431300	0.050442
C	0.056982	6.012734	0.245491
C	-0.635760	6.323854	1.434364
C	-1.644837	7.290158	1.396094
H	-2.177079	7.537558	2.309971
C	-1.968011	7.940093	0.210239
C	-1.280041	7.630677	-0.957774
H	-1.532881	8.138062	-1.884217
C	-0.263850	6.671754	-0.960196
H	0.770590	5.698546	2.960723
H	-2.753408	8.689543	0.196981
Si	-5.256027	2.694990	-0.203814

C	-1.291355	0.604916	-0.051136
C	-2.561012	1.242307	-0.099653
C	-3.635816	1.811868	-0.140546
C	-6.631963	1.406348	-0.227186
H	-6.553065	0.750927	-1.099179
H	-6.605790	0.774995	0.665440
H	-7.616211	1.884197	-0.263328
C	-5.398866	3.788052	1.324331
H	-4.599901	4.533854	1.358170
H	-5.342161	3.200950	2.245068
H	-6.352819	4.325319	1.332541
C	-5.303314	3.741656	-1.769933
H	-6.254284	4.277794	-1.853243
H	-5.190202	3.127358	-2.667407
H	-4.502863	4.486529	-1.776940
C	-0.297732	5.636431	2.736790
H	-0.551688	4.572764	2.711625
H	-0.842289	6.087606	3.568716
C	0.461453	6.340971	-2.243447
H	0.069186	6.927300	-3.076752
H	0.359884	5.282812	-2.500593
H	1.533600	6.543136	-2.168014
C	-1.198133	-0.785288	-0.100175
C	-2.377084	-1.608252	-0.198490
H	-3.341749	-1.114431	-0.231178
C	-2.274909	-2.960386	-0.247085
C	-3.269581	-4.026014	-0.343470
C	-4.655646	-4.012597	-0.424720
H	-5.206309	-3.076690	-0.420415
C	-5.340055	-5.228112	-0.514378
H	-6.423301	-5.231145	-0.578123
C	-4.643307	-6.441923	-0.524961
H	-5.195506	-7.373549	-0.597842
C	-3.251935	-6.470616	-0.445213
H	-2.716862	-7.414896	-0.458185
C	-2.556757	-5.261053	-0.351022
C	-1.131548	-4.989137	-0.262524
C	-0.968246	-3.607671	-0.200980
C	0.193186	-2.814132	-0.099815
H	1.166251	-3.289455	-0.057640
C	0.106375	-1.431300	-0.050442
C	-0.056982	-6.012734	-0.245491
C	0.635760	-6.323854	-1.434364
C	1.644837	-7.290158	-1.396094
H	2.177079	-7.537558	-2.309971

C	1.968011	-7.940093	-0.210239
C	1.280041	-7.630677	0.957774
H	1.532881	-8.138062	1.884217
C	0.263850	-6.671754	0.960196
H	-0.770590	-5.698546	-2.960723
H	2.753408	-8.689543	-0.196981
Si	5.256027	-2.694990	0.203814
C	1.291355	-0.604916	0.051136
C	2.561012	-1.242307	0.099653
C	3.635816	-1.811868	0.140546
C	6.631963	-1.406348	0.227186
H	6.553065	-0.750927	1.099179
H	6.605790	-0.774995	-0.665440
H	7.616211	-1.884197	0.263328
C	5.398866	-3.788052	-1.324331
H	4.599901	-4.533854	-1.358170
H	5.342161	-3.200950	-2.245068
H	6.352819	-4.325319	-1.332541
C	5.303314	-3.741656	1.769933
H	6.254284	-4.277794	1.853243
H	5.190202	-3.127358	2.667407
H	4.502863	-4.486529	1.776940
C	0.297732	-5.636431	-2.736790
H	0.551688	-4.572764	-2.711625
H	0.842289	-6.087606	-3.568716
C	-0.461453	-6.340971	2.243447
H	-0.069186	-6.927300	3.076752
H	-0.359884	-5.282812	2.500593
H	-1.533600	-6.543136	2.168014

Table S4. Optimized geometry of **DIAn**$^{\bullet+}$ calculated at UB3LYP/6-311G* level of theory.

Zero-point correction = 0.837848 (Hartree/Particle)
Thermal correction to Energy = 0.894313
Thermal correction to Enthalpy = 0.895257
Thermal correction to Gibbs Free Energy = 0.737820
Sum of electronic and zero-point Energies = –2665.109046
Sum of electronic and thermal Energies = –2665.052581
Sum of electronic and thermal Enthalpies = –2665.051637
Sum of electronic and thermal Free Energies = –2665.209074
NImag = 0

	x	*y*	*z*
C	1.197885	0.780993	0.099923
C	2.380549	1.591726	0.196157
H	3.342093	1.092756	0.223776
C	2.280379	2.947053	0.247011
C	3.272937	4.018649	0.336140
C	4.656423	4.009612	0.414512
H	5.215666	3.079965	0.413455
C	5.331387	5.233019	0.498645
H	6.414213	5.239635	0.560414
C	4.636704	6.451030	0.508379
H	5.191044	7.380139	0.578539
C	3.249404	6.476561	0.432018
H	2.707552	7.416052	0.444651
C	2.559976	5.257790	0.341157
C	1.149261	4.997109	0.262969
C	0.981642	3.584513	0.205617
C	-0.174742	2.824148	0.104623
H	-1.144850	3.305204	0.064164
C	-0.096291	1.418884	0.051731
C	0.069781	6.009360	0.246476
C	-0.629351	6.299499	1.437805
C	-1.641479	7.261275	1.398512
H	-2.177032	7.503096	2.311154
C	-1.961364	7.916669	0.214715
C	-1.266715	7.621361	-0.952859
H	-1.518704	8.134655	-1.875447
C	-0.241898	6.672648	-0.959954
H	0.774590	5.712802	2.985608
H	-2.749361	8.662398	0.203265
Si	-5.273663	2.698146	-0.208275
C	-1.285658	0.623368	-0.049169
C	-2.549887	1.264750	-0.097724

C	-3.628647	1.827020	-0.140434
C	-6.614509	1.378175	-0.230581
H	-6.525372	0.725865	-1.103819
H	-6.579002	0.749904	0.663779
H	-7.607480	1.836660	-0.267196
C	-5.405580	3.781180	1.323952
H	-4.614452	4.535309	1.354439
H	-5.341301	3.193474	2.243546
H	-6.363548	4.310312	1.338990
C	-5.303944	3.730684	-1.780101
H	-6.258660	4.257367	-1.875223
H	-5.179355	3.113706	-2.673930
H	-4.512192	4.484654	-1.783691
C	-0.286726	5.614030	2.740506
H	-0.507934	4.542979	2.711534
H	-0.855901	6.042560	3.566480
C	0.493057	6.360676	-2.242917
H	0.079859	6.930046	-3.076467
H	0.426217	5.300008	-2.502772
H	1.557226	6.603986	-2.175103
C	-1.197885	-0.780993	-0.099923
C	-2.380549	-1.591726	-0.196157
H	-3.342093	-1.092756	-0.223776
C	-2.280379	-2.947053	-0.247011
C	-3.272937	-4.018649	-0.336140
C	-4.656423	-4.009612	-0.414512
H	-5.215666	-3.079965	-0.413455
C	-5.331387	-5.233019	-0.498645
H	-6.414213	-5.239635	-0.560414
C	-4.636704	-6.451030	-0.508379
H	-5.191044	-7.380139	-0.578539
C	-3.249404	-6.476561	-0.432018
H	-2.707552	-7.416052	-0.444651
C	-2.559976	-5.257790	-0.341157
C	-1.149261	-4.997109	-0.262969
C	-0.981642	-3.584513	-0.205617
C	0.174742	-2.824148	-0.104623
H	1.144850	-3.305204	-0.064164
C	0.096291	-1.418884	-0.051731
C	-0.069781	-6.009360	-0.246476
C	0.629351	-6.299499	-1.437805
C	1.641479	-7.261275	-1.398512
H	2.177032	-7.503096	-2.311154
C	1.961364	-7.916669	-0.214715
C	1.266715	-7.621361	0.952859

H	1.518704	-8.134655	1.875447
C	0.241898	-6.672648	0.959954
H	-0.774590	-5.712802	-2.985608
H	2.749361	-8.662398	-0.203265
Si	5.273663	-2.698146	0.208275
C	1.285658	-0.623368	0.049169
C	2.549887	-1.264750	0.097724
C	3.628647	-1.827020	0.140434
C	6.614509	-1.378175	0.230581
H	6.525372	-0.725865	1.103819
H	6.579002	-0.749904	-0.663779
H	7.607480	-1.836660	0.267196
C	5.405580	-3.781180	-1.323952
H	4.614452	-4.535309	-1.354439
H	5.341301	-3.193474	-2.243546
H	6.363548	-4.310312	-1.338990
C	5.303944	-3.730684	1.780101
H	6.258660	-4.257367	1.875223
H	5.179355	-3.113706	2.673930
H	4.512192	-4.484654	1.783691
C	0.286726	-5.614030	-2.740506
H	0.507934	-4.542979	-2.711534
H	0.855901	-6.042560	-3.566480
C	-0.493057	-6.360676	2.242917
H	-0.079859	-6.930046	3.076467
H	-0.426217	-5.300008	2.502772
H	-1.557226	-6.603986	2.175103

Table S5. Optimized geometry of **DIAn**$^{\bullet-}$ calculated at UB3LYP/6-311G* level of theory.

Zero-point correction = 0.834184 (Hartree/Particle)
Thermal correction to Energy = 0.890242
Thermal correction to Enthalpy = 0.891186
Thermal correction to Gibbs Free Energy = 0.736072
Sum of electronic and zero-point Energies = –2665.405928
Sum of electronic and thermal Energies = –2665.349870
Sum of electronic and thermal Enthalpies = –2665.348926
Sum of electronic and thermal Free Energies = –2665.504041
NImag = 0

	x	*y*	*z*
C	1.189774	0.795155	0.081653
C	2.358846	1.616968	0.156750
H	3.328225	1.130400	0.173781
C	2.257700	2.977482	0.201692
C	3.259692	4.030147	0.271874
C	4.648607	3.997912	0.334868
H	5.178825	3.048983	0.329093
C	5.361130	5.196576	0.409453
H	6.445935	5.181016	0.457875
C	4.678514	6.422094	0.427443
H	5.245902	7.347060	0.493150
C	3.289078	6.475534	0.367726
H	2.775738	7.432528	0.397333
C	2.556195	5.279357	0.281221
C	1.137296	5.030289	0.223218
C	0.953973	3.631405	0.175817
C	-0.196945	2.839657	0.088523
H	-1.173867	3.307240	0.043475
C	-0.111454	1.440136	0.044501
C	0.072835	6.060410	0.217845
C	-0.757389	6.235882	1.349141
C	-1.760125	7.209662	1.322031
H	-2.391593	7.344487	2.196500
C	-1.950501	8.012269	0.202516
C	-1.133071	7.842856	-0.909501
H	-1.285526	8.460824	-1.790842
C	-0.124187	6.875917	-0.920686
H	0.490183	5.376935	2.891588
H	-2.733516	8.765537	0.196377
Si	-5.249753	2.658241	-0.171683
C	-1.281339	0.610233	-0.038926
C	-2.556455	1.234245	-0.077451

C	-3.640462	1.790724	-0.111100
C	-6.642501	1.383047	-0.100016
H	-6.587167	0.685596	-0.940821
H	-6.594508	0.791853	0.818964
H	-7.625164	1.865725	-0.133574
C	-5.386358	3.834013	1.299659
H	-4.589616	4.583004	1.282597
H	-5.309718	3.294854	2.248157
H	-6.343853	4.366264	1.294523
C	-5.373997	3.642771	-1.778682
H	-6.330530	4.172352	-1.847268
H	-5.290594	2.990130	-2.652342
H	-4.576037	4.387227	-1.848608
C	-0.560727	5.401320	2.592565
H	-0.861166	4.361428	2.436265
H	-1.147590	5.797539	3.425407
C	0.718940	6.688920	-2.159966
H	0.329814	7.283356	-2.990811
H	0.739741	5.640363	-2.467817
H	1.759888	6.982144	-1.995378
C	-1.189774	-0.795155	-0.081653
C	-2.358846	-1.616968	-0.156750
H	-3.328225	-1.130400	-0.173781
C	-2.257700	-2.977482	-0.201692
C	-3.259692	-4.030147	-0.271874
C	-4.648607	-3.997912	-0.334868
H	-5.178825	-3.048983	-0.329093
C	-5.361130	-5.196576	-0.409453
H	-6.445935	-5.181016	-0.457875
C	-4.678514	-6.422094	-0.427443
H	-5.245902	-7.347060	-0.493150
C	-3.289078	-6.475534	-0.367726
H	-2.775738	-7.432528	-0.397333
C	-2.556195	-5.279357	-0.281221
C	-1.137296	-5.030289	-0.223218
C	-0.953973	-3.631405	-0.175817
C	0.196945	-2.839657	-0.088523
H	1.173867	-3.307240	-0.043475
C	0.111454	-1.440136	-0.044501
C	-0.072835	-6.060410	-0.217845
C	0.757389	-6.235882	-1.349141
C	1.760125	-7.209662	-1.322031
H	2.391593	-7.344487	-2.196500
C	1.950501	-8.012269	-0.202516
C	1.133071	-7.842856	0.909501

H	1.285526	-8.460824	1.790842
C	0.124187	-6.875917	0.920686
H	-0.490183	-5.376935	-2.891588
H	2.733516	-8.765537	-0.196377
Si	5.249753	-2.658241	0.171683
C	1.281339	-0.610233	0.038926
C	2.556455	-1.234245	0.077451
C	3.640462	-1.790724	0.111100
C	6.642501	-1.383047	0.100016
H	6.587167	-0.685596	0.940821
H	6.594508	-0.791853	-0.818964
H	7.625164	-1.865725	0.133574
C	5.386358	-3.834013	-1.299659
H	4.589616	-4.583004	-1.282597
H	5.309718	-3.294854	-2.248157
H	6.343853	-4.366264	-1.294523
C	5.373997	-3.642771	1.778682
H	6.330530	-4.172352	1.847268
H	5.290594	-2.990130	2.652342
H	4.576037	-4.387227	1.848608
C	0.560727	-5.401320	-2.592565
H	0.861166	-4.361428	-2.436265
H	1.147590	-5.797539	-3.425407
C	-0.718940	-6.688920	2.159966
H	-0.329814	-7.283356	2.990811
H	-0.739741	-5.640363	2.467817
H	-1.759888	-6.982144	1.995378

Table S6. Optimized geometry of **DIAn^{2+}** calculated at RB3LYP/6-311G* level of theory.

Zero-point correction = 0.839521 (Hartree/Particle)
Thermal correction to Energy = 0.895793
Thermal correction to Enthalpy = 0.896737
Thermal correction to Gibbs Free Energy = 0.741682
Sum of electronic and zero-point Energies = –2664.797085
Sum of electronic and thermal Energies = –2664.740813
Sum of electronic and thermal Enthalpies = –2664.739869
Sum of electronic and thermal Free Energies = –2664.894924
NImag = 0

	x	*y*	*z*
C	1.199236	0.775802	0.070328
C	2.388828	1.580722	0.120795
H	3.348576	1.078656	0.100223
C	2.292344	2.936138	0.174602
C	3.294257	4.006721	0.185213
C	4.675841	3.987810	0.229721
H	5.231922	3.057321	0.246073
C	5.358593	5.212461	0.268519
H	6.442573	5.211134	0.305290
C	4.678359	6.440333	0.281553
H	5.243875	7.363034	0.333724
C	3.293240	6.474273	0.242036
H	2.759659	7.416678	0.277567
C	2.592223	5.255039	0.172316
C	1.184612	5.012842	0.187662
C	1.001809	3.574445	0.188244
C	-0.153712	2.834893	0.096909
H	-1.123095	3.316748	0.057604
C	-0.086558	1.413138	0.044620
C	0.128657	6.017176	0.200929
C	-0.775116	6.068104	1.301503
C	-1.752265	7.059428	1.305288
H	-2.415095	7.143635	2.160228
C	-1.875592	7.957267	0.248076
C	-1.002248	7.888684	-0.831300
H	-1.117474	8.578877	-1.660593
C	0.021289	6.943983	-0.874939
H	0.357331	4.815527	2.691745
H	-2.650789	8.715460	0.269690
Si	-5.314997	2.650780	-0.193353
C	-1.283523	0.638321	-0.029516
C	-2.545496	1.279022	-0.067130

C	-3.633590	1.825283	-0.109701
C	-6.600981	1.281265	-0.147091
H	-6.499986	0.600298	-0.996827
H	-6.537055	0.692422	0.772114
H	-7.609535	1.703197	-0.190693
C	-5.448439	3.782791	1.300801
H	-4.681817	4.562514	1.289755
H	-5.355599	3.233281	2.241164
H	-6.421211	4.283809	1.311454
C	-5.374414	3.611734	-1.806447
H	-6.342731	4.109787	-1.915404
H	-5.243377	2.961460	-2.675174
H	-4.603494	4.385694	-1.850086
C	-0.659613	5.166161	2.512694
H	-1.301816	4.284624	2.427539
H	-0.978314	5.700870	3.408650
C	0.902378	6.903493	-2.105033
H	0.308519	7.108900	-2.997504
H	1.394795	5.943406	-2.256629
H	1.680950	7.670972	-2.065639
C	-1.199236	-0.775802	-0.070328
C	-2.388828	-1.580722	-0.120795
H	-3.348576	-1.078656	-0.100223
C	-2.292344	-2.936138	-0.174602
C	-3.294257	-4.006721	-0.185213
C	-4.675841	-3.987810	-0.229721
H	-5.231922	-3.057321	-0.246073
C	-5.358593	-5.212461	-0.268519
H	-6.442573	-5.211134	-0.305290
C	-4.678359	-6.440333	-0.281553
H	-5.243875	-7.363034	-0.333724
C	-3.293240	-6.474273	-0.242036
H	-2.759659	-7.416678	-0.277567
C	-2.592223	-5.255039	-0.172316
C	-1.184612	-5.012842	-0.187662
C	-1.001809	-3.574445	-0.188244
C	0.153712	-2.834893	-0.096909
H	1.123095	-3.316748	-0.057604
C	0.086558	-1.413138	-0.044620
C	-0.128657	-6.017176	-0.200929
C	0.775116	-6.068104	-1.301503
C	1.752265	-7.059428	-1.305288
H	2.415095	-7.143635	-2.160228
C	1.875592	-7.957267	-0.248076
C	1.002248	-7.888684	0.831300

H	1.117474	-8.578877	1.660593
C	-0.021289	-6.943983	0.874939
H	-0.357331	-4.815527	-2.691745
H	2.650789	-8.715460	-0.269690
Si	5.314997	-2.650780	0.193353
C	1.283523	-0.638321	0.029516
C	2.545496	-1.279022	0.067130
C	3.633590	-1.825283	0.109701
C	6.600981	-1.281265	0.147091
H	6.499986	-0.600298	0.996827
H	6.537055	-0.692422	-0.772114
H	7.609535	-1.703197	0.190693
C	5.448439	-3.782791	-1.300801
H	4.681817	-4.562514	-1.289755
H	5.355599	-3.233281	-2.241164
H	6.421211	-4.283809	-1.311454
C	5.374414	-3.611734	1.806447
H	6.342731	-4.109787	1.915404
H	5.243377	-2.961460	2.675174
H	4.603494	-4.385694	1.850086
C	0.659613	-5.166161	-2.512694
H	1.301816	-4.284624	-2.427539
H	0.978314	-5.700870	-3.408650
C	-0.902378	-6.903493	2.105033
H	-0.308519	-7.108900	2.997504
H	-1.394795	-5.943406	2.256629
H	-1.680950	-7.670972	2.065639

Table S7. Optimized geometry of **DIAn^{2-}** calculated at RB3LYP/6-311G* level of theory.

Zero-point correction = 0.831428 (Hartree/Particle)
Thermal correction to Energy = 0.887184
Thermal correction to Enthalpy = 0.888128
Thermal correction to Gibbs Free Energy = 0.736709
Sum of electronic and zero-point Energies = –2665.395095
Sum of electronic and thermal Energies = –2665.339339
Sum of electronic and thermal Enthalpies = –2665.338395
Sum of electronic and thermal Free Energies = –2665.489814
NImag = 0

	x	*y*	*z*
C	1.186081	0.805294	0.078916
C	2.345067	1.627846	0.143700
H	3.318942	1.148662	0.145583
C	2.243090	2.996093	0.191839
C	3.249456	4.039062	0.242614
C	4.638509	3.991564	0.300277
H	5.150989	3.031342	0.297661
C	5.376974	5.175950	0.368486
H	6.462820	5.144483	0.411099
C	4.703734	6.409508	0.392318
H	5.281898	7.330127	0.461517
C	3.316185	6.484315	0.339148
H	2.823488	7.452120	0.391739
C	2.548664	5.300274	0.247781
C	1.136804	5.069454	0.212912
C	0.940380	3.654574	0.180476
C	-0.201114	2.858150	0.092270
H	-1.181315	3.317727	0.031704
C	-0.115152	1.449239	0.047220
C	0.088907	6.104582	0.215610
C	-0.847119	6.194282	1.281518
C	-1.835304	7.182233	1.263279
H	-2.537992	7.240867	2.092159
C	-1.918870	8.102865	0.222697
C	-1.003492	8.026966	-0.822241
H	-1.073313	8.728390	-1.651855
C	-0.012046	7.042591	-0.847357
H	0.278471	5.186032	2.815511
H	-2.692244	8.867485	0.224296
Si	-5.247603	2.620615	-0.153143
C	-1.276246	0.612924	-0.034134
C	-2.552282	1.225602	-0.066973

C	-3.645902	1.770173	-0.094709
C	-6.647195	1.376348	0.131622
H	-6.638727	0.589535	-0.628324
H	-6.549002	0.886990	1.104981
H	-7.628933	1.862740	0.098572
C	-5.332965	3.956351	1.184246
H	-4.534825	4.693177	1.056943
H	-5.218918	3.522268	2.181917
H	-6.290054	4.490363	1.157398
C	-5.501748	3.440005	-1.841581
H	-6.465702	3.959376	-1.896254
H	-5.472371	2.700401	-2.647133
H	-4.715015	4.172663	-2.042526
C	-0.754763	5.265287	2.466901
H	-1.067178	4.246619	2.219857
H	-1.380640	5.620093	3.291812
C	0.903571	6.949609	-2.044207
H	0.533841	7.569068	-2.867834
H	0.981521	5.915354	-2.389144
H	1.925634	7.267326	-1.815119
C	-1.186081	-0.805294	-0.078916
C	-2.345067	-1.627846	-0.143700
H	-3.318942	-1.148662	-0.145583
C	-2.243090	-2.996093	-0.191839
C	-3.249456	-4.039062	-0.242614
C	-4.638509	-3.991564	-0.300277
H	-5.150989	-3.031342	-0.297661
C	-5.376974	-5.175950	-0.368486
H	-6.462820	-5.144483	-0.411099
C	-4.703734	-6.409508	-0.392318
H	-5.281898	-7.330127	-0.461517
C	-3.316185	-6.484315	-0.339148
H	-2.823488	-7.452120	-0.391739
C	-2.548664	-5.300274	-0.247781
C	-1.136804	-5.069454	-0.212912
C	-0.940380	-3.654574	-0.180476
C	0.201114	-2.858150	-0.092270
H	1.181315	-3.317727	-0.031704
C	0.115152	-1.449239	-0.047220
C	-0.088907	-6.104582	-0.215610
C	0.847119	-6.194282	-1.281518
C	1.835304	-7.182233	-1.263279
H	2.537992	-7.240867	-2.092159
C	1.918870	-8.102865	-0.222697
C	1.003492	-8.026966	0.822241

H	1.073313	-8.728390	1.651855
C	0.012046	-7.042591	0.847357
H	-0.278471	-5.186032	-2.815511
H	2.692244	-8.867485	-0.224296
Si	5.247603	-2.620615	0.153143
C	1.276246	-0.612924	0.034134
C	2.552282	-1.225602	0.066973
C	3.645902	-1.770173	0.094709
C	6.647195	-1.376348	-0.131622
H	6.638727	-0.589535	0.628324
H	6.549002	-0.886990	-1.104981
H	7.628933	-1.862740	-0.098572
C	5.332965	-3.956351	-1.184246
H	4.534825	-4.693177	-1.056943
H	5.218918	-3.522268	-2.181917
H	6.290054	-4.490363	-1.157398
C	5.501748	-3.440005	1.841581
H	6.465702	-3.959376	1.896254
H	5.472371	-2.700401	2.647133
H	4.715015	-4.172663	2.042526
C	0.754763	-5.265287	-2.466901
H	1.067178	-4.246619	-2.219857
H	1.380640	-5.620093	-3.291812
C	-0.903571	-6.949609	2.044207
H	-0.533841	-7.569068	2.867834
H	-0.981521	-5.915354	2.389144
H	-1.925634	-7.267326	1.815119

TD-DFT Calculations

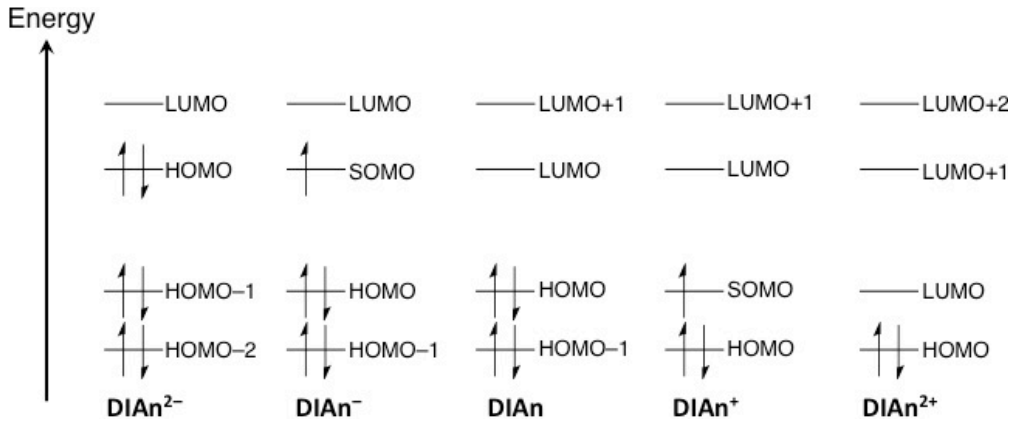

Figure S21. Orbital diagrams of **DIAn** series.

Table S8. TD-UB3LYP/6-311+G** result of low lying states with non-zero f in neutral state.

state	Configuration	E	f
2	H-1a => La (0.43) Ha => La (-0.28) Ha => L+1a (0.46) H-1a => Lb (-0.43) Hb => Lb (0.28) Hb => L+1b (0.46)	1.5490 eV (800.43 nm)	0.0950
3	H-1a => La (-0.14) H-1a => L+1a (0.13) Ha => La (-0.62) Ha => L+1a (-0.27) H-1b => Lb (0.14) H-1b => L+1b (0.13) Hb => Lb (0.62) Hb => L+1b (-0.27)	1.7264 eV (718.17 nm)	0.5228

Table S9. TD-UB3LYP/6-311+G** result of low lying states with non-zero f in mono-anionic state.

state	configuration	E	f
1	H-1a=>La (-0.10) Sa=>La (0.51) Hb=>Sb (0.84)	0.8595 eV (1442.58 nm)	0.1841
2	H-1a=>La (0.17) Sa=>La (0.84) H-2b=>Lb (0.11) Hb=>Sb (-0.49)	1.0229 eV (1212.05 nm)	0.2244

Table S10. TD-U(R)B3LYP/6-311+G** result of low lying states with non-zero f in dianionic state [restricted wavefunction]

state	configuration	E	f
2	Ha=>La (0.71) Hb=>Lb (-0.71)	0.9589 eV (1293.00 nm)	0.0785

Table S11. TD-UB3LYP/6-311+G** result of low lying states with non-zero f in mono-cationic state

state	configuration	E	f
1	Sa=>La (0.90) H-1b=>Sb (-0.13) Hb=>Sb (0.39) Hb=>L+1b (-0.12)	0.8524 eV (1454.59 nm)	0.1663
3	Sa=>La (-0.31) H-6b=>Lb (-0.12) H-3b=>Sb (-0.20) H-1b=>Sb (-0.30) Hb=>Sb (0.87)	1.3178 eV (940.87 nm)	0.1183

Table S12. TD-U(R)B3LYP/6-311+G** result of low lying states with non-zero f in dicationic state [restricted wavefunction]

state	configuration	E	f
2	Ha=>La (0.68) Hb=>Lb (0.68) H-3a=>La (0.19) H-3b=>Lb (0.19)	1.0894 eV (1138.13 nm)	0.1811

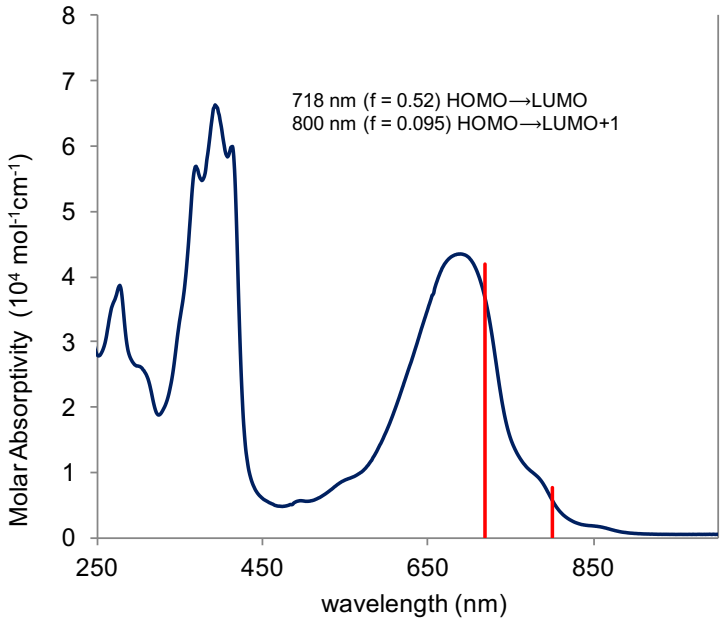

Figure S22. Electronic absorption spectra of neutral DIAn and and electronic transitions from TDDFT calculation.

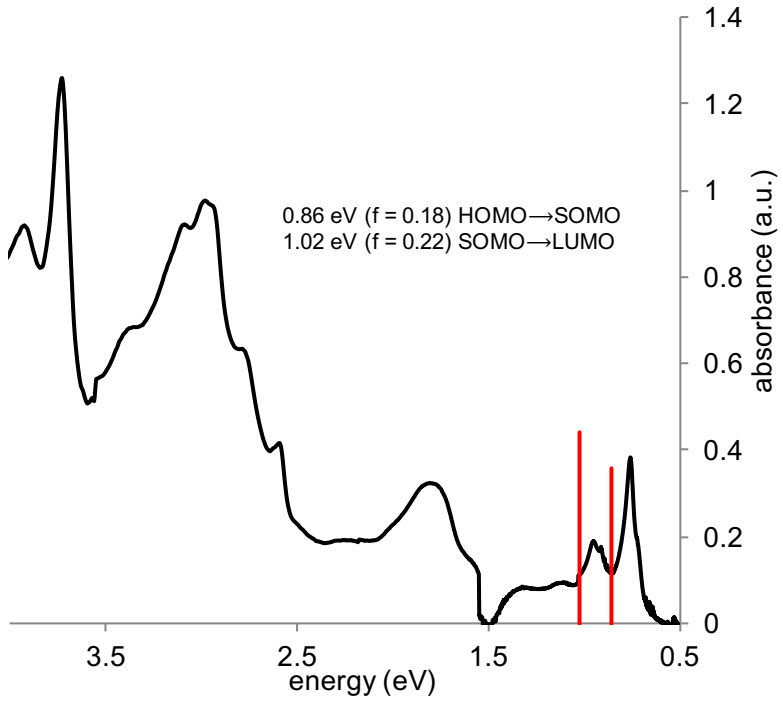

Figure S23. DIAn radical anion generated by electrolysis and electronic transitions from TDDFT calculation.

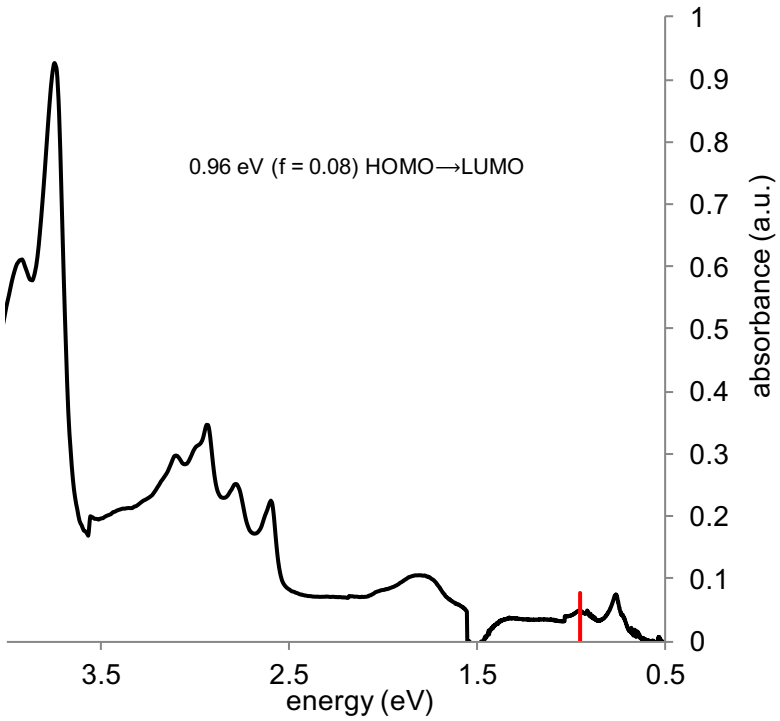

Figure S24. DIAn dianion generated by electrolysis and electronic transitions from TDDFT calculation.

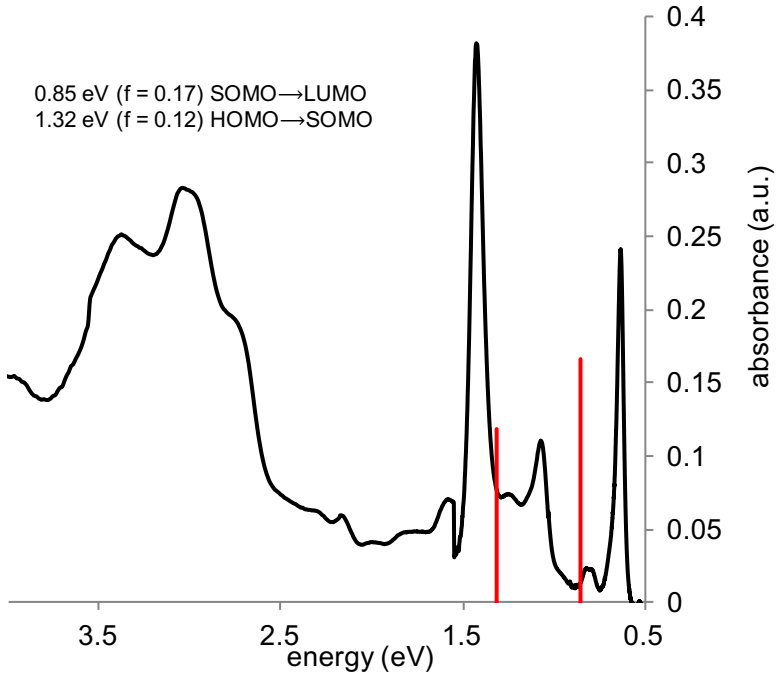

Figure S25. DIAn radical cation generated by electrolysis and electronic transitions from TDDFT calculation.

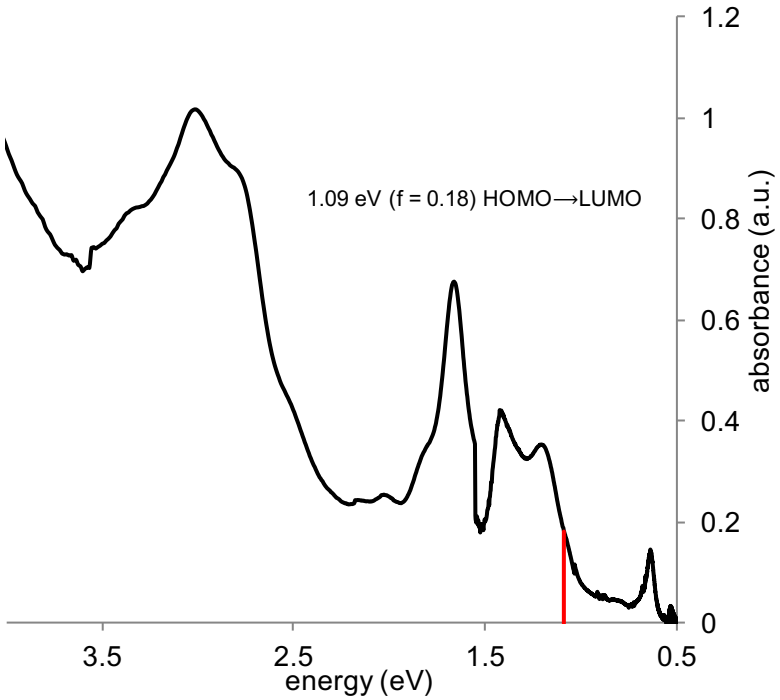

Figure S26. DIAn dication generated by electrolysis and electronic transitions from TDDFT calculation.

Hirshfeld Charge

Atomic Hirshfeld charges are also calculated at LC-UBLYP/6-311+G** level of theory for each optimized geometry (Table S8). It is found that the largest difference upon ionization occurs at the carbon atoms of the five-membered rings at which the dimethylphenyl substituents are bonded (atom number 15 and 67 in Figure S26). More exactly, the carbon atom in the cationic **DIAn**$^{+}$ system exhibits 0.11 a.u. less, and that in the anionic **DIAn**$^{-}$ system does 0.11 more electrons. This observation also substantiates the charge localization at the five-membered rings in mono-ionic states.

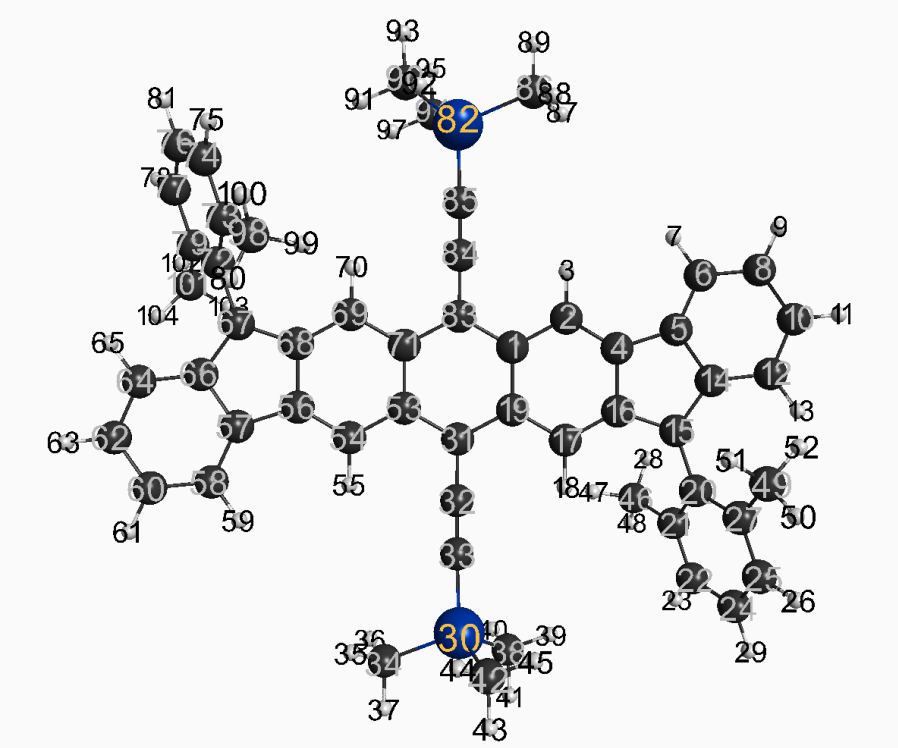

Figure S27. Atomic numbering.

Table S13. Hirshfeld charges of each state calculated at LC-UBLYP/6-311+G** method.

Atom Number	**DIAn**$^{+}$	**DIAn**	**DIAn**$^{-}$
1	0.017406	0.000852	-0.020148
2	-0.004518	-0.029016	-0.060802
3	0.064263	0.049505	0.031908
4	-0.003251	-0.009163	-0.028217
5	0.028278	-0.012766	-0.047212
6	-0.015471	-0.039281	-0.063385
7	0.069401	0.049597	0.031467
8	0.032272	-0.046990	-0.115948
9	0.079963	0.045302	0.010180
10	-0.012840	-0.047294	-0.084501
11	0.074408	0.045632	0.016346

12	0.019351	-0.040857	-0.086072
13	0.075162	0.050323	0.024874
14	-0.012184	-0.015863	-0.023090
15	0.122832	0.010704	-0.103894
16	-0.010212	-0.021843	-0.025473
17	0.033220	-0.028300	-0.090364
18	0.069335	0.049098	0.026864
19	0.012613	-0.006389	-0.017872
20	-0.024164	-0.017272	-0.006787
21	0.014528	0.000052	-0.007537
22	-0.036601	-0.057218	-0.075782
23	0.061114	0.042262	0.025646
24	-0.004804	-0.047889	-0.082799
25	-0.034391	-0.057306	-0.079000
26	0.063366	0.042184	0.022896
27	0.017251	-0.000267	-0.010854
28	0.041852	0.042174	0.037770
29	0.070106	0.045627	0.022686
30	0.422340	0.414828	0.403890
31	0.030542	0.007240	-0.022117
32	-0.056913	-0.036753	-0.016017
33	-0.122158	-0.160376	-0.203130
34	-0.189076	-0.194486	-0.200641
35	0.039738	0.037171	0.033574
36	0.040416	0.037420	0.032878
37	0.050563	0.036526	0.021795
38	-0.188632	-0.193625	-0.199576
39	0.037559	0.039184	0.038712
40	0.043559	0.038254	0.031677
41	0.049675	0.036062	0.021966
42	-0.187586	-0.193405	-0.199996
43	0.049547	0.036069	0.021756
44	0.044543	0.038417	0.031514
45	0.040923	0.039887	0.037127
46	-0.083609	-0.089603	-0.098855
47	0.046255	0.041632	0.037155
48	0.057447	0.038061	0.019393
49	-0.082821	-0.089814	-0.100046
50	0.057486	0.038080	0.018217
51	0.039831	0.042691	0.040468
52	0.052121	0.040578	0.029256
53	0.017406	0.000852	-0.020148
54	-0.004518	-0.029016	-0.060802
55	0.064263	0.049505	0.031908
56	-0.003251	-0.009163	-0.028217
57	0.028279	-0.012766	-0.047212
58	-0.015471	-0.039281	-0.063385
59	0.069401	0.049597	0.031467
60	0.032272	-0.046990	-0.115948

61	0.079963	0.045302	0.010180
62	-0.012840	-0.047294	-0.084501
63	0.074408	0.045632	0.016346
64	0.019351	-0.040857	-0.086072
65	0.075162	0.050323	0.024874
66	-0.012183	-0.015863	-0.023090
67	0.122832	0.010704	-0.103894
68	-0.010212	-0.021843	-0.025473
69	0.033220	-0.028300	-0.090364
70	0.069335	0.049098	0.026864
71	0.012613	-0.006389	-0.017872
72	-0.024164	-0.017272	-0.006787
73	0.014528	0.000052	-0.007537
74	-0.036601	-0.057218	-0.075782
75	0.061114	0.042262	0.025646
76	-0.004804	-0.047889	-0.082799
77	-0.034391	-0.057306	-0.079000
78	0.063366	0.042184	0.022896
79	0.017251	-0.000267	-0.010854
80	0.041852	0.042174	0.037770
81	0.070106	0.045627	0.022686
82	0.422340	0.414828	0.403890
83	0.030542	0.007240	-0.022117
84	-0.056913	-0.036753	-0.016017
85	-0.122158	-0.160376	-0.203130
86	-0.189076	-0.194486	-0.200641
87	0.039738	0.037171	0.033574
88	0.040416	0.037420	0.032878
89	0.050563	0.036526	0.021795
90	-0.188632	-0.193625	-0.199576
91	0.037559	0.039184	0.038712
92	0.043559	0.038254	0.031677
93	0.049675	0.036062	0.021966
94	-0.187586	-0.193405	-0.199996
95	0.049547	0.036069	0.021756
96	0.044543	0.038417	0.031514
97	0.040923	0.039887	0.037127
98	-0.083609	-0.089603	-0.098855
99	0.046255	0.041632	0.037155
100	0.057447	0.038061	0.019393
101	-0.082821	-0.089814	-0.100046
102	0.057486	0.038080	0.018217
103	0.039831	0.042691	0.040468
104	0.052121	0.040578	0.029256

References

(1) Kozhemyakina, N. V.; Nuss, J.; Jansen, M. *Z. Anorg. Allg. Chem.* **2009**, *635*, 1355–1361.

(2) Rudebusch, G. E.; Zafra, J. L.; Jorner, K.; Fukuda, K.; Marshall, J. L.; Arrechea-Marcos, I.; Espejo, G. L.; Ortiz, R. P.; Gómez-García, C. J.; Zakharov, L. N.; Nakano, M.; Ottosson, H.; Casado, J.; Haley, M. M. *Nat. Chem.* **2016**, *8*, 753–759.

(3) *SADABS, Bruker AXS*. **2001**.

(4) Sheldrick, G. M. *SHELXTL, Version 6.14, University of Göttingen, Germany* **2000**.

(5) Spek, A. L. *Acta Cryst.* **2015**, *C71*, 9–19.

(6) Baonza, V. G.; Taravillo, M.; Arencibia, A.; Cáceres, M.; Núñez, J. *J. Raman Spectrosc.* **2003**, *34*, 264-270.

(7) del Corro, E.; González, J.; Taravillo, M.; Flahaut, E.; Baonza, V. G. *Nano Lett.* **2008**, *8*, 2215.

(8) Bannon, E.; Williams, Q. *Phys. Chem. Minerals* **2016**, *43*, 181-208.

(9) Zhao, L.; Baer, B. J.; Chronister, E. L. *J. Phys. Chem. A* **1999**, *103*, 1728-1733.

(10) Huan, W.; Zhang, J.; Berlie, A.; Qin, Z. X.; Zhao, X. M.; Zhang, J. B.; Tang, L. Y.; Luin, J.; Zhang, C.; Zhong, G. J.; Lin, H. Q.; Chen, X. J. *J. Chem. Phys.* **2013**, *139*, 10432.