Rigidification of a Macrocyclic *Tris*-Catecholate Scaffold Leads to Electronic Localisation of its Mixed Valent Redox Product

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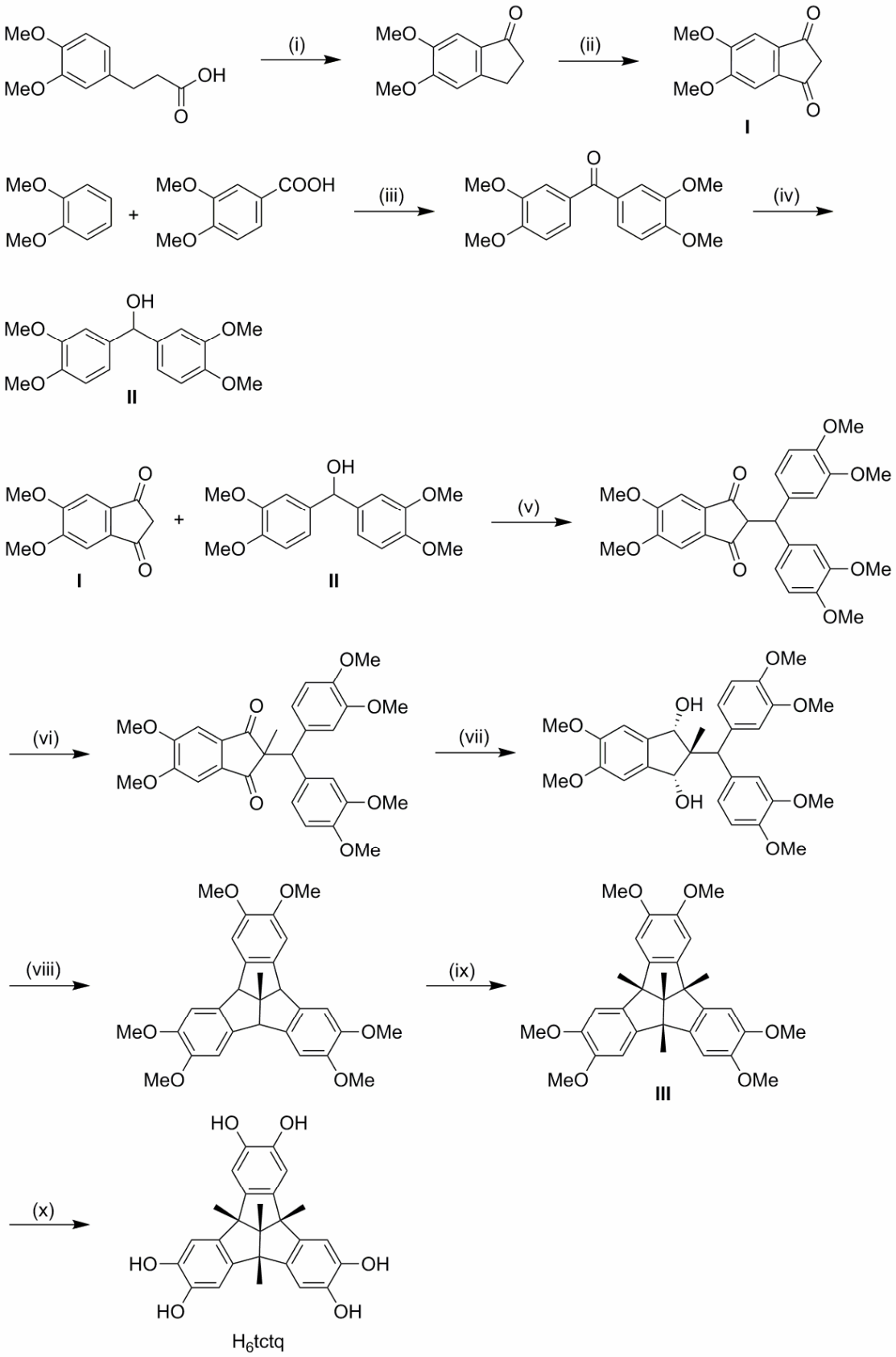
Supporting Information



Scheme S1. Synthesis of H_6tctq. Steps (i)-(ix) are taken from ref. 1. Reagents and conditions: (i) $(COCl)_2$, dmf, CH_2Cl_2, rt, 18 hrs then $AlCl_3$, CH_2Cl_2, rt, 2 hrs, 34 %; (ii) CrO_3, AcOH/H_2O, 0 °C→rt, 3 days, 19 %; (iii) Polyphosphoric acid, 80 °C, 30 min then ice, 75 %; (iv) 10 bar H_2, Pd/C, pyridine, MeOH, rt, 4 days, 70 %; (v) TsOH, toluene/CH_2Cl_2, reflux, 18 hrs, 89 %; (vi) MeI, KF/celite, MeCN, reflux, 18 hrs, 74 %; (vii) DIBAL, toluene, 0 °C→rt, 18 hrs, 81 %; (viii) H_3PO_4, chlorobenzene, reflux, 1 hr, 36 %; (ix) NBS/AIBN, benzene, *hν*, 45 mins then $AlMe_3$, toluene, 50 °C, 1 hr, 25 %; (x) BBr_3, CH_2Cl_2, 0 °C, 6 hrs, 98 %.

Experimental

2,3,6,7,10,11-Hexamethoxy-4b,8b,12b,12d-tetramethyltribenzotriquinacene (compound **III**, Scheme S1)[1] and $[PtCl_2L]$ (L = dppb, dppe)[2] were prepared by the literature procedures. Other reagents and solvents were purchased commercially and used as supplied.

Synthesis of 2,3,6,7,10,11-hexahydroxy-4b,8b,12b,12d-tetramethyltribenzotriquinacene (H_6tctq). To a stirred solution of 2,3,6,7,10,11-hexamethoxy-4b,8b,12b,12d-tetramethyltribenzotriquinacene (0.12 g, 0.23 mmol) in dry dichloromethane (6.5 cm^3) in an ice bath under N_2 was added boron tribromide (0.38 g, 1.52 mmol). After stirring for 6 hrs the mixture was poured onto ice (40 g) and stirred at room temperature until the ice melted. The resultant pale red precipitate was collected by filtration, washed with water (3 x 5 cm^3) and dried *in vacuo*. Yield 0.094 g, 98 %. Mp 350 °C dec. ^{1}H NMR ($\{CD_3\}_2CO$) δ 1.23 (s, 3H, C*H*$_3$), 1.34 (s, 9H, C*H*$_3$), 6.63 (s, 6H, C*H*), 7.37 (br s, 6H, O*H*). HR-ESMS *m/*z: 453.1265 (calcd for $[C_{26}H_{22}O_6Na]^+$ 453.1309).

Synthesis of $[\{Pt(dppb)\}_3(\mu_3\text{-tctq})]$ (2a). A mixture of H_6tctq (0.018 g, 0.043 mmol) and $[PtCl_2(dppb)]$ (0.10 g, 0.14 mmol) in dry deoxygenated *N*,*N*-dimethylacetamide (10 cm^3) was stirred for 30 mins under a nitrogen atmosphere, before potassium *tert*-butoxide (0.040 g, 0.36 mmol) in dry deoxygenated methanol (5 cm^3) was added dropwise. The mixture turned from yellow to green and was stirred for 18 hours. Dry deoxygenated diethyl ether (20 cm^3) was added, and the mixture was cooled in an ice bath for 30 minutes before being filtered by cannula to afford a pale green powder. The product was recrystallised from a chloroform/pentane solvent mixture. Yield 0.064 g, 63 %. Found C, 49.0; H, 3.47; N, 0.00 %. Calculated for $C_{116}H_{90}O_6P_6Pt_3\cdot 4CHCl_3$ C, 49.3; H, 3.25; N, 0.00 %. ESMS *m/*z: 685.1 ($[Pt(dppb)(O_2CH)–H]^+$), 856.2 ($[\{Pt(dppb)\}_2(H_2tctq)+2H]^{2+}$), 1175.2 ($[\{Pt(dppb)\}_3(tctq)+H]^{2+}$), 1398.1 ($[\{Pt(dppb)\}_3(dppb)(tctq)+H]^{2+}$), 1711.3 ($[\{Pt(dppb)\}_2(H_2tctq)+H]^+$), 2350.4 (calcd for $[\{Pt(dppb)\}_3(tctq-)+H]^+$) . ^{1}H NMR ($CD_2Cl_2$) δ 1.12 (s, 3H, tctq C*H*$_3$), 1.36 (s, 9H, tctq C*H*$_3$), 6.47 (s, 6H, tctq C*H*), 7.40-7.85 (m, 72H, dppb C*H*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 29.9 ($J_{P\text{-}195Pt}$ = 3358 Hz).

Synthesis of $[\{Pt(dppe)\}_3(\mu_3\text{-tctq})]$ (2b). Method as for **2a**, using $[PtCl_2(dppe)]$ (0.093 g, 0.14 mmol). The product was isolated as a sparingly soluble pale green powder, of which small amounts could be purified by recrystallisation from chloroform/pentane. Yield 0.047 g, 50 %. Found C, 48.4; H, 3.15; N, 0.00 %. Calculated for $C_{104}H_{90}O_6P_6Pt_3\cdot 4CHCl_3$ C, 48.3; H, 3.52; N, 0.00 %. ESMS (dmso) *m/z*: 636.1 ($[Pt(dppe)(O_2CH)]^+$), 670.1 ($[Pt(dppe)(dmso)]^+$), 1693.2 ($[\{Pt(dppe)\}_2(H_2tctq)(dmso)+H]^+$).

The compound was insufficiently soluble to afford useful NMR spectra.

Single crystal X-ray structure determination of H_6tctq·thf·*n*MeOH

The crystals were obtained by storage of a solution of H_6tctq in a thf/methanol mixture, at –15 °C. Diffraction data were collected with an Agilent Supernova diffractometer, using monochromated Cu-K_α radiation (λ = 1.54184 Å). The diffractometer is fitted with an Oxford Cryosystems low-temperature device. Experimental details of the structure determination are given in Table S1. The structure was solved by direct methods (*SHELXS97*[3]), and developed by least-squares refinement on F^2 (*SHELXL97*[3]). Crystallographic figures were prepared using *X-SEED*.[4]

The asymmetric unit contains one molecule of interest, and one fully occupied molecule of thf. Two weak residual Fourier peaks near the crystallographic inversion centre ½, ½, 0 were also included in the model as a 0.15-occupied molecule of methanol. All fully occupied non-H atoms were refined anisotropically. The tctq O-bound hydroxyl H atoms were located in the Fourier map and were allowed to refine, with U_{iso} restrained to 1.5x U_{eq} of the corresponding O atom. Other H atoms were placed in calculated positions and refined using a riding model. An antibumping restraint was applied to the fractional methanol OH group, to ensure a reasonable geometry.

Table S1 Crystallographic experimental data for H_6tctq·thf·nMeOH ($n \approx 0.15$).

Molecular formula	$C_{30.75}H_{33.80}O_7$	V / Å^3	1273.1(3)
M_r	515.38	Z	2
Crystal system	triclinic	μ\{Cu-K_α\} / mm^{-1}	0.772
Space group	$P\bar{1}$	T / K	120(2)
a / Å	11.1115(13)	Measured reflections	9545
b / Å	11.3585(16)	Independent reflections	4773
c / Å	12.7308(15)	R_{int}	0.060
α / °	67.602(12)	R_1, $I > 2\sigma(I)$[a]	0.082
β / °	67.891(11)	wR_2, all data[b]	0.247
γ/ °	62.042(13)		

[a]$R = \Sigma[|F_o| - |F_c|] / \Sigma|F_o|$ [b]$wR = [\Sigma w(F_o^2 - F_c^2) \ / \ \Sigma wF_o^4]^{1/2}$

Other measurements

Elemental microanalyses were performed by the London Metropolitan University microanalytical service. Electrospray mass spectra (MS) were obtained on a Bruker MicroTOF spectrometer, from MeCN feed solutions. All mass peaks have the correct isotopic distributions for the proposed assignments. Alkali metal cations and formate anions in the molecular ion assignments originate from calibrants in the spectrometer feed solutions. NMR spectra were run using a Bruker Avance 500 spectrometer operating at 500.1 MHz (^{1}H) or 125.6 MHz (^{31}P). UV/vis/NIR spectra for redox titrations were run on a Perkin Elmer Lambda900 spectrophotometer using 1 cm quartz cells.

Electrochemical measurements were carried out using an Autolab PGSTAT204 voltammetric analyser, under an argon atmosphere, in predried CH_2Cl_2 containing 0.1 M ^{n}Bu$_4$NPF$_6$ as supporting electrolyte. Voltammetry experiments used a Pt disk working electrode, a Pt rod counter electrode and an Ag/AgCl reference electrode. All potentials quoted are referenced to internal ferrocene and were obtained at a scan rate (v) of 100 mV s^{-1}. The Fc$^{+/0}$ couple under these conditions was observed at $E_{1/2}$ = +0.48 ±0.01 V *vs.* Ag/AgCl. UV/vis/NIR spectroelectrochemistry experiments were conducted using a Shimadzu UV-3600 plus spectrophotometer, fitted with an optically transparent thin layer electrode (OTTLE) cell. The working electrode was platinum gauze in the path of the beam, the counter electrode was platinum wire, and silver wire was used as the reference electrode. The electrolysis was controlled by an Autolab PGSTAT 100N.

Multifrequency EPR measurements were carried out at the EPSRC National UK EPR Facility and Service in the Photon Science Institute at The University of Manchester. Samples were prepared by oxidation of the neutral complex by ferrocenium hexafluorophosphate in CH_2Cl_2 solution at –78 °C with a concentration of 3-5 mM. A small amount of THF was added to the reaction mixture before samples were loaded into the appropriately sized quartz tubes. S-band (v = 3.86 GHz) and X-band (v = 9.41 GHz) continuous wave spectra were collected using a Bruker EMX spectrometer. Spectrum simulations were performed using *Easyspin*.[5]

Calculations

The ORCA program package was used for all calculations.[6] The geometries of all molecules were fully optimised by a spin-unrestricted DFT method employing the BP86 functional[7] and the D3 dispersion correction.[8] Starting coordinates were adapted from the crystallographic coordinates of **1a**[9] with the Ph rings of dppb replaced with H atoms. Split-valence basis sets with one set of polarisation functions (def2-SVP) were used for all atoms.[10] Auxiliary basis sets used to expand the electron density in the calculations were chosen to match the orbital basis. The self-consistent field calculations were tightly converged (1×10^{-8} E_h in energy, 1×10^{-7} E_h in the charge density, and 1×10^{-7} in the maximum element of the DIIS[11] error vector). The geometry was converged with the following convergence criteria: change in energy $<10^{-5}$ E_h, average force $<5 \times 10^{-4}$ E_h Bohr^{-1}, and the maximum force 10^{-4} E_h Bohr^{-1}. The geometry search for all complexes was carried out in redundant internal coordinates without imposing geometry constraints.

Electronic properties were calculated on the optimised coordinates at the B3LYP level of theory.[12] Calculations with this hybrid functional used the RIJCOSX algorithm to speed the calculation of Hartree–Fock exchange.[13] A segmented all-electron relativistically contracted SARC-ZORA-TZVP basis set was used for platinum with increased integration accuracy (SPECIALGRIDINTACC 10).[14] The scalar relativistically recontracted ZORA-def2-

TZVP basis set was used for all other atoms.[15] Calculations included the zeroth-order regular approximation (ZORA) for relativistic effects[16] as implemented by van Wüllen.[17] The conductor-like polarizable continuum model (CPCM) was employed using an infinite continuum.[18]

We used the broken symmetry (BS) approach to describe our computational results for **[2••]**$^{2+}$ and **[2•••]**$^{3+}$.[19] We adopt the following notation: the given system was divided into two fragments. The notation BS(*m, n*) refers then to a broken symmetry state with *m* unpaired α-spin electrons essentially on fragment 1 and *n* unpaired β-spin electrons localized on fragment 2. In most cases, fragments 1 and 2 correspond to the metal and the ligands, respectively. In this notation the standard high-spin, open-shell solution is written as BS(*m*+*n*, 0). The BS(*m*,*n*) notation refers to the initial guess to the wave function. The variational process does, however, have the freedom to converge to a solution of the form BS(*m*–*n*, 0) in which effectively the *nβ*-spin electrons pair up with $n < m$ *α*-spin electrons on the partner fragment. Such a solution is then a standard $M_s \cong (m-n)/2$ spin-unrestricted Kohn-Sham solution. As explained elsewhere,[20] the nature of the solution is investigated from the corresponding orbital transformation (COT) which, from the corresponding orbital overlaps, displays whether the system should be described as a spin-coupled or a closed-shell solution. Corresponding[16] and canonical orbitals and density plots were obtained using Molekel.[21]

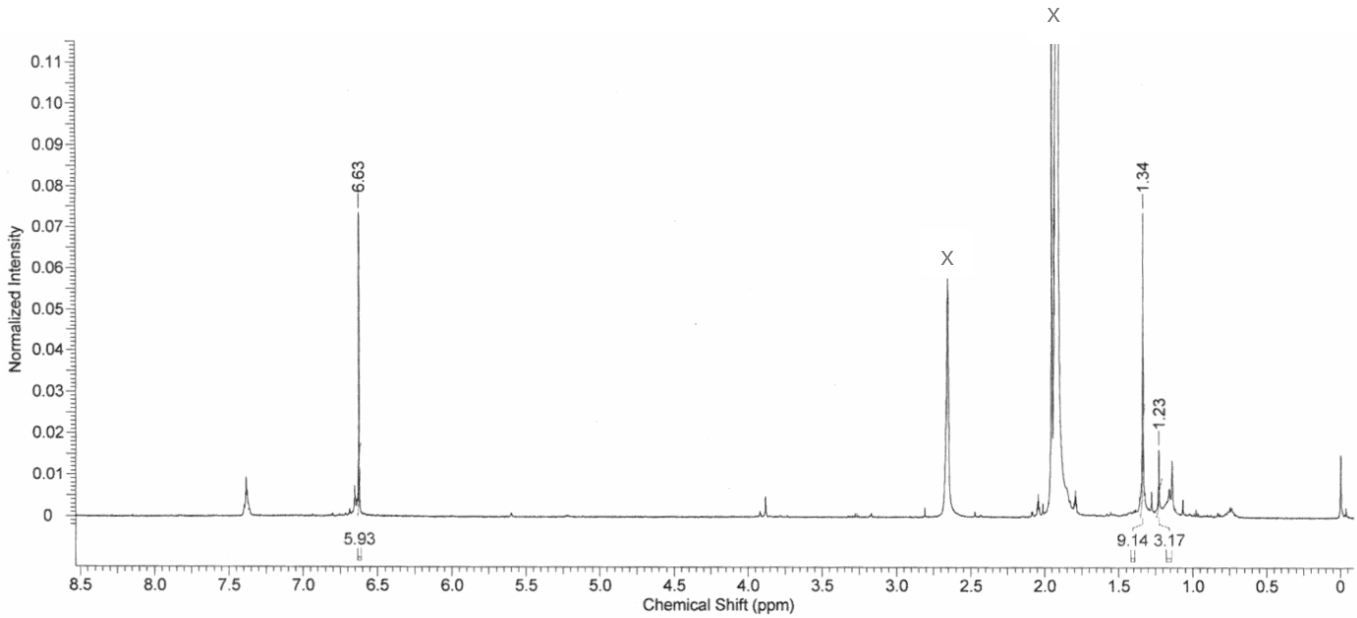


Figure S1. ^{1}H NMR spectrum of H_6tctq ({CD_3}$_2$CO).

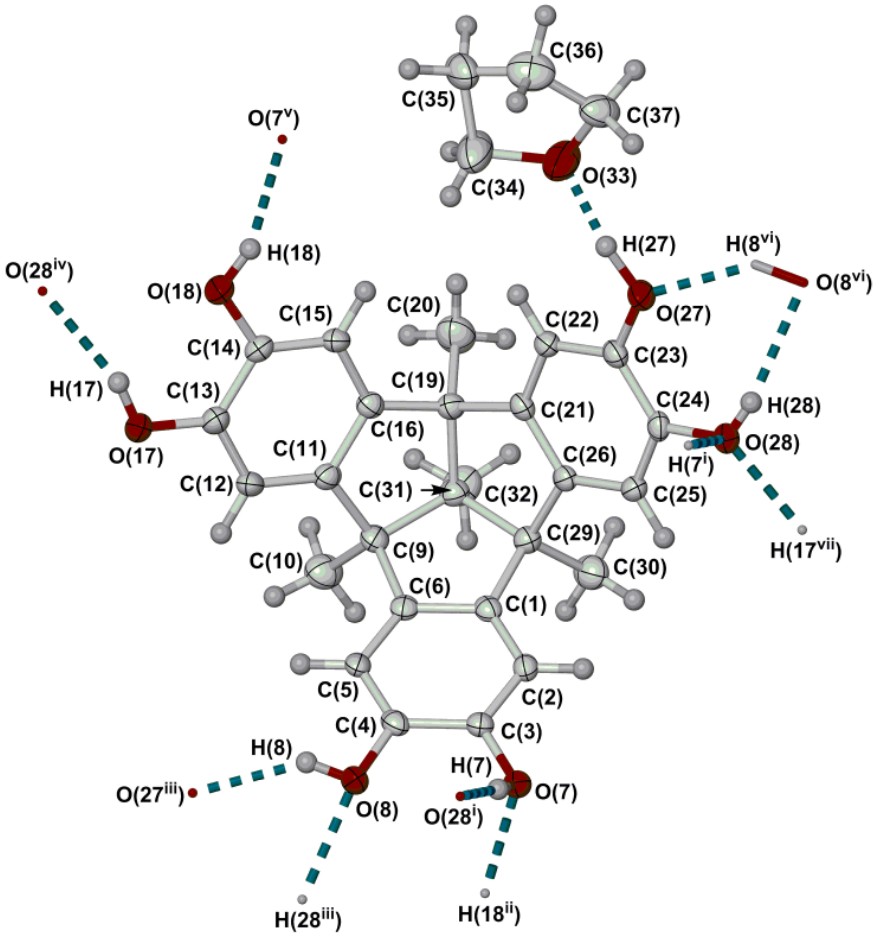


Figure S2. View of the H_6tctq·thf moiety in the structure of H_6tctq·thf·*n*MeOH. Displacement ellipsoids are at the 50 % probability level, and the partial methanol molecule (which does not form any obvious hydrogen bonds) is not shown. Colour code: C, white; H, pale grey; O, red.

Symmetry codes: (i) 1–*x*, 2–*y*, 1–*z*; (ii) *x*, 1+*y*, *z*; (iii) 1+*x*, *y*, *z*; (iv) 1+*x*, –1+*y*, *z*; (v) *x*, –1+*y*, *z*; (vi) –1+*x*, *y*, *z*; (vii) –1+*x*, 1+*y*, *z*.

Table S2 Hydrogen bond parameters in the structure of H_6tctq·thf·*n*MeOH (Å, °). See Figure S2 for the atom numbering scheme. Symmetry codes: (i) 1–*x*, 2–*y*, 1–*z*; 1+*x*, *y*, *z*; (iv) 1+*x*, –1+*y*, *z*; (v) *x*, –1+*y*, *z*; (vi) –1+*x*, *y*, *z*.

	O–H	H…O	O…O	O–H…O
O(7)–H(7)…O(28^{i})	0.90(5)	1.88(5)	2.776(4)	178(4)
O(8)–H(8)…O(27^{iii})	0.86(5)	1.95(5)	2.693(3)	144(5)
O(17)–H(17)…O(28^{iv})	0.85(6)	2.03(6)	2.859(4)	165(5)
O(18)–H(18)…O(7^{v})	0.85(6)	1.96(6)	2.766(3)	158(5)
O(27)–H(27)…O(33)	1.00(6)	1.60(6)	2.588(4)	172(5)
O(28)–H(28)…O(8^{vi})	0.73(5)	2.17(5)	2.882(3)	168(5)

The fractional methanol site C(38)/O(39) does not have an obvious hydrogen-bond acceptor, but is positioned to accept two weak C–H…O interactions from the H_6tctq and thf molecules [C(20)…O(39) = 3.34(4), C(34)…O(39) = 3.26(3) Å].

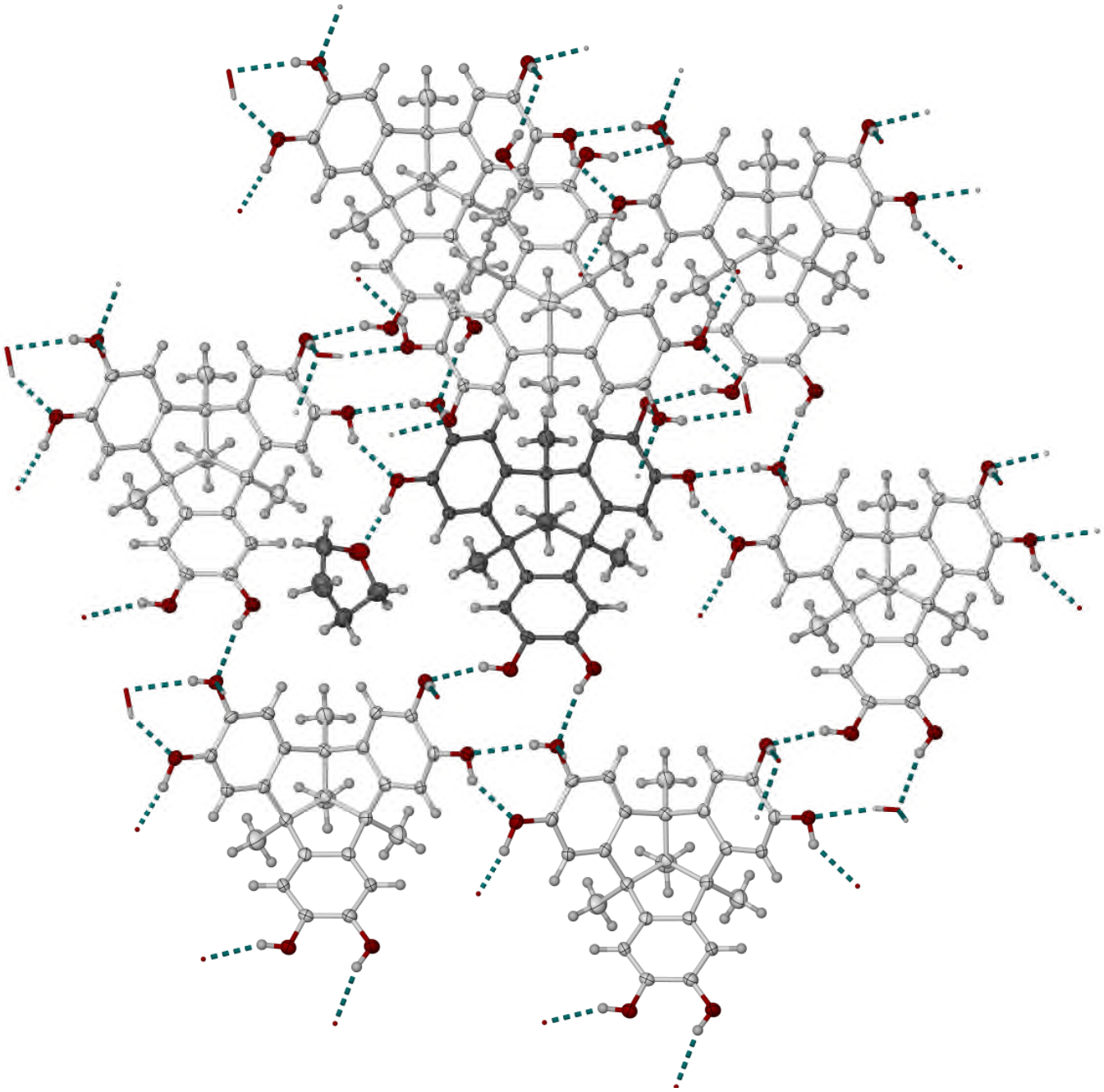


Figure S3. View of the hydrogen bond connectivity in H_6tctq·thf·*n*MeOH. A central H_6tctq·thf moiety is shown in dark colouration, surrounded by its seven nearest neighbour H_6tctq molecules with paler colouration. Displacement ellipsoids are at the 50 % probability level, and the partial methanol molecule (which does not form any obvious hydrogen bonds) is not shown. Colour code: C, white or dark grey; H, pale grey; O, red.

Six of the seven connected molecules are disposed about the central molecule in an approximately hexagonal arrangement, within the same half of the hydrogen bonded bilayer (Figure S4). An additional connection to a seventh molecule is the link to the other half of the bilayer structure.

The connectivity of the hydrogen bonded bilayers is most simply described as a pair of 2D 6^3 hydrogen bonded sheets, which are linked into bilayers by the seventh connection in the third dimension.

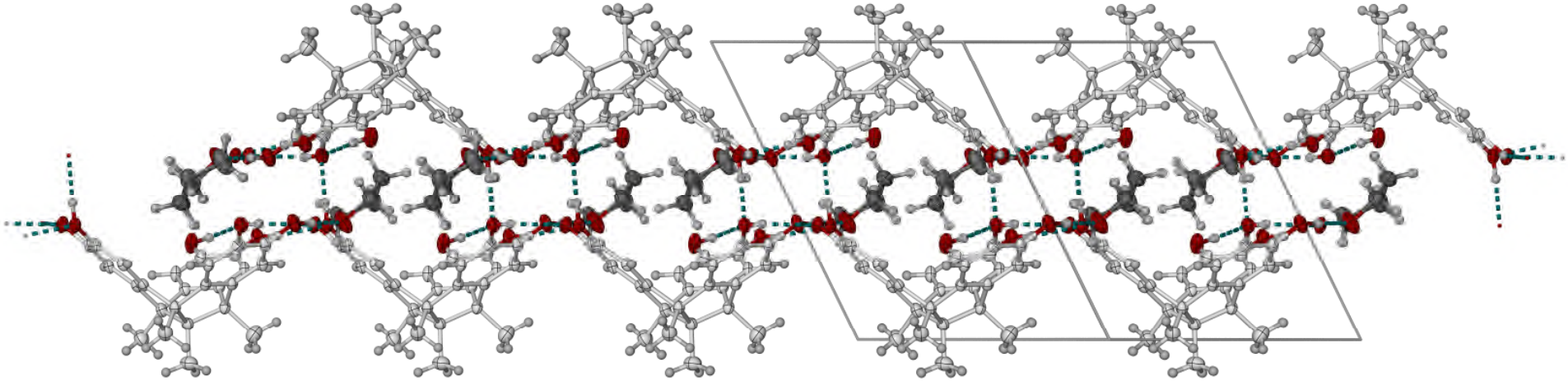


Figure S4. A hydrogen bonded bilayer in the lattice of H_6tctq·thf·*n*MeOH. The view is parallel to the $(1\,\bar{1}\,0)$ crystal vector. Displacement ellipsoids are at the 50 % probability level. The thf molecules are highlighted with dark colouration, and the partial methanol molecule (which does not form any obvious hydrogen bonds) is not shown.

Colour code: C{H_6tctq}, white; C{solvent}, dark gray; H, pale gray; O, red.

Similar hydrogen bonded bilayer crystal packing is also shown by several solvent clathrates of H_6ctc.[22,23] The two halves of the bilayer are also linked by inclusion of the thf solvent molecules in the H_6tctq bowl-shaped cavities (Figure S5).

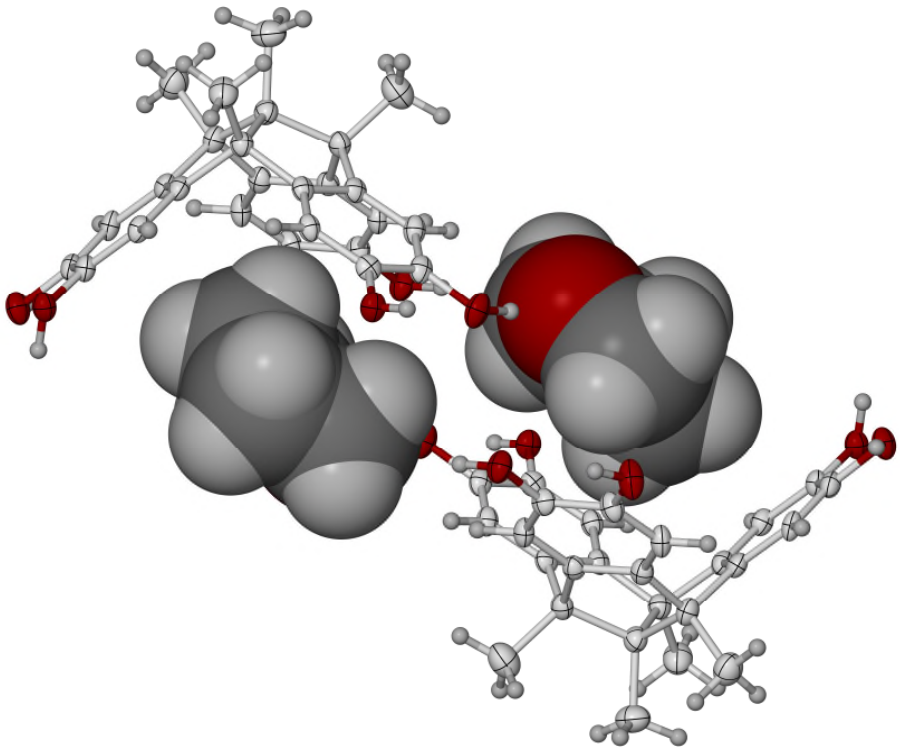


Figure S5. View of the inclusion of thf molecules inside the H_6tctq bowl-shaped cavities in H_6tctq·thf·*n*MeOH. Each thf molecule is hydrogen bonded to one half of the bilayer structure, and included into the other half. Colour code: C{H_6tctq}, white; C{solvent}, dark gray; H, pale gray; O, red.

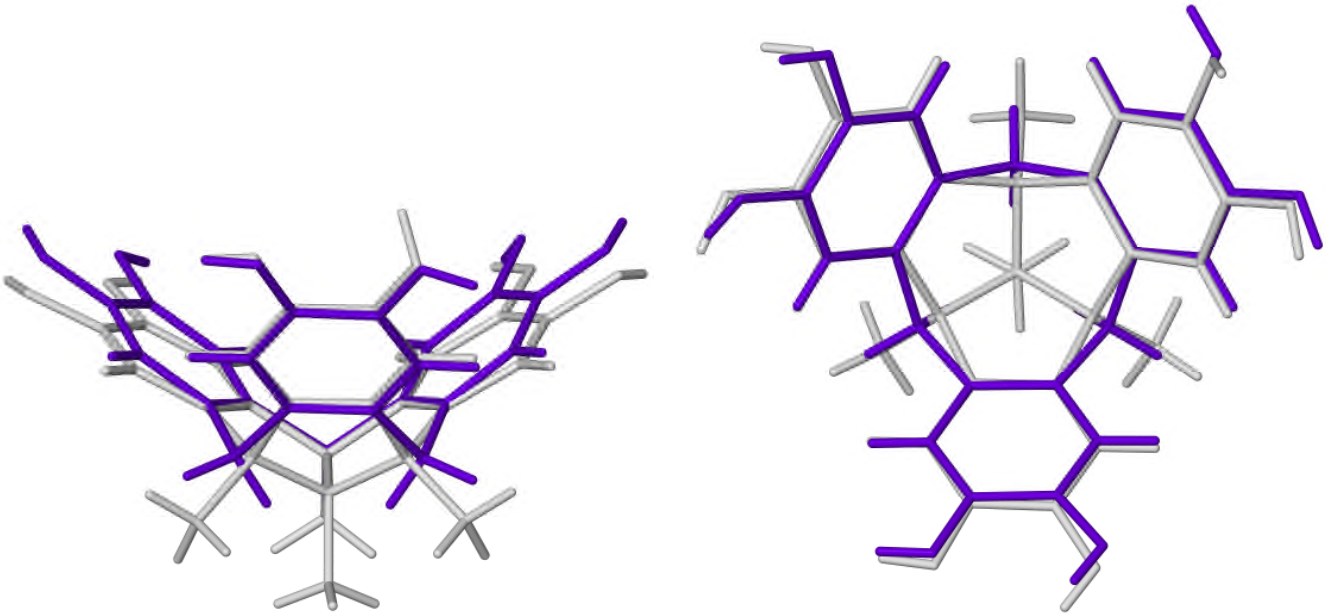


Figure S6. Overlays of the crystallographic molecular structures of H_6tctq (white) and H_6ctc (purple), showing the shallower bowl-shaped conformation of the H_6tctq macrocycle. The left view is the same as Figure 3 of the main article.

The H_6ctc molecule in the Figure is from H_6ctc·5dmso.[23]

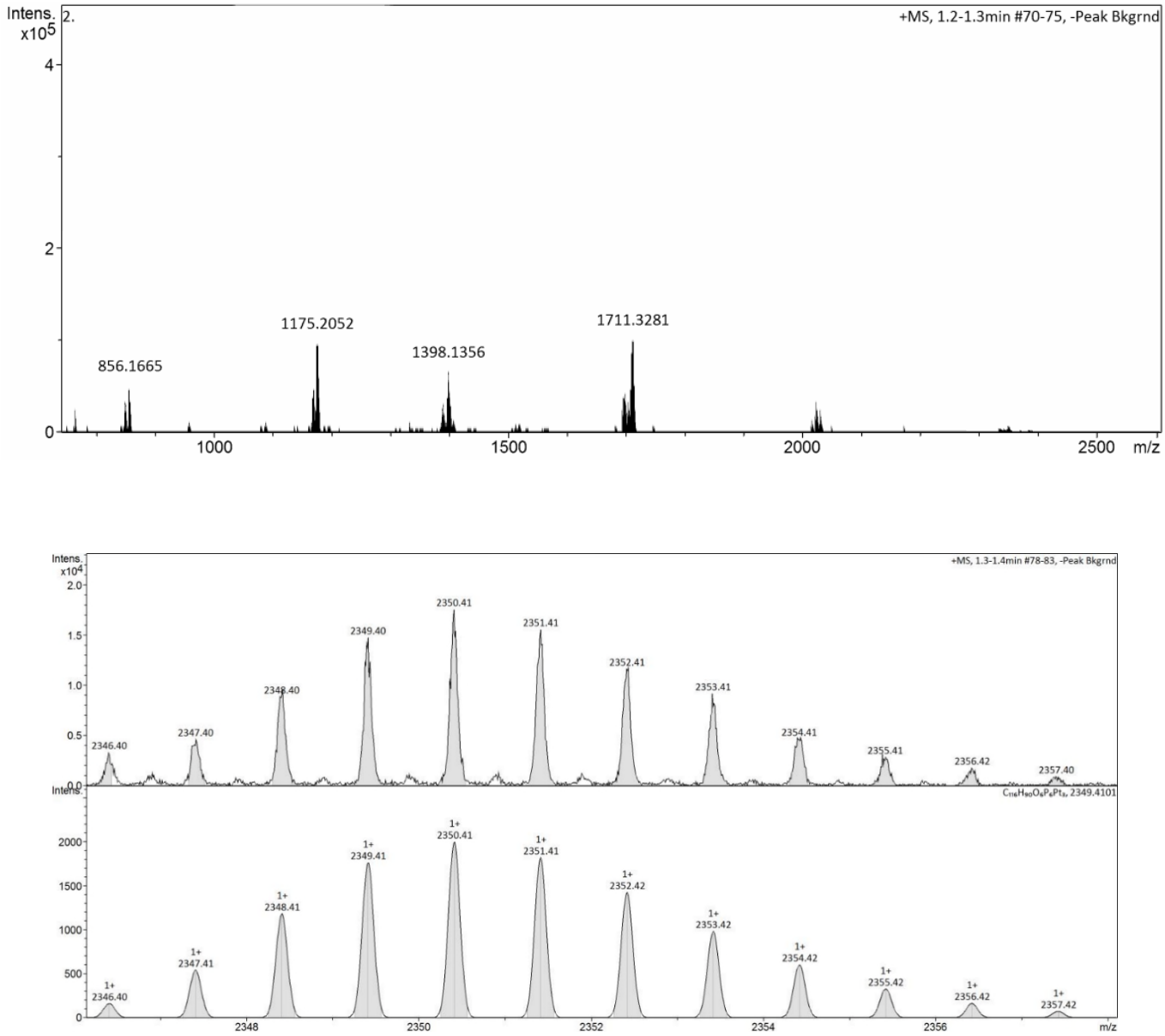


Figure S7. Top: the high-nuclearity species in the high-resolution electrospray mass spectrum of **2a** (more intense mononuclear fragments at lower mass are not shown). Bottom: the observed and simulated molecular ion for the intact $[\{Pt(dppb)\}_3(tctq)+H]^+$ molecular ion. Other peak assignments are listed in the Experimental Section.

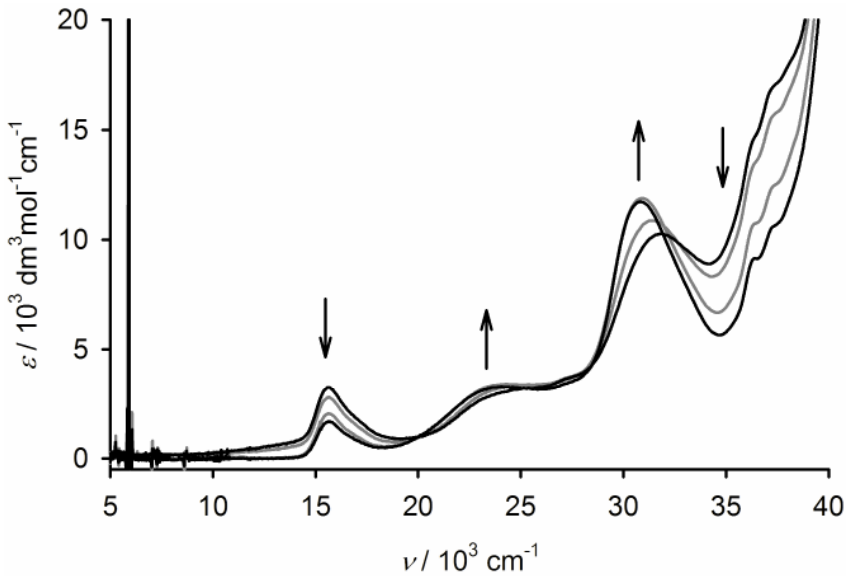


Figure S8. The **2a→[2a•]**$^+$ oxidation in CH_2Cl_2, monitored by titration with $[FeCp_2]PF_6$ at 298 K with UV/vis/NIR spectroscopy. The starting and final spectra are highlighted in black while the intermediate spectra are paler.

Although the reaction is not isosbestic under these conditions, the spectral changes during the reaction broadly resemble those in the spectroelectrochemical oxidation (Figure 2, main article). This includes the absence of the IVCT absorption below 10 x10^3 cm^{-1} which is shown by **[1a•]**$^+$.[24]

The exception to the above statement is the feature near 16 x10^3 cm^{-1}, which is not present in the spectro-elecrochemical data and is of uncertain origin. While $[FeCp_2]PF_6$ exhibits an absorption near that energy,[25] that assignment is unlikely since the peak is also observed in the starting **2a** spectrum.

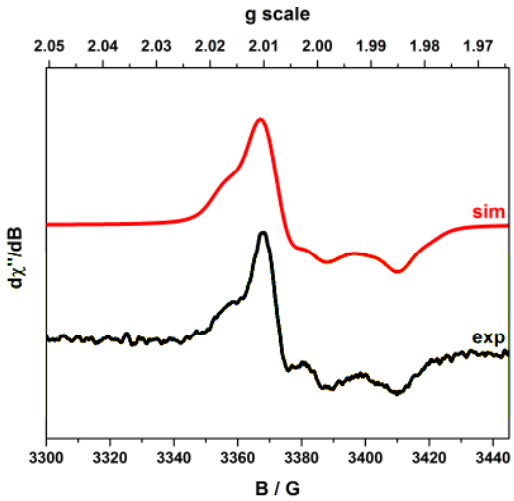


Figure S9. Measured (black) and simulated (red) X-band EPR spectrum of [**2a**$^{\bullet}$]$^{+}$ in CH_2Cl_2 solution at 150 K.

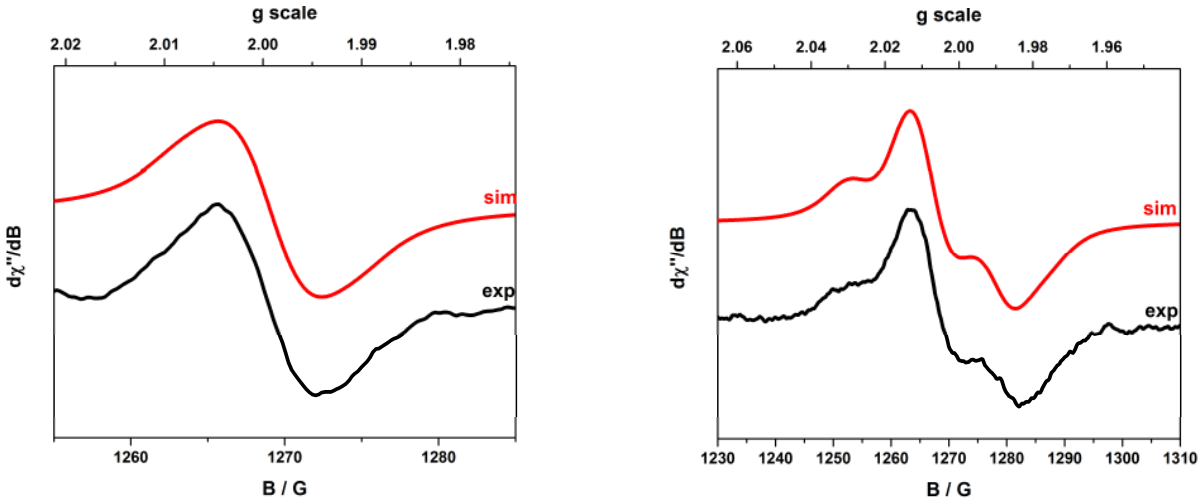


Figure S10. Measured (black) and simulated (red) S-band EPR spectra of [**2a**$^{\bullet}$]$^{+}$ in CH_2Cl_2 solution at 300 K (left) and 45 K (right).

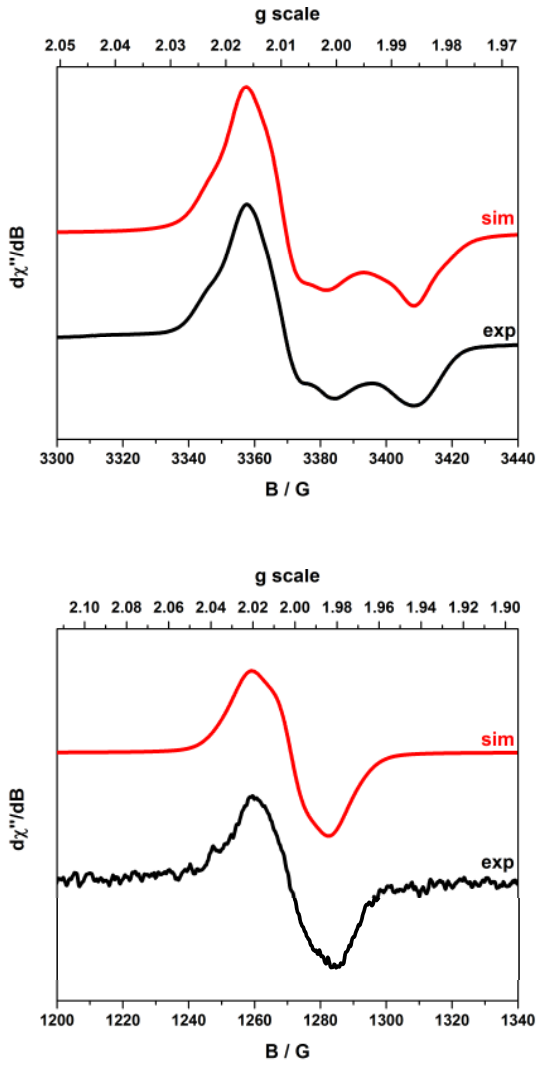


Figure S11. Measured (black) and simulated (red) EPR spectra of [**2b**•]$^+$ in CH_2Cl_2 solution. Top, X-band spectrum at 150 K: bottom, S-band spectrum at 45 K (frozen solution).

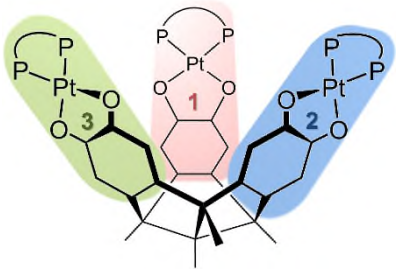
A spectrum of this radical in fluid solution was not achieved, because of its instability towards decomposition at elevated temperatures.

Table S3 Simulated EPR parameters for [**2a**•]$^+$ and [**2b**•]$^+$ in CH_2Cl_2 solution (Figures S9-S11).

	T / K	g_1	g_2	g_3	$A_1\{^{195}Pt\}$ / 10^{-4} cm^{-1}	$A\{^{31}P\}$ / 10^{-4} cm^{-1}
[**2a**•]$^+$	300	2.006	–	–	20	5
	45	2.010	2.006	1.984	60	8
[**2b**•]$^+$	150	2.016	2.009	1.985	60	7

These parameters resemble those of [**1a**•]$^+$ [24] and other platinum(II)/semiquinonate radical species.[26]

Table S4 Calculated mean bond distances (Å) and angles (°) in the different oxidation states of **2a**. Data in square brackets are from the corresponding calculation of **1a**$^{z+}$ in ref. 24. Relevant experimental data from **1a**/**1b** are also listed in ref. 24.



$[\{Pt(dppb)\}_3(\mu_3\text{-tctq})]^{z+}$		$z = 0$ $M_S = 1$	$z = 1$ $M_S = 2$	$z = 2$ BS(1,1) $M_S = 3$	$z = 3$ BS(2,1) $M_S = 2$
	Pt–P	2.242 [2.221]	2.244 [2.232]	2.247 [2.228]	2.251 [2.234]
	Pt–O	2.018 [2.015]	2.035 [2.054]	2.054 [2.055]	2.081 [2.081]
	C–O	1.361 [1.363]	1.342 [1.337]	1.327 [1.327]	1.308 [1.308]
1	C–C_{arom}	1.409 [1.405]	1.413 [1.412]	1.416 [1.413]	1.421 [1.418]
	τ^a	1.1 [0.4]	1.7 [1.3]	1.7 [2.2]	1.5 [0.4]
	α^b	54.1 [56.5]	45.1 [55.9]	47.8 [58.9]	49.7 [60.8]
	θ^c	0.8 [0.4]	3.4 [2.8]	4.3 [4.9]	5.1 [4.9]
	Pt–P	2.242 [2.221]	2.244 [2.232]	2.247 [2.228]	2.251 [2.234]
	Pt–O	2.019 [2.017]	2.033 [2.047]	2.056 [2.056]	2.082 [2.080]
	C–O	1.361 [1.364]	1.346 [1.347]	1.326 [1.326]	1.308 [1.308]
2	C–C_{arom}	1.409 [1.405]	1.412 [1.410]	1.417 [1.413]	1.421 [1.418]
	τ^a	0.9 [0.5]	0.9 [0.4]	1.2 [2.5]	1.6 [0.3]
	α^b	53.4 [56.5]	55.6 [55.9]	54.6 [58.9]	56.0 [60.8]
	θ^c	0.5 [0.7]	1.4 [1.4]	4.1 [4.3]	5.5 [1.8]
	Pt–P	2.242 [2.221]	2.244 [2.232]	2.247 [2.229]	2.251 [2.234]
	Pt–O	2.017 [2.017]	2.033 [2.047]	2.056 [2.056]	2.082 [2.081]
	C–O	1.360 [1.364]	1.346 [1.346]	1.326 [1.326]	1.308 [1.308]
3	C–C_{arom}	1.409 [1.405]	1.412 [1.410]	1.417 [1.413]	1.421 [1.418]
	τ^a	0.8 [0.5]	0.8 [0.4]	1.3 [2.2]	1.5 [0.3]
	α^b	49.1 [56.5]	55.0 [55.9]	53.9 [58.9]	54.8 [60.8]
	θ^c	1.4 [0.7]	1.4 [1.4]	4.2 [5.5]	5.3 [2.2]
	Pt⋯Pt	10.57 [10.37]	10.16 [10.33]	10.43 [10.62]	10.80 [10.62]
		10.14 [10.37]	10.84 [10.33]	10.84 [10.69]	11.11 [10.83]
		10.20 [10.52]	10.11 [10.58]	10.38 [10.69]	10.72 [10.88]
	Average	10.30 [10.42]	10.37 [10.41]	10.55 [10.67]	10.88 [10.78]

[a]Dihedral angle between $\{PtO_2\}$ and $\{PtP_2\}$ mean planes. [b]Angle between $\{PtO_2C_6\}$ plane and molecular C_3 axis. [c]Dihedral angle between $\{PtO_2\}$ and $\{O_2C_6\}$ mean planes.

Table S5 Geometry optimized coordinates for **2a**.

Pt	5.24599651944574	-2.82177386034587	-0.41889214504644
Pt	0.06201213565145	5.88762465510134	-0.39373685626443
Pt	-5.32604056080638	-2.76784024015213	-0.40959795736022
P	7.23282918755966	-2.14839425926704	-1.20765986253635
P	5.60830463272476	-4.72341057948104	-1.54915019635748
P	-1.45041234302043	7.14789163285633	-1.46545166635659
P	1.61329655939562	7.15123458806947	-1.40438633766257
P	-5.72369839978210	-4.67560603371592	-1.51751562032226
P	-7.30659269342503	-2.07256356356474	-1.19490555934082
O	4.88421206909552	-1.12541852859956	0.61174843560563
O	3.46648511092363	-3.39667533526150	0.34128641533946
O	-1.30053680594094	4.72004827649853	0.52649534616711
O	1.38964624501313	4.71405319811726	0.56882305411961
O	-3.55426293608222	-3.36347895742401	0.35120931346178
O	-4.93421020634811	-1.06693784374143	0.60135151329998
C	1.24259933101437	-1.51496143356515	2.59211624050080
C	1.97932314891001	-0.32508652448230	2.72477006431035
C	3.21233936741285	-0.16378159041510	2.07040903200077
C	3.69504891148397	-1.21156359920998	1.26674450766992
C	2.94448794058455	-2.41299687217337	1.12352087468409
C	1.71628960707435	-2.56780247519595	1.79058883179084
C	-0.03053107237560	-1.50466721078106	3.42849920736962
C	-1.29744558511201	0.72083061025956	3.58311244207936
C	1.27285084206667	0.69917927993834	3.60239799013421
C	0.70591665186236	1.83625110127308	2.75983215123942
C	-0.69872512581698	1.84262533854784	2.74198900814242
C	-1.40459662503568	2.80562506176839	2.00057491022214
C	-0.68105756210719	3.76432428756111	1.27053680635594
C	0.74278370938125	3.76051758039889	1.29211418150746
C	1.43896503350166	2.79521895442630	2.03986053460073
C	-2.01753279079755	-0.29644945807164	2.70907104031691
C	-1.30178270921566	-1.50048480551764	2.58926496886365
C	-1.79220035822139	-2.55195494811404	1.79605060329882
C	-3.01623222883612	-2.38174880579993	1.12498075325567
C	-3.74623492995963	-1.16652624563788	1.25653058512641
C	-3.24630234256113	-0.11963474466556	2.05079190730067
C	7.99886808643976	-3.47746144567494	-2.22737894114046
C	7.24886848860444	-4.66612637530471	-2.38538749945823
C	7.76889837354339	-5.72958061095402	-3.14769768912409
C	9.03475005472093	-5.60587871023063	-3.74663298475410
C	9.78029638068891	-4.42549069435378	-3.58895585951734
C	9.26512482706351	-3.35875112349055	-2.83154734639783
C	-0.60571184600960	8.40916276196560	-2.50950673227454
C	0.80840215850383	8.41100600702654	-2.48092456243499
C	1.52615771334328	9.34740517623379	-3.24962146584842
C	0.83289965269830	10.27776490455761	-4.04383421686330
C	-0.57178477512504	10.27540843423777	-4.07278111083412
C	-1.29416545035673	9.34297051021830	-3.30756383770985
C	-7.37305912014432	-4.60640469570337	-2.33536305575101
C	-8.10431658228646	-3.40515575040346	-2.18522531909368
C	-9.37635833546561	-3.27726739617903	-2.77511072077121
C	-9.91604241317296	-4.34743804525398	-3.51021411520439
C	-9.18900779618720	-5.54023609758904	-3.66035845406858
C	-7.91739184944702	-5.67307751439054	-3.07584065810099
C	-0.03706065426931	-2.72075991141926	4.37974313421629
C	2.22292552970509	1.25459283231615	4.68108217756119
C	-2.24574583997833	1.30517655087375	4.64817435993735
H	7.31982577480181	-0.99625167628883	-2.05741699887057
H	4.72222476432564	-5.11397983512613	-2.60729206548768
H	-2.39804300189164	7.92897274721516	-0.72418941056967
H	2.56775211517151	6.53624249392106	-2.28051405423642
H	-4.85469874399604	-5.08787370651935	-2.58160863217753
H	-7.38185302407129	-0.93375061215390	-2.06384360585364
H	3.81209842834241	0.75301914094252	2.16605652326956
H	1.16377773871478	-3.51136527096036	1.67369868311094
H	-2.50414496311906	2.82792384096792	1.96154469689442
H	2.53930752959441	2.81017612176780	2.03082582225156

H	-1.25663917201981	-3.50642696897758	1.68938655542717
H	-3.83139939186586	0.80737839428755	2.13870587596433
H	7.18795715284579	-6.65660115351044	-3.27302089615510
H	9.44159471048416	-6.43950278393151	-4.33878247978319
H	10.77160037114235	-4.33461734544459	-4.05719306544790
H	9.85241897941875	-2.43517945181466	-2.70962255876846
H	2.62776149212418	9.35281618102982	-3.22904162940044
H	1.39491935390726	11.01005859184384	-4.64321252447247
H	-1.11120517749142	11.00578314354392	-4.69487567651913
H	-2.39566184591288	9.34450747979167	-3.33284639465212
H	-9.94930327673686	-2.34394018037660	-2.65914526497148
H	-10.91203044455453	-4.24939640034796	-3.96687702712641
H	-9.61498555052373	-6.37645889045624	-4.23509633890257
H	-7.35096778048741	-6.60983208308981	-3.19517436024237
H	-0.93954710473574	-2.73560919323297	5.02309696096555
H	0.86519380338461	-2.74399430668349	5.02321206505179
H	-0.04103489627408	-3.65808944306343	3.78735321376806
H	-1.72476332394750	2.03554360588969	5.29866506404304
H	-2.69506442292126	0.51294560448851	5.27984279199579
H	-3.07979472591929	1.84550287120236	4.15581094864016
H	1.71108748307111	1.99039845990301	5.33257995611464
H	3.07335119115857	1.78084573197247	4.20163265716550
H	2.64843565616853	0.44736715238972	5.30990435647890
C	-0.02295849475037	-0.07041883299874	4.14475433223417
C	-0.03596715686693	-0.18765248992243	5.66958628033154
H	-0.02991715943626	0.80444979449085	6.15930763752350
H	0.84742741632006	-0.74160586288496	6.04073974363138
H	-0.93608298735865	-0.72405944904081	6.02625412133965
H	-2.36809317706747	6.53121285796942	-2.37882364321572
H	2.52932520110321	7.93359349077095	-0.62576595854193
H	5.64508299494609	-5.97332679543556	-0.84836100011723
H	8.27892618387880	-1.80160189011344	-0.29077362562948
H	-5.76786650913263	-5.91772018099791	-0.80342441113883
H	-8.33724478134954	-1.69140240713228	-0.27421637780562

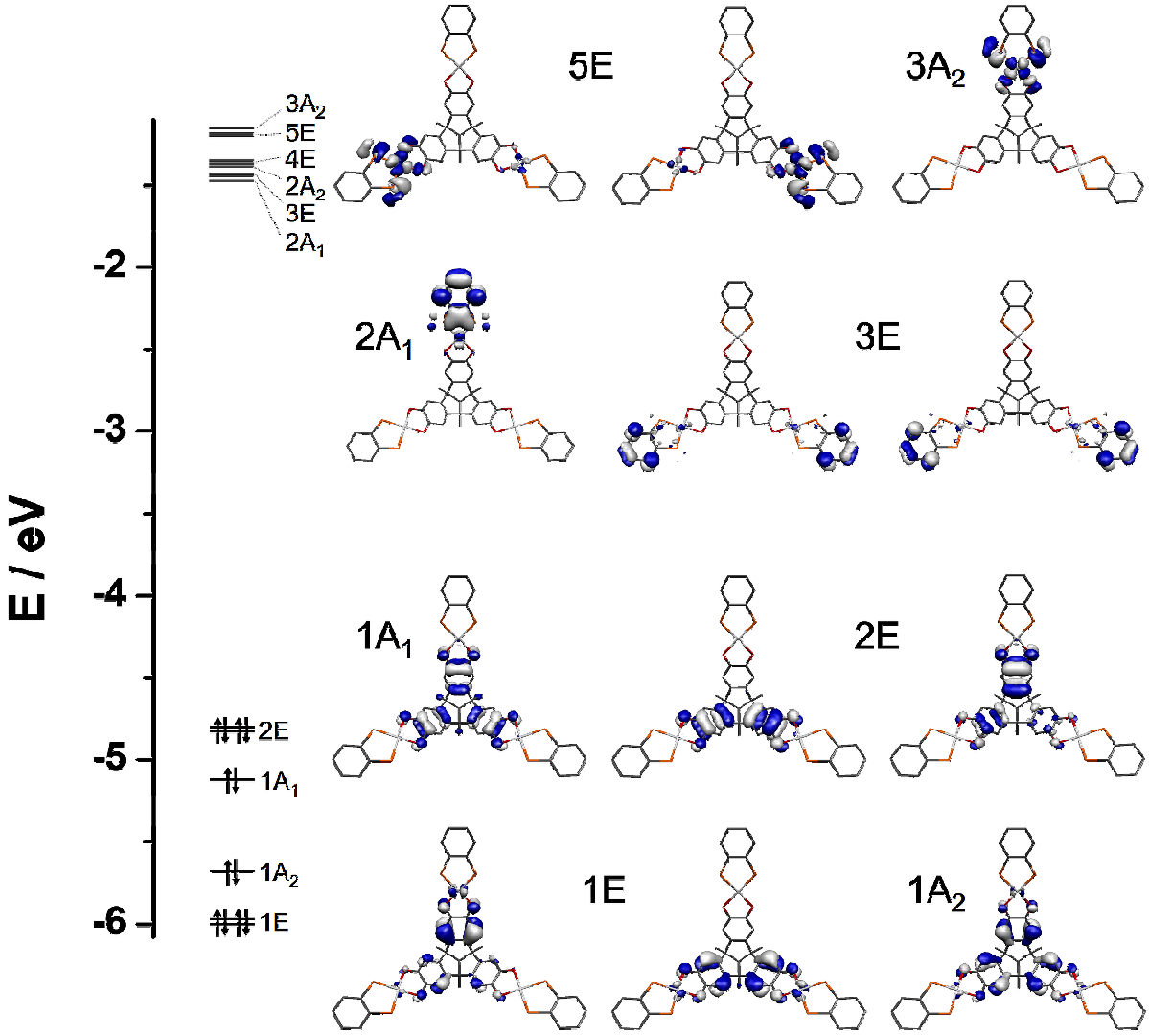


Figure S12. MO energy level scheme of frontier Kohn-Sham orbitals for **2a** with C_{3v} symmetry labels.

Table S6 Geometry Optimized Coordinates for **[2a•]**$^{+}$

Pt	5.37997534203993	-2.84554034086670	-0.38248926581373
Pt	0.05271272730177	5.74572539411352	-0.68352881327806
Pt	-5.45849987323997	-2.77879153758979	-0.36646019458886
P	7.42423787985497	-2.21116855940339	-1.05292979897718
P	5.76631604513920	-4.74855938713029	-1.50792465712083
P	-1.46480898910844	7.09539170353490	-1.63873898787136
P	1.59912018215504	7.08783291389820	-1.60238582798799
P	-5.87981144984886	-4.68197314755156	-1.47916948251561
P	-7.49282865752913	-2.11350145173619	-1.03710913549258
O	4.99088915622314	-1.14517721295867	0.65780814051370
O	3.53074048416026	-3.37767530529859	0.27710162530957
O	-1.30743076128404	4.52451828185117	0.21052600259334
O	1.38567479842797	4.51701926469779	0.24034866713728
O	-3.61844470436527	-3.33916161776508	0.29566988311572
O	-5.03841333262604	-1.07819883044803	0.66087984196509
C	1.25856752412775	-1.50092224579292	2.45172844569804
C	2.02231462327904	-0.32823156133008	2.64807481263785
C	3.28358978777333	-0.17520805908331	2.05344713081275
C	3.78268224979895	-1.21583114260535	1.24875841390520
C	3.00541042731048	-2.40741107711089	1.04563014584468
C	1.74180098091328	-2.54732855483147	1.65730520950577
C	-0.02543107067603	-1.49034610798490	3.26844090512153
C	-1.29251931751433	0.72027726008937	3.47607539140155
C	1.27829616745166	0.69909428476835	3.48851549080548
C	0.71515578847471	1.75432263249700	2.54651793623154
C	-0.70319203172429	1.76052696118858	2.53346518601375
C	-1.41275806984621	2.67465601750807	1.74375208205530
C	-0.69288960260527	3.60159424020636	0.96721310144788
C	0.74930686461268	3.59729799543839	0.98282396573793
C	1.44681915756556	2.66467243659496	1.77267870350034
C	-2.05416727459607	-0.29893363481370	2.64244626202007
C	-1.31156511649777	-1.48646669729872	2.45499624138240
C	-1.81414914949861	-2.53037423601273	1.66916185270795
C	-3.07539502296040	-2.37263678867213	1.05683956009036
C	-3.83105002662223	-1.16602279950350	1.25130360862591
C	-3.31292557592280	-0.12821576859515	2.04759471472851
C	8.20946097735750	-3.54120711277063	-2.05187449482764
C	7.44391080989138	-4.71228672683283	-2.26271677891745
C	7.97760174475637	-5.77544549819606	-3.01520889597251
C	9.27016916421940	-5.66811786012902	-3.55262702665137
C	10.03134704470479	-4.50453107067251	-3.34260180169798
C	9.50451703935728	-3.43971838498989	-2.59394232600708
C	-0.62693990131031	8.51312162780325	-2.45848570545056
C	0.78796577119315	8.51013165211250	-2.44084578587613
C	1.50158823771636	9.56330461357691	-3.04292447762549
C	0.80333551233329	10.61560892649166	-3.65626465650043
C	-0.60283466521952	10.61845800731349	-3.67405083296778
C	-1.32072385876235	9.56917675606067	-3.07849637430118
C	-7.55968661115113	-4.62304961340396	-2.22747874977819
C	-8.30451728653948	-3.43768499588939	-2.02251142351552
C	-9.59997236017454	-3.31858683590050	-2.55993547162246
C	-10.14791207897365	-4.38012083100914	-3.29795937154526
C	-9.40736101695960	-5.55790329629111	-3.50218353146129
C	-8.11444658122356	-5.68277363818884	-2.96948513609163
C	-0.02934110787966	-2.72723112211193	4.20182272508665
C	2.17440894610317	1.34140236878593	4.55928504904669
C	-2.18025338503950	1.38886656584653	4.53799655695144
H	7.54949677128460	-1.04262843560946	-1.86893848823108
H	4.90592524341583	-5.09934708526694	-2.59647100682306
H	-2.44517457214957	7.70367556801671	-0.79372392999854
H	2.48129243527919	6.55362285105280	-2.59545263390852
H	-5.02941504450311	-5.05215750941364	-2.56911258900806
H	-7.59985124271371	-0.94972131318661	-1.86255638726169
H	3.90136093759355	0.72137851711929	2.20436125252793
H	1.17995201921558	-3.47905223501350	1.50074779637804
H	-2.51174676203894	2.70316327000791	1.71859013165437

H	2.54623224806602	2.68545533767519	1.76879743523842
H	-1.26930291530377	-3.47323228549685	1.51937681643905
H	-3.91499871748902	0.77997449675869	2.19256624829309
H	7.38698001450147	-6.68960610484518	-3.18203053551237
H	9.68747559620727	-6.50058031582108	-4.13861452694864
H	11.04411588680782	-4.42687256758341	-3.76432803711287
H	10.10580033823802	-2.53148638781666	-2.43197648047127
H	2.60298925649336	9.56736221610056	-3.03153286343049
H	1.36047812775571	11.44189752037190	-4.12263380883286
H	-1.14471090571862	11.44696952621876	-4.15431378537058
H	-2.42202526809233	9.57775307925394	-3.09526570675491
H	-10.18528360969204	-2.39916770811548	-2.40250584392488
H	-11.16114195484962	-4.28867209360688	-3.71576756779223
H	-9.84118775883120	-6.38776008527758	-4.07978556172679
H	-7.53999478666129	-6.60799797892142	-3.13173702015156
H	-0.93014034668273	-2.75029641089626	4.84549542680246
H	0.87377471788366	-2.75786826800448	4.84196389872791
H	-0.03410284254169	-3.65341046562523	3.59364466859282
H	-1.61346352164181	2.13280255598513	5.13201566148238
H	-2.62805682088589	0.64523077738690	5.22638973894956
H	-3.01517715446264	1.93067649476148	4.05001767984788
H	1.61925639206596	2.09167965678160	5.15612291357777
H	3.02274436750807	1.87024886555569	4.08014538568998
H	2.60344228453843	0.58324680986830	5.24361527198264
C	-0.01623548733988	-0.07444022205865	4.02008527212490
C	-0.02567922658851	-0.22104359511469	5.54186876040618
H	-0.02055828920699	0.76227664278371	6.04731465631175
H	0.85962265512728	-0.77893711317768	5.90131101040014
H	-0.92413814533324	-0.76453327002209	5.89074548349030
H	-2.32553708477881	6.56437237554466	-2.65212059381644
H	2.56184003984675	7.69019423536333	-0.73312757226443
H	5.73668069170468	-5.98347254553139	-0.78682489208182
H	8.40025333657773	-1.90145199936931	-0.05418688606106
H	-5.86703565074201	-5.91340250854729	-0.75163016331677
H	-8.46006224740691	-1.77790319589339	-0.03814736965469

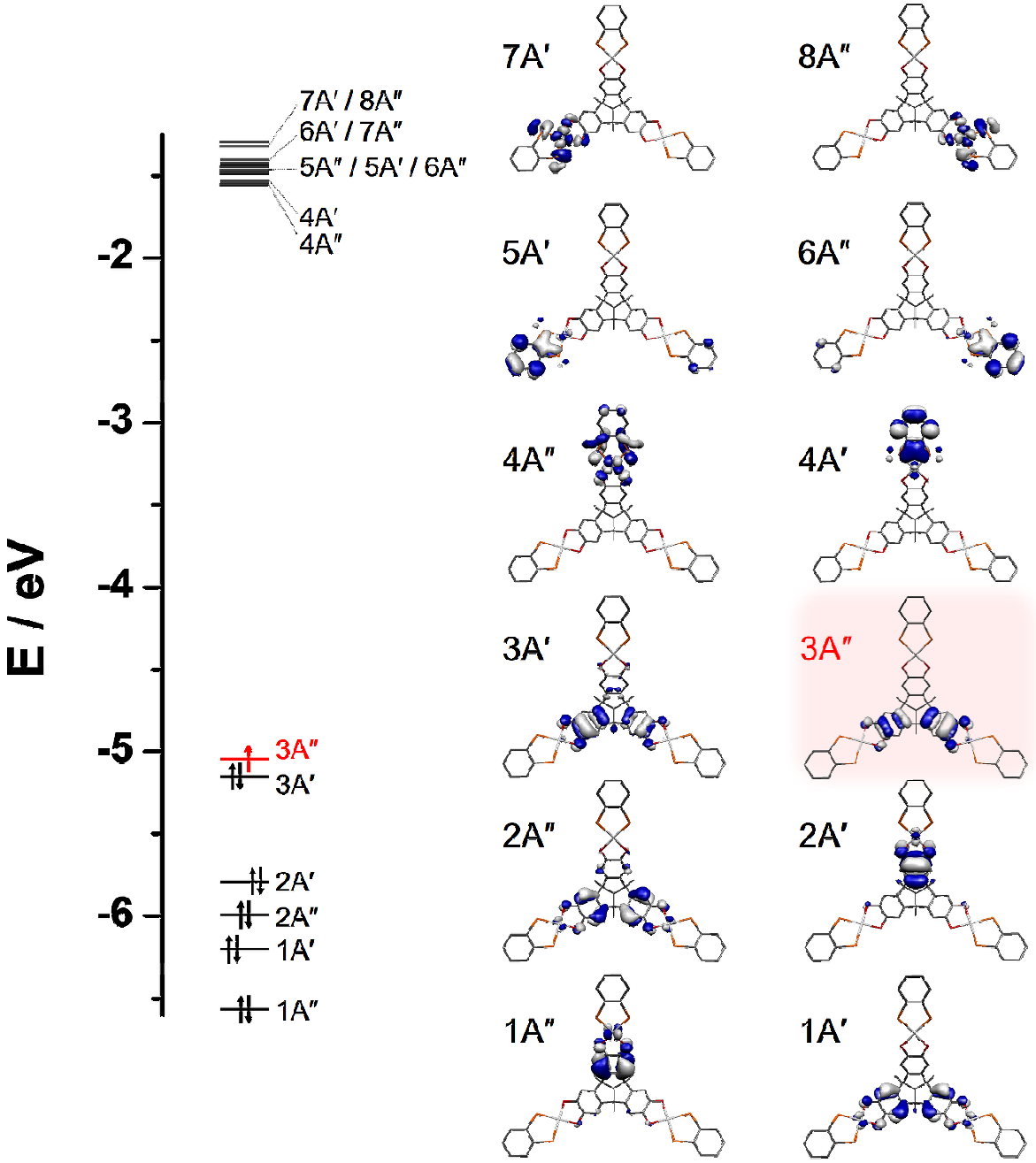


Figure S13. MO energy level scheme of frontier Kohn-Sham orbitals for **[2a•]**$^{+}$ with C_s symmetry labels.

Table S7 Geometry Optimized Coordinates for **[2a•]**$^{2+}$

Pt	5.37881192726361	-2.93161915560328	-0.48148668126795
Pt	0.05491346040035	5.97829545486790	-0.63739277879165
Pt	-5.46295135619219	-2.86769094674581	-0.45323216225532
P	7.45771172647013	-2.35089808368056	-1.10539272814045
P	5.80412845370965	-4.90108108477036	-1.47692547557739
P	-1.46285260989665	7.38664089318741	-1.51071701130788
P	1.59803085287425	7.38173613728719	-1.47346454577548
P	-5.92546156517615	-4.83615717963647	-1.43422496463502
P	-7.53066351807131	-2.25241098727607	-1.08128212038402
O	4.93657674522701	-1.16408511657774	0.46858788573120
O	3.48287342748572	-3.40814742649530	0.15611430578663
O	-1.30441736115251	4.68038010124024	0.19127672879872
O	1.38785982955498	4.67486123338300	0.22522924345550
O	-3.57493986662749	-3.37386533330786	0.18613746665193
O	-4.98584071047271	-1.09998556476813	0.47962172816737
C	1.23370626303014	-1.49001340030424	2.28749913392223
C	1.99298405137134	-0.29179659911929	2.43164656903640
C	3.24313395660740	-0.14835665313608	1.82765941087933
C	3.74554584693394	-1.21445234424276	1.04815912028246
C	2.96045531096891	-2.42903834163471	0.88125615387469
C	1.70201458933345	-2.55251552140716	1.51323718668489
C	-0.02378611653310	-1.47052504281962	3.14312915681172
C	-1.28928647789472	0.75286650900244	3.28605590017266
C	1.27918566614847	0.73154224072385	3.29894366084786
C	0.72015401957082	1.81867610430356	2.39042831412302
C	-0.70331413993116	1.82427769939113	2.37580785598095
C	-1.41519277856540	2.76687456512719	1.63125512064147
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C	1.45442702718909	2.75842560570059	1.66417634702411
C	-2.02200080954320	-0.26358414711356	2.42729870533666
C	-1.28525687924539	-1.47702840904104	2.29336711523819
C	-1.77527191330668	-2.53831319415294	1.53097702664890
C	-3.03267107010280	-2.39755016466250	0.90032303867297
C	-3.79454466278567	-1.16686734411304	1.05675498368793
C	-3.27055182899790	-0.10272660599901	1.82467313251076
C	8.27877816653796	-3.74626807768994	-1.96729117249247
C	7.51406447185165	-4.92484085524358	-2.13994561776454
C	8.07515042822265	-6.04064903441580	-2.78875476101734
C	9.39550945406323	-5.97550252841693	-3.26103044370569
C	10.15563064515694	-4.80447761635782	-3.08932509823872
C	9.60181588166115	-3.68744742319548	-2.44372607477941
C	-0.62870500851069	8.83681193167389	-2.26283537789678
C	0.78669275566887	8.83483027521801	-2.24507729394160
C	1.50050350887008	9.91319713343198	-2.80021987378605
C	0.79927533254036	10.98862139186975	-3.36820398233835
C	-0.60719818191123	10.99047604751692	-3.38602278476852
C	-1.32541861969811	9.91699860029743	-2.83591779990182
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C	-8.37556400647726	-3.63609318266438	-1.93894711936199
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C	-10.26936385648436	-4.66403359722707	-3.06057351781108
C	-9.53177744117055	-5.85061302487903	-3.22320214837670
C	-8.21435808435532	-5.93870450515011	-2.74654913814972
C	-0.02595592031317	-2.68292237574850	4.09857001087588
C	2.21384984048616	1.33619469363227	4.36144943321085
C	-2.21531524013387	1.38650352100692	4.33950570423099
H	7.59152696313611	-1.23113389673020	-1.98283860863648
H	4.96754530081347	-5.27528639663938	-2.57316002196015
H	-2.42569231700966	7.92774631869388	-0.60474162132109
H	2.48393320248471	6.87049334137824	-2.47238831620389
H	-5.09321985745550	-5.23460278141838	-2.52510382052101
H	-7.64391988493892	-1.13328797624219	-1.96241839046113
H	3.86488169507061	0.74799693271014	1.95767112106707
H	1.15406145688682	-3.49886125546482	1.40852151700538
H	-2.51377412812185	2.80653806032244	1.61656676000099

H	2.55328451240897	2.79146024043889	1.67398722735074
H	-1.24554536843557	-3.49583696304699	1.43448231687341
H	-3.87556339957283	0.80590835583114	1.94833452045006
H	7.48796212806683	-6.96176401487520	-2.92648459938610
H	9.83595882848054	-6.84768574992101	-3.76634971519115
H	11.18979584475514	-4.76176524792052	-3.46082416452198
H	10.20407921420136	-2.77522991127321	-2.31145581975764
H	2.60172621880307	9.92040597396925	-2.78908882868647
H	1.35480494983816	11.83465466382617	-3.79944128146803
H	-1.14943567353964	11.83795975760607	-3.83115831576873
H	-2.42653856878390	9.92703192986266	-2.85291899854572
H	-10.28060287000623	-2.62979769514656	-2.29455829705109
H	-11.30145521557005	-4.60333563573364	-3.43526935004046
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H	-2.65959521531049	0.62225149980067	5.00615835845921
H	-3.05121517630255	1.92129351850388	3.84647923651106
H	1.68401387139301	2.08369509533799	4.98242012764593
H	3.06310916970586	1.85806254224719	3.87734291563052
H	2.63871892416310	0.55641433336309	5.02245054438357
C	-0.01435303619044	-0.03271599097675	3.85189960631751
C	-0.02359842716641	-0.14005811141362	5.37695438857218
H	-0.01739420236454	0.85353538575917	5.86116606577047
H	0.86027729719014	-0.69024849919423	5.74970261693125
H	-0.92144923543320	-0.67438092440396	5.73944406690272
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H	5.69714889088270	-6.06882594367992	-0.66145449227866
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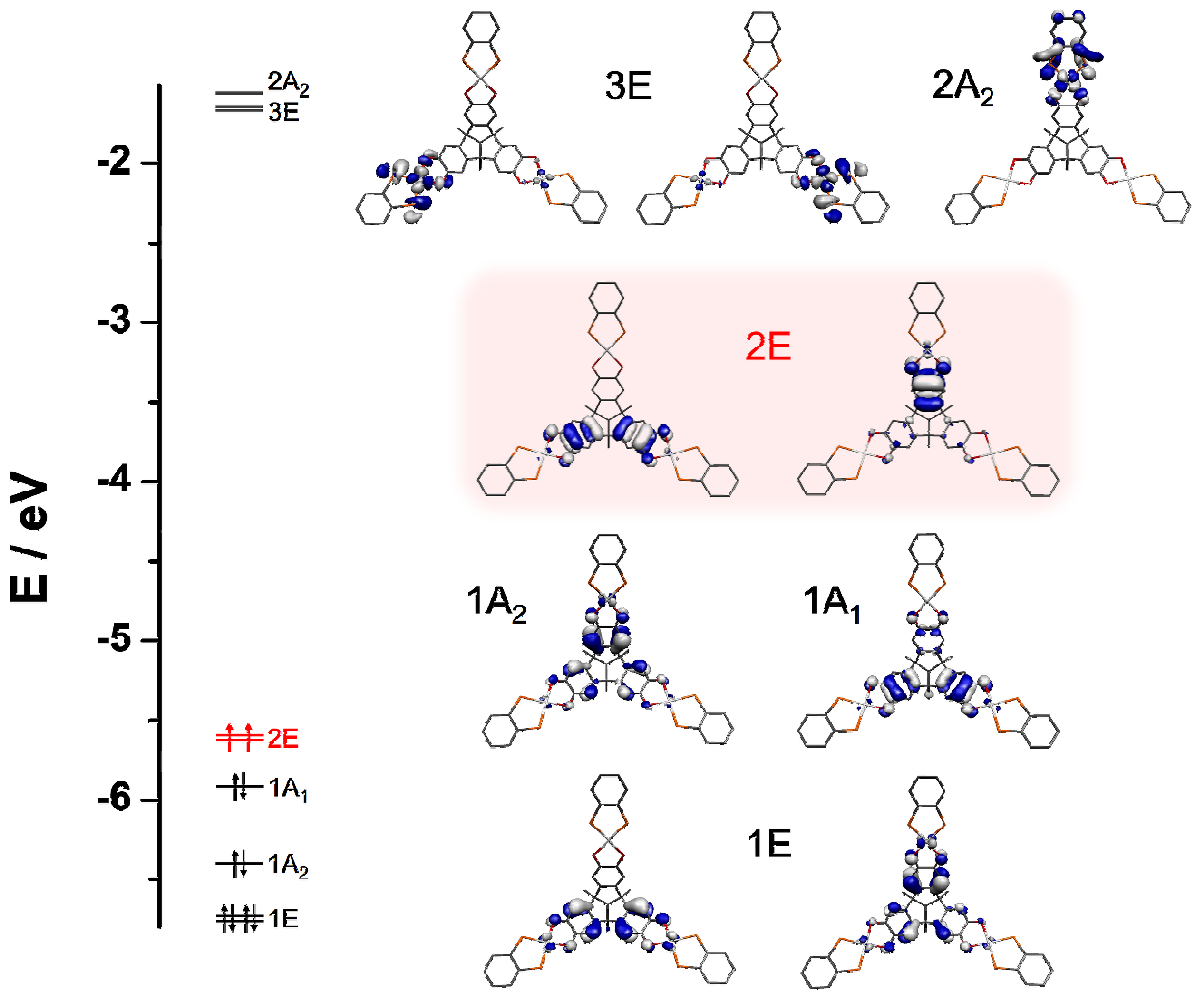

Figure S14. MO energy level scheme of frontier Kohn-Sham orbitals for **[2a•]**$^{2+}$ with C_{3v} symmetry labels.

Table S8 Geometry Optimized Coordinates for **[2a‴]**$^{3+}$

Pt	5.51173062358761	-3.02067426532468	-0.50639681739674
Pt	0.07837118716684	6.21456878206667	-0.60794029121142
Pt	-5.60027282383056	-2.97320473778080	-0.49118121315418
P	7.63082022867040	-2.47805701982424	-1.03870981887031
P	5.98616183361203	-5.03025517269662	-1.40386113545504
P	-1.43171011341094	7.67636942637959	-1.41501379529211
P	1.62428529345435	7.68624070725527	-1.32405505936560
P	-6.11602750771197	-4.99177757291124	-1.34464773562137
P	-7.70960323410338	-2.40069616352985	-1.03105148855483
O	4.99748380849536	-1.20629580630571	0.37289652951024
O	3.55580361781390	-3.45188788357221	0.06022460066409
O	-1.28383722425413	4.82129862400233	0.12217463656040
O	1.40227079167859	4.82760002306105	0.20052102458112
O	-3.65358753517420	-3.43165341024527	0.08590354381595
O	-5.05030324838209	-1.15177757537403	0.35141751496954
C	1.23984091130018	-1.49588718784134	2.05502287543698
C	2.00068111915222	-0.28632452424441	2.20042658391523
C	3.26325802338416	-0.14958467458996	1.63734078162312
C	3.80179778104672	-1.24009309982819	0.90225135059634
C	3.01372040983642	-2.46925446886299	0.73274192596583
C	1.72288716384889	-2.57058840477233	1.31891484408324
C	-0.03321887044814	-1.46184171537854	2.88902815139955
C	-1.29772326895009	0.76221852461142	3.01921569809484
C	1.26999440362730	0.73931110620038	3.05439514368279
C	0.72511309189006	1.86192669702367	2.17918799439968
C	-0.70929228799011	1.86394174174153	2.14539527069922
C	-1.41674076247114	2.83055355052075	1.44165252505045
C	-0.69157549859902	3.85212997872566	0.77141545951555
C	0.77776110949173	3.85482514453757	0.81299371888926
C	1.46769332281264	2.83217930458627	1.51802460893538
C	-2.04174200044655	-0.25939102785491	2.17329684579473
C	-1.30504229604542	-1.48672798533017	2.05312653261098
C	-1.80755049226312	-2.56474308243580	1.33514007717362
C	-3.09371448452482	-2.44764160409024	0.74154733741742
C	-3.85689558601716	-1.19962691396413	0.88478781206531
C	-3.29887875745366	-0.10703188893952	1.60211663266077
C	8.48370235474264	-3.90264506209822	-1.80425199083363
C	7.72195464414436	-5.08446115549448	-1.97350113635397
C	8.30701618920509	-6.22609678026532	-2.55211533898406
C	9.65040253377937	-6.18055205087334	-2.95851752467353
C	10.40717530200148	-5.00663550504402	-2.79070196760006
C	9.82949532217583	-3.86375674798344	-2.21394398708614
C	-0.59584376209485	9.15800981056594	-2.08380217724172
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C	1.53835031226061	10.26822844433851	-2.53306570416455
C	0.83824290517628	11.36322163909278	-3.06512007020429
C	-0.56784979341546	11.35807098244529	-3.10814865339104
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C	-8.46609828808205	-6.16980888437991	-2.45087586759983
C	-0.03506216152587	-2.67214696671696	3.85548414716758
C	2.20486648511140	1.32498724094628	4.13497785082262
C	-2.23381398517187	1.38943415290014	4.07569108146348
H	7.78207285432921	-1.37864485900651	-1.93718789415092
H	5.17726965590388	-5.41665843806279	-2.51504223845511
H	-2.39234823139915	8.14030047338752	-0.46631282103038
H	2.53537038991244	7.19734582227301	-2.30939807231722
H	-5.32116824143025	-5.41550587172434	-2.45230183828513
H	-7.84238339177797	-1.32120916139953	-1.95641849172006
H	3.87928780393011	0.75106388940786	1.76443762331474
H	1.17393227191251	-3.51568770193967	1.20886057611871
H	-2.51504577653193	2.86362605702741	1.40791003666247

H	2.56626298625661	2.86613728805425	1.54164257113194
H	-1.27872356729663	-3.52336106485347	1.24561625000066
H	-3.89792464244763	0.80714733127570	1.71293218520413
H	7.72456322469902	-7.15049272774742	-2.68771400789639
H	10.11135599776923	-7.07147029744436	-3.40996263188203
H	11.45876583304505	-4.98105454066420	-3.11170107895164
H	10.43117499745713	-2.95074969706560	-2.08507312654516
H	2.63901900240954	10.28356591215721	-2.50249431823057
H	1.39557040870130	12.23071408644510	-3.44870971258245
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H	-2.39167749624684	10.26509224162894	-2.65680048693451
H	-10.52492827144691	-2.84441780438114	-2.05002329260725
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H	-10.29125652461737	-7.00061576306199	-3.27828124048307
H	-7.90207559182793	-7.10811128566304	-2.56769783223751
H	-0.93438836690146	-2.67401992651250	4.49991318557473
H	0.86472841629456	-2.67618021595757	4.49932868401671
H	-0.03564151036710	-3.61896272713850	3.28129295608369
H	-1.69545594731707	2.12711980456535	4.69998462968017
H	-2.67672130055116	0.61825733529034	4.73382461168143
H	-3.06815539510030	1.92489536971452	3.58191133213658
H	1.67573249083007	2.06682895945356	4.76194745924120
H	3.06145228386223	1.84532811419112	3.66345697414475
H	2.61585007294234	0.53172282239542	4.78709053554071
C	-0.02833329309667	-0.02379641349629	3.59469555669758
C	-0.05084050838414	-0.12921060911606	5.12058359873261
H	-0.04707035082869	0.86431354530723	5.60382500953904
H	0.82820087568519	-0.67981836547615	5.50234036658768
H	-0.95193313326211	-0.66132015159825	5.47677654612723
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H	2.52380933542105	8.15594280323870	-0.31987099773313
H	5.80677463236290	-6.14207206620519	-0.52685457965291
H	8.44094510715529	-2.05754621646143	0.05836058447418
H	-5.95096174163213	-6.08817712042136	-0.44565222647679
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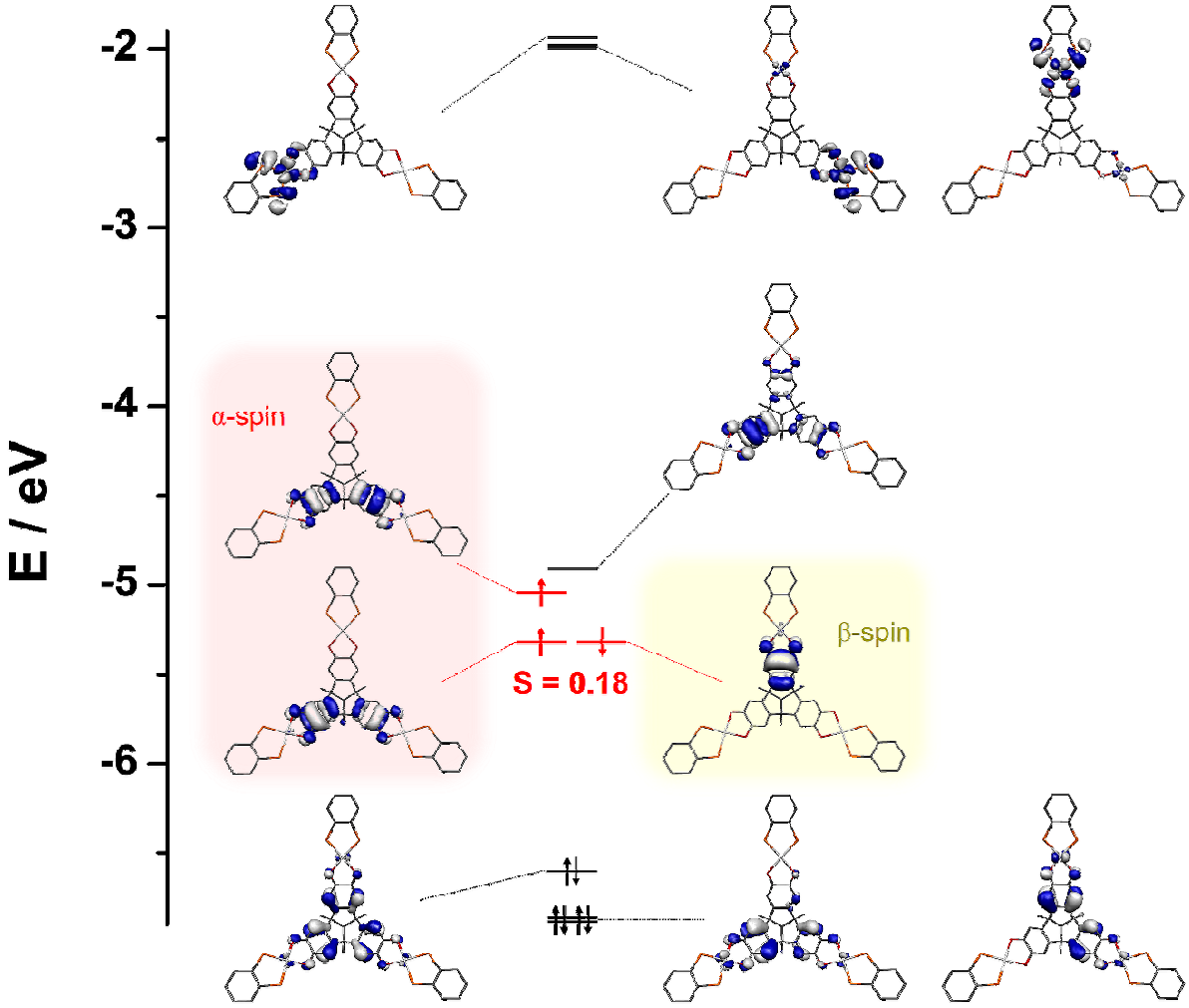

Figure S15. MO energy level scheme of frontier Kohn-Sham orbitals for **[2a•••]**$^{3+}$. α-spin and β-spin magnetic orbitals (SOMOs) are highlighted red and yellow, respectively.

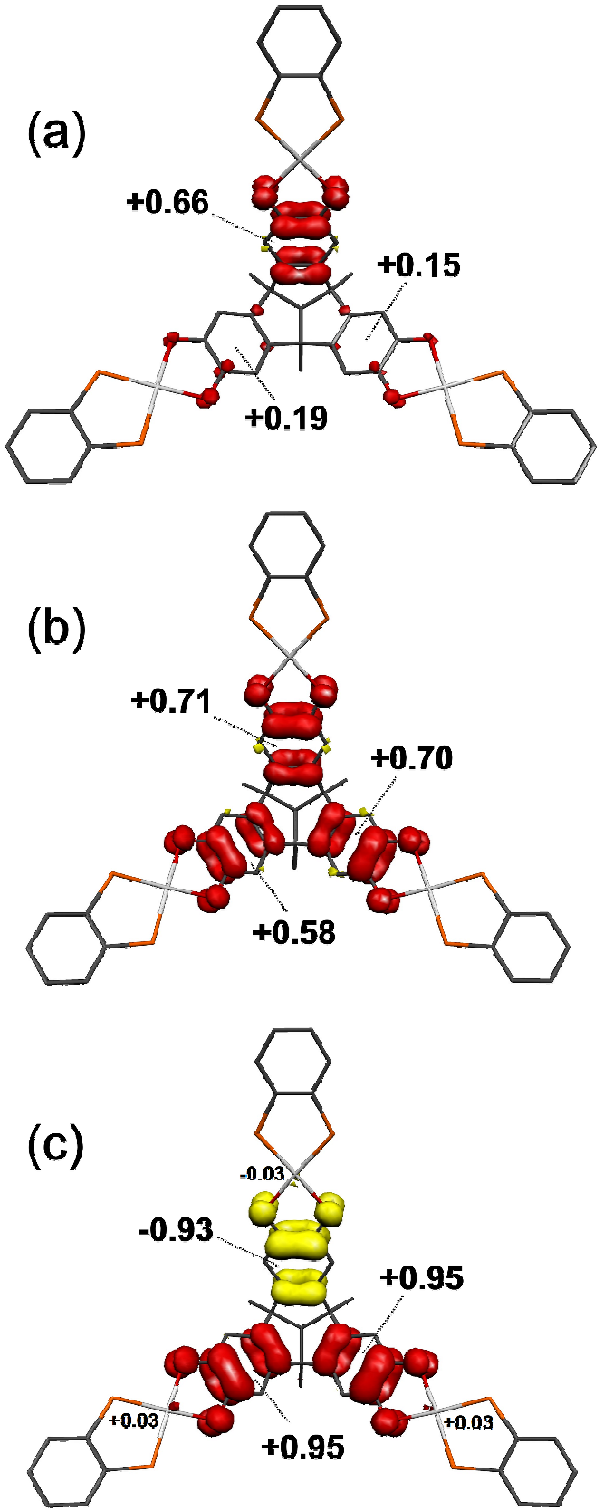

Figure S16. Mulliken spin population analyses for: (a) **[2a•]**$^{+}$, (b) **[2a••]**$^{+}$, and (c) **[2a•••]**$^{3+}$ (red: α-spin; yellow: β-spin).

Corresponding data for **[1a•]**$^{+}$, **[1a••]**$^{+}$ and **[1a•••]**$^{3+}$ are in Figure 8 of ref. 24.

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