Supporting Information

Directing Energy Transfer in Pt(bodipy)(mercaptopyrene) Dyads

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NMR-Spectra

Brief Discussion of the Spectroscopic trends

The (pyrS)Pt(PEt_3)$_2$ moiety of the dyad molecules acts as a net electron donor towards the respective BDP ligand. The ^{31}P and ^{195}Pt NMR data of Table 1 indicate that the coupling constant J_{PtP} increases with an increasing electron-richness of the Pt-fragment, which is due to stronger back-bonding to the PEt_3 coligands. Such observations have been pivotal in elucidating the *cis*-effect of ligands in Pt(II) chemistry.[1] This sequence is, however, not reflected by the chemical shifts, which follow an inverse ordering for ^{195}Pt and ^{31}P NMR data with extreme positions for the mesityl (mesityl = 2,4,6-tripmethylphenyl) and krypto-BDP (KBDP) complexes. For **BPtSPyr** and **BPtSPyrSPtB**, the chemical shifts and coupling constants are very similar, which indicates that the pyrene-1,6-dithiolate ligand does not differ appreciably from mercaptopyrene in terms of net electron-donation to every individual Pt ion.

Table S1. ^{195}Pt, ^{31}P and ^{13}C NMR Spectroscopic Data for the complexes

	δ(^{195}Pt) / ppm	δ(^{31}P) / ppm	J_{PtP} / Hz	δ(^{13}C)[a] / ppm	J_{PtC} / Hz
MesPtSPyr[b]	-4494	9.32	2734	144.8	864
KBPtSPyr	-4249[c]	-4.90[c]	2611[c]	169.0[d]	n.o.
BPtSPyrSPtB	-4344[b]	6.46[d]	2491[b] / 2493[d]	188.3[d]	n.o.
BPtSPyr[d]	-4378	6.84	2486	188.0	848
KBPtI[b]	-4432	-4.90	2583	161.7	n.o.
BPtI[c]	-4503	4.02	2450	181.1	n.o.

[a]Chemical shift of the carbon atom attached to the platinum via a direct Pt-C σ-bond. Measured in [b]$CDCl_3$, [c]C_6D_6, or [d]THF-*d8* solution.

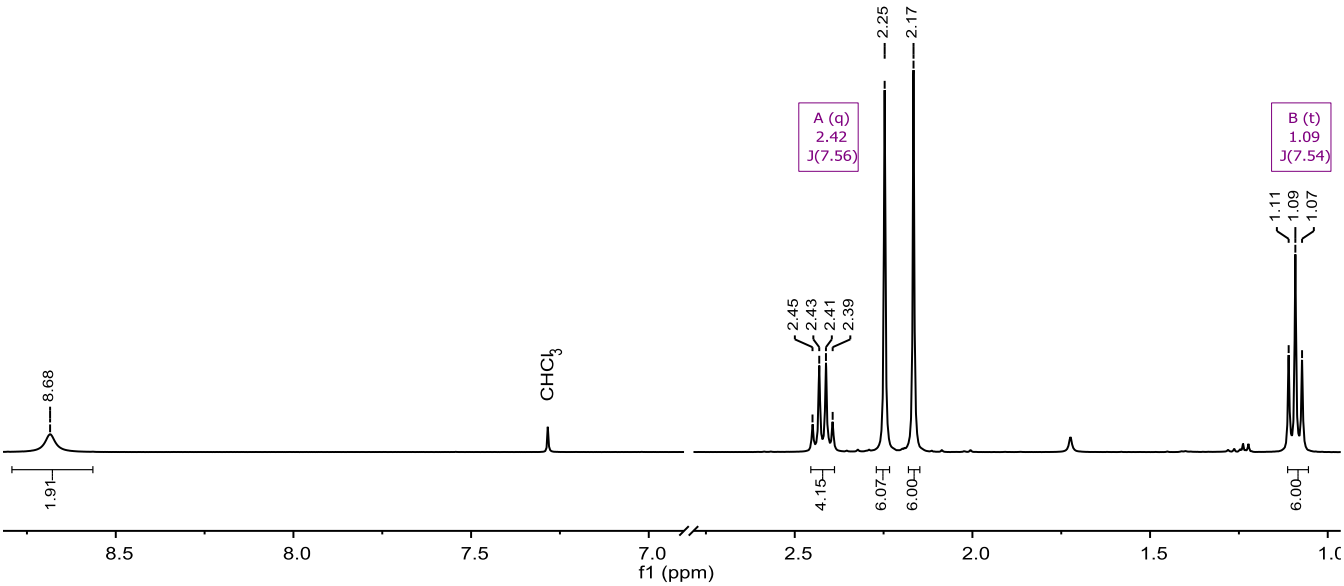

Figure S1. ^{1}H NMR spectrum of bis-(4-ethyl-3,5-dimethyl-pyrrol-2-yl)-ketone in $CDCl_3$.

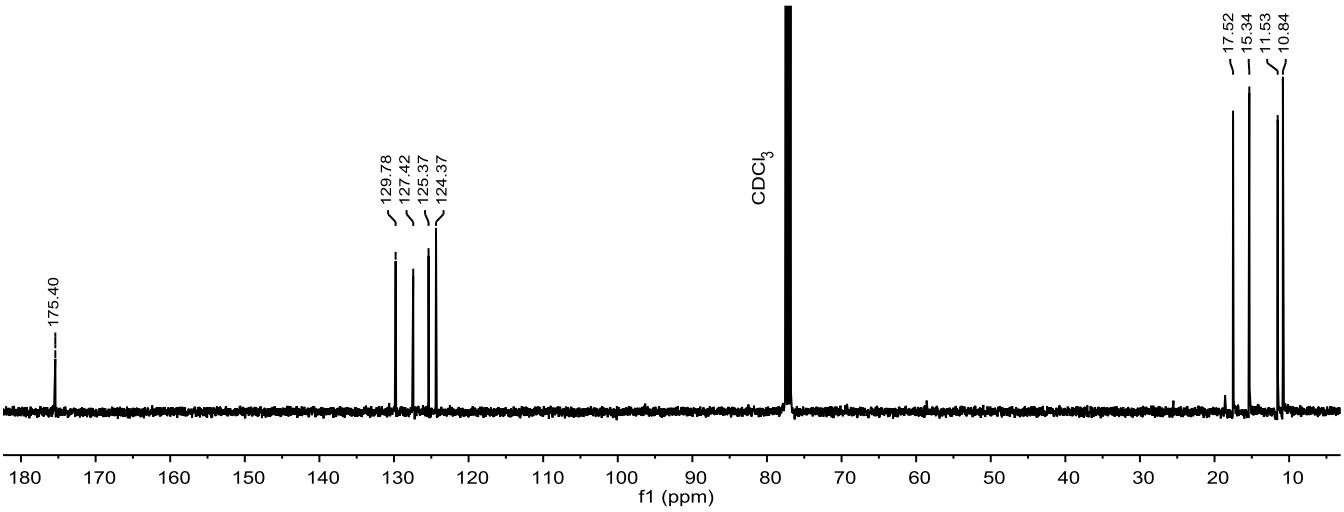

Figure S2. ^{13}C {^{1}H} NMR spectrum of bis-(4-ethyl-3,5-dimethyl-pyrrol-2-yl)-ketone in $CDCl_3$.

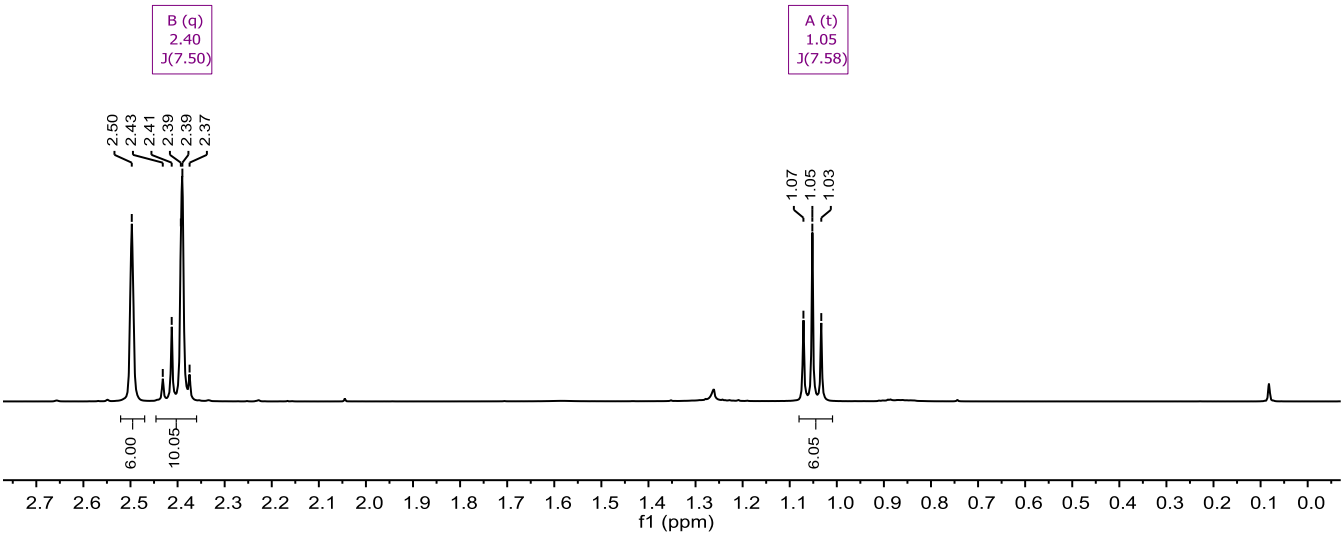

Figure S3. ^{1}H NMR spectrum of 8-cloro-2,6-diethyl-1,3,5,7-tetramethyl-bodipy in $CDCl_3$.

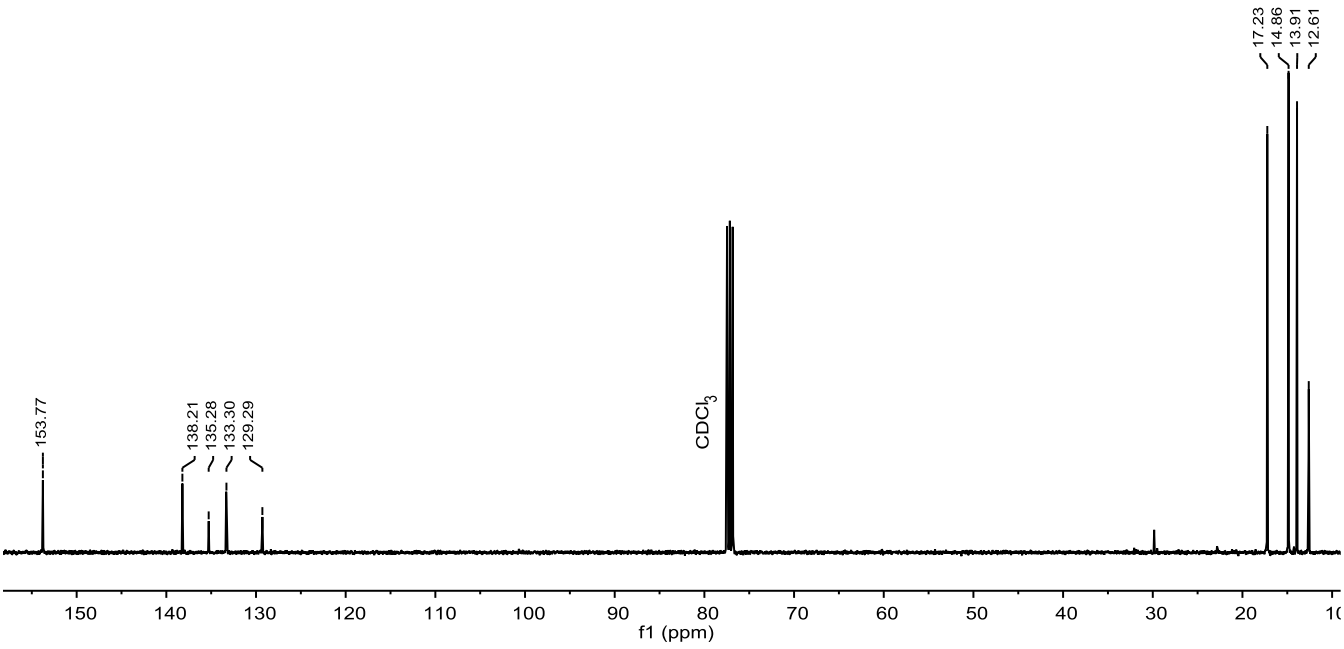

Figure S4. ^{13}C {^{1}H} NMR spectrum of 8-cloro-2,6-diethyl-1,3,5,7-tetramethyl-bodipy in $CDCl_3$.

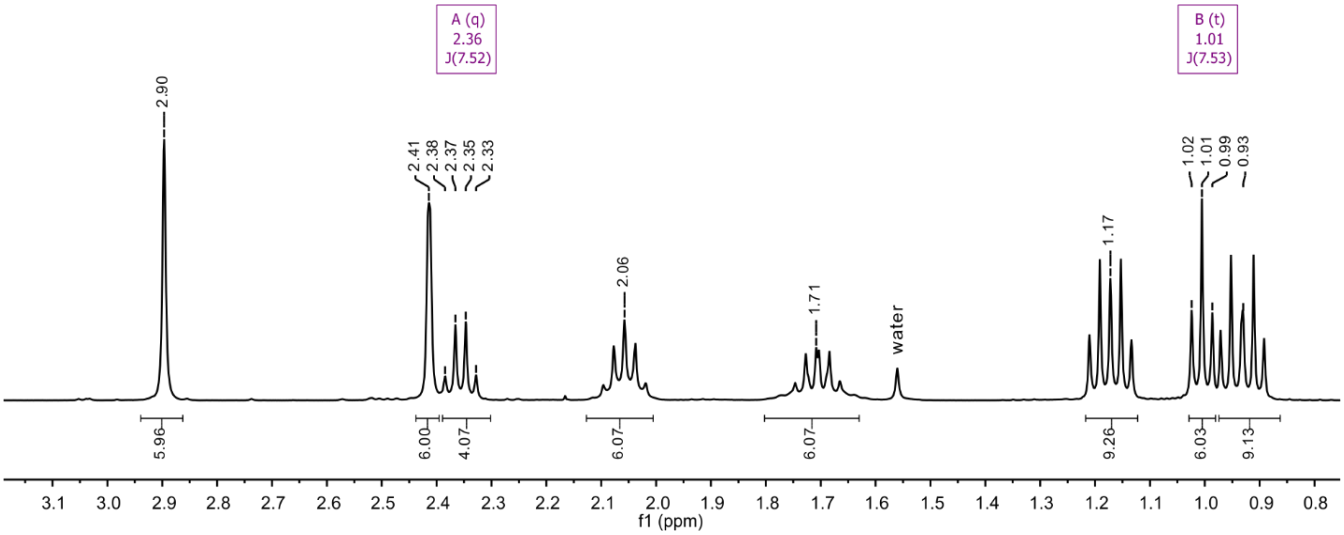

Figure S5. ^{1}H NMR spectrum of ***cis*-KBPtCl** in $CDCl_3$.

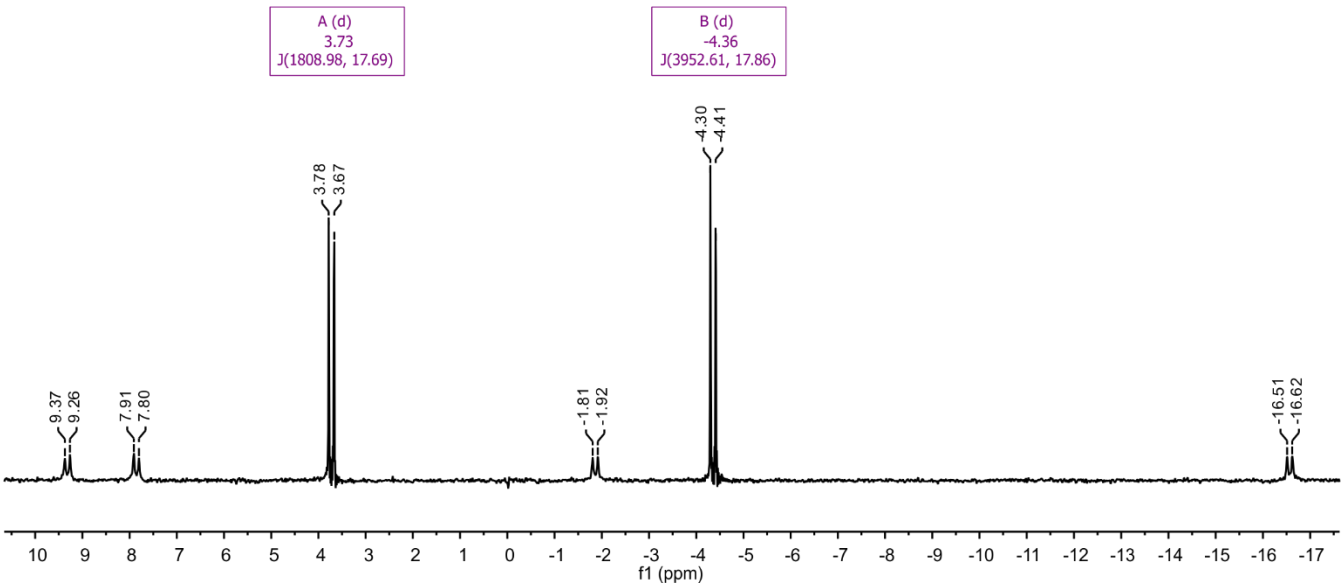

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of ***cis*-KBPtCl** in $CDCl_3$.

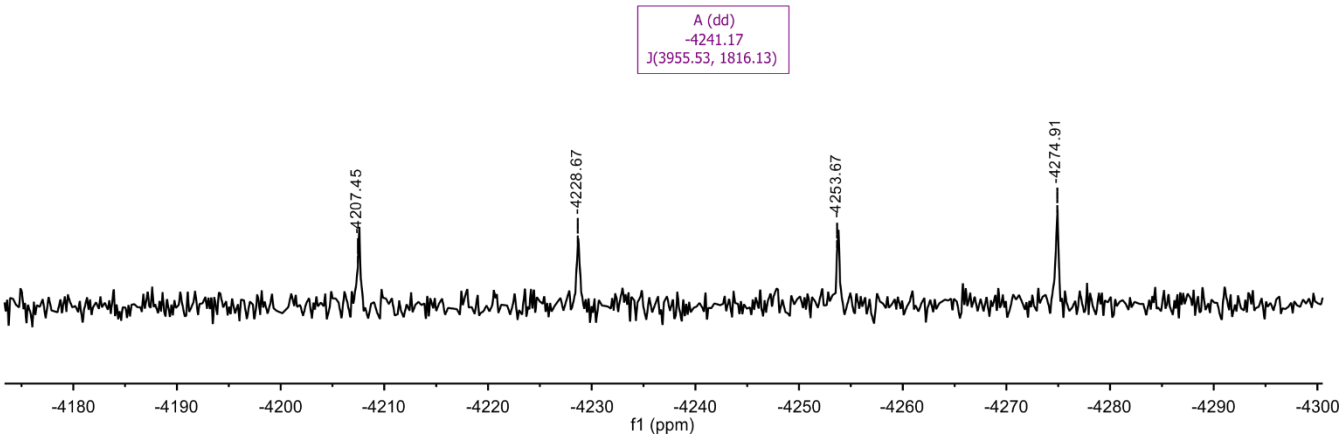

Figure S7. $^{195}Pt\{^{1}H\}$ NMR spectrum of ***cis*-KBPtCl** in $CDCl_3$.

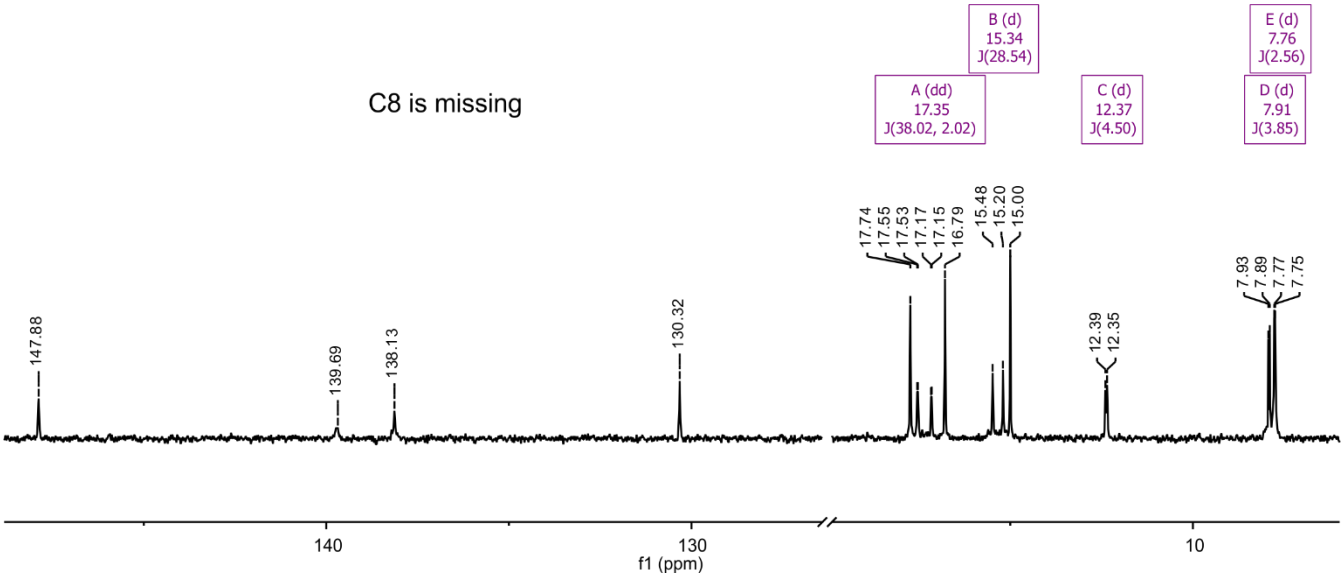

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of ***cis*-KBPtCl** in $CDCl_3$.

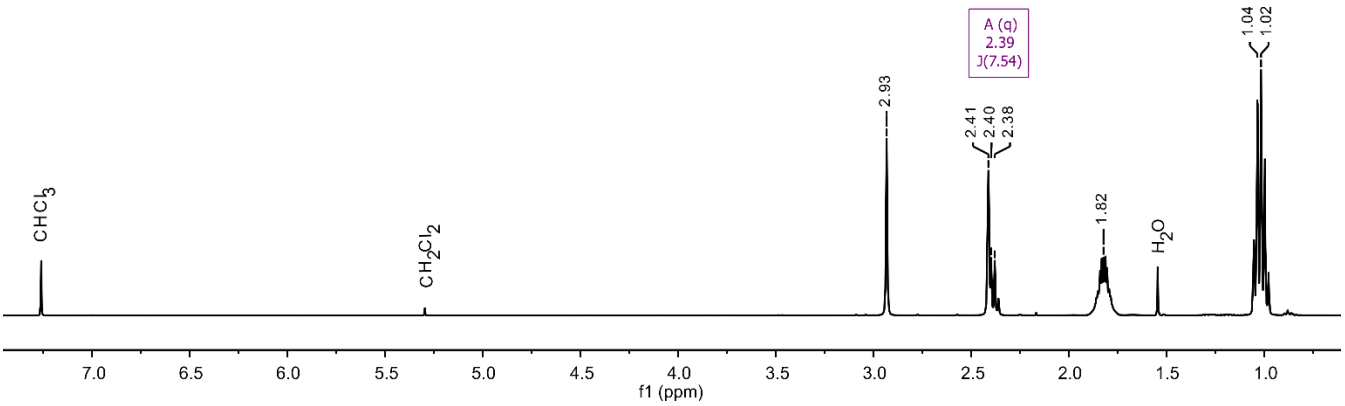

Figure S9. ^{1}H NMR spectrum of **KBPtI** in $CDCl_3$.

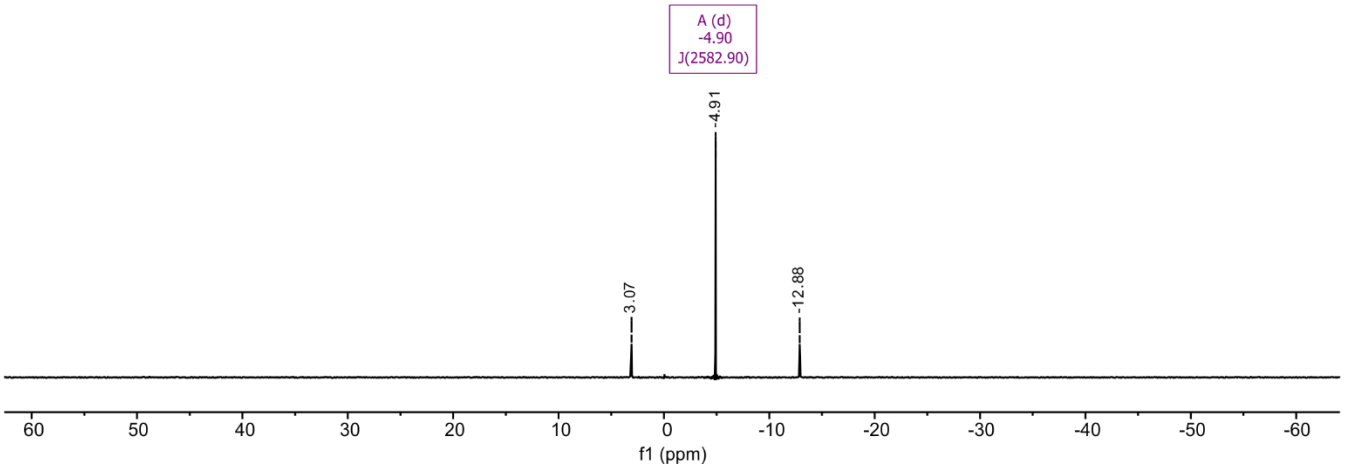

Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **KBPtI** in $CDCl_3$.

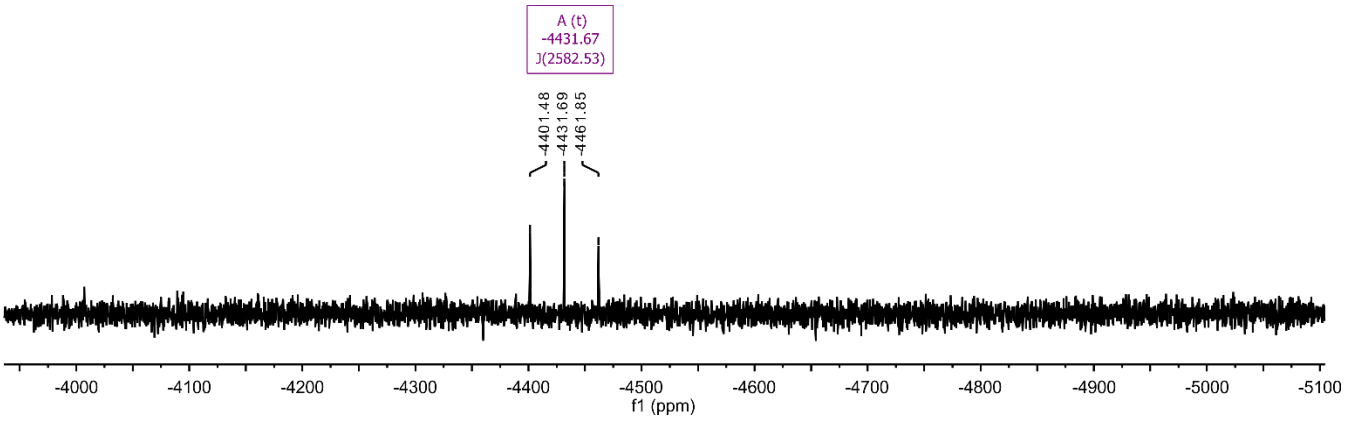

Figure S11. $^{195}Pt\{^{1}H\}$ NMR spectrum of **KBPtI** in $CDCl_3$.

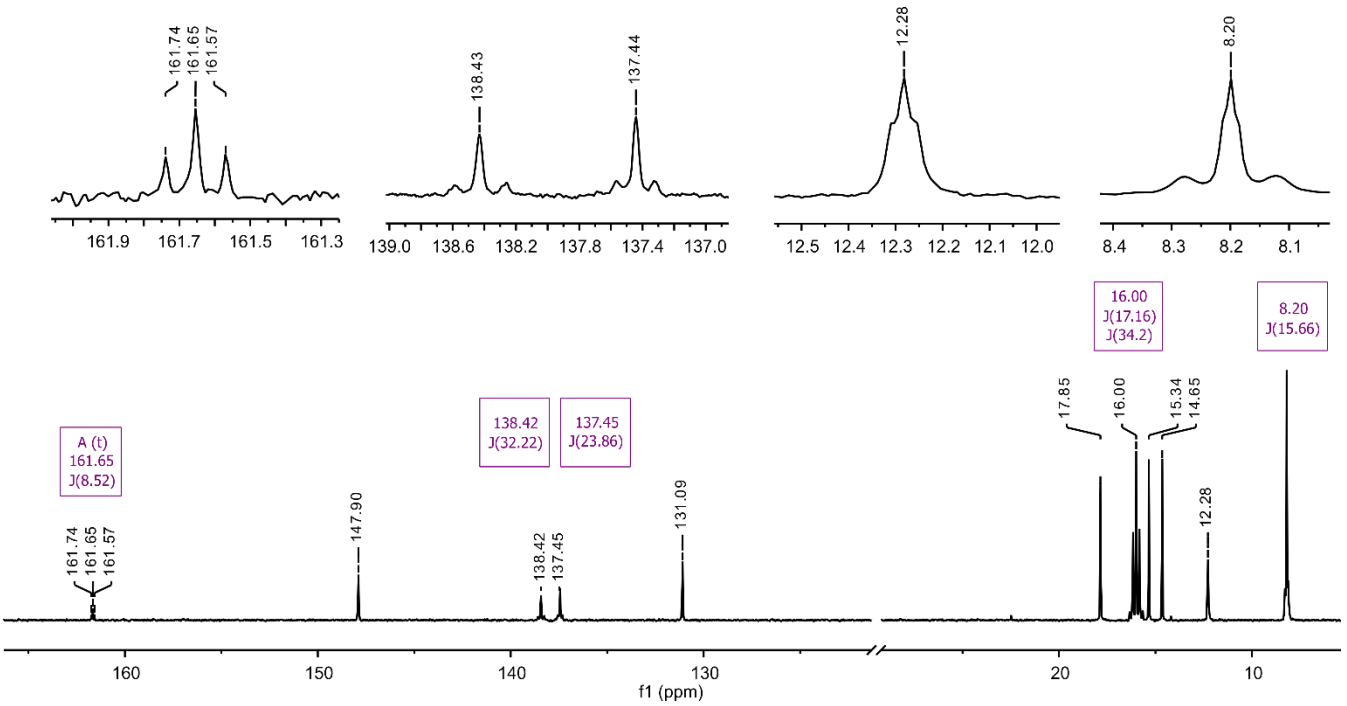

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **KBPtI** in $CDCl_3$.

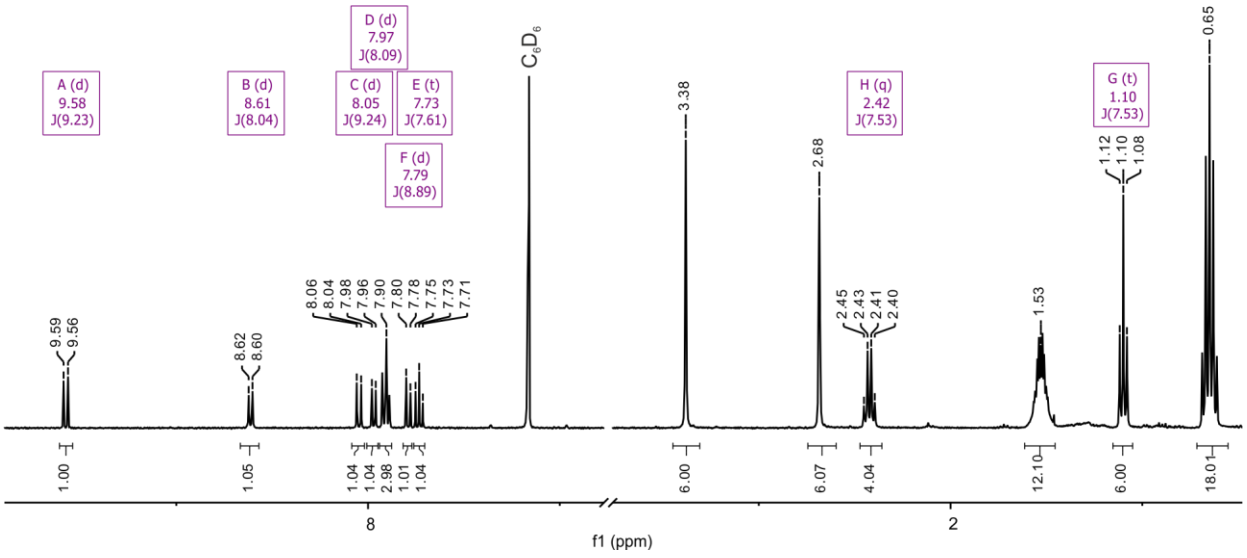

Figure S13. ^{1}H NMR spectrum of **KBPtSPyr** in C_6D_6.

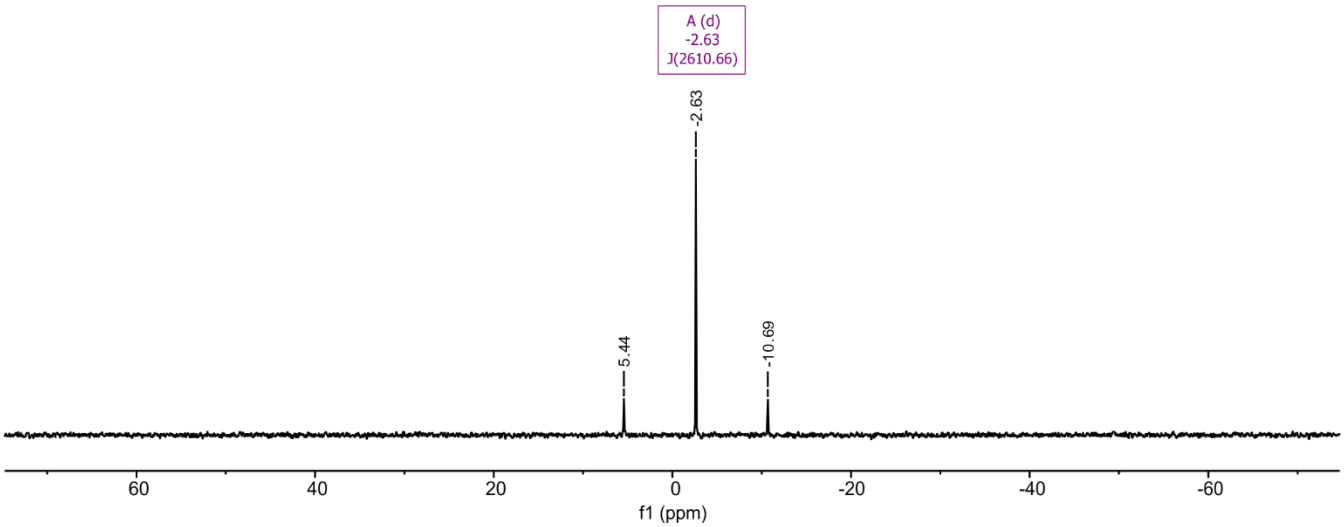

Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum of **KBPtSPyr** in C_6D_6.

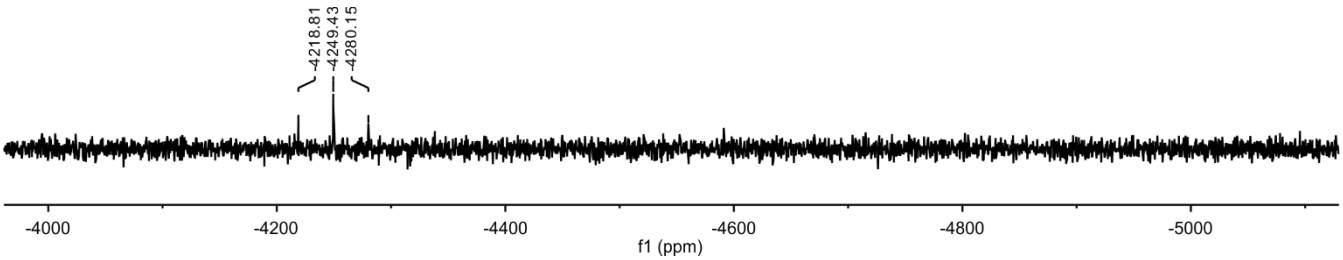

Figure S15. $^{195}Pt\{^{1}H\}$ NMR spectrum of **KBPtSPyr** in C_6D_6.

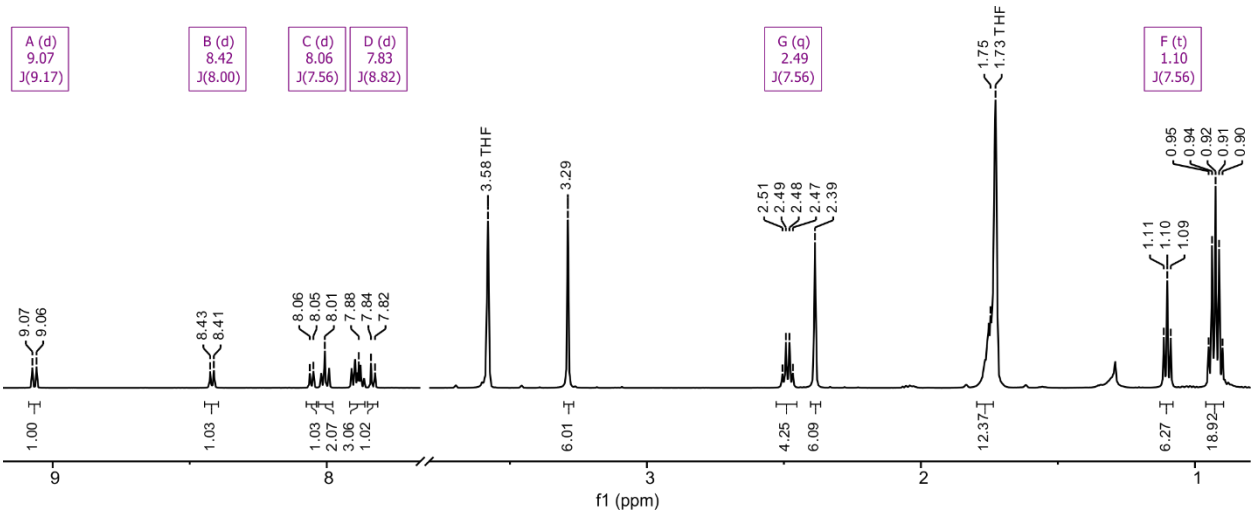

Figure S16. ^{1}H NMR spectrum of **KBPtSPyr** in THF-*d8*.

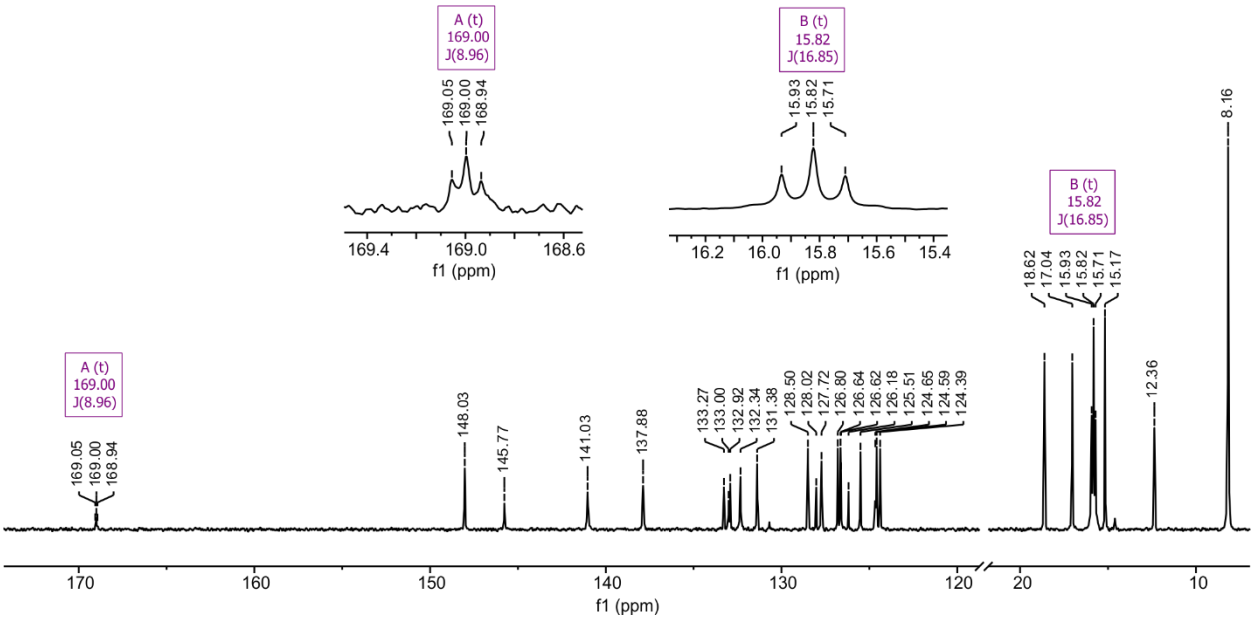

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **KBPtSPyr** in THF-*d8*.

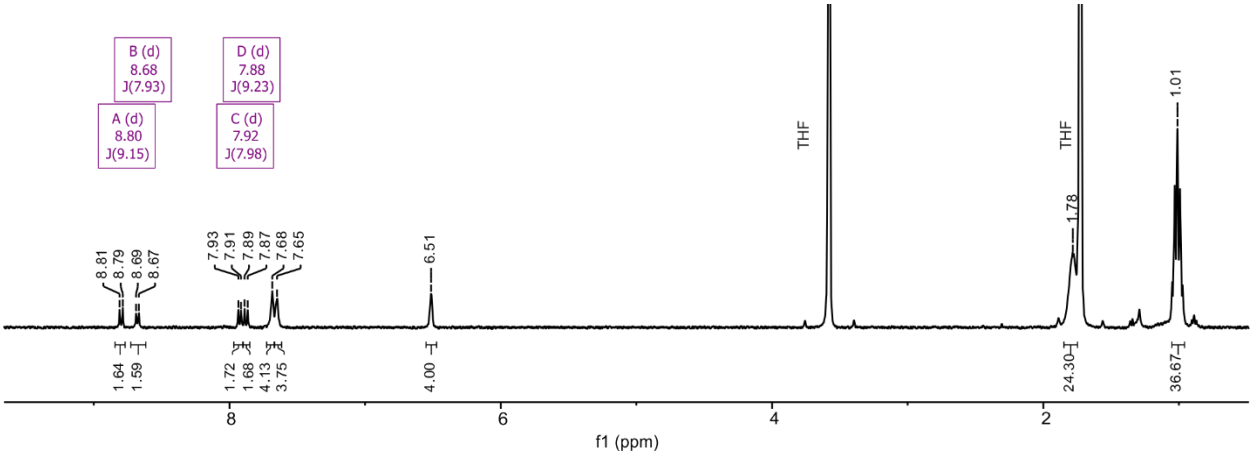

Figure S18. ^{1}H NMR spectrum of **BPtSPyrSPtB** in THF-*d8*.

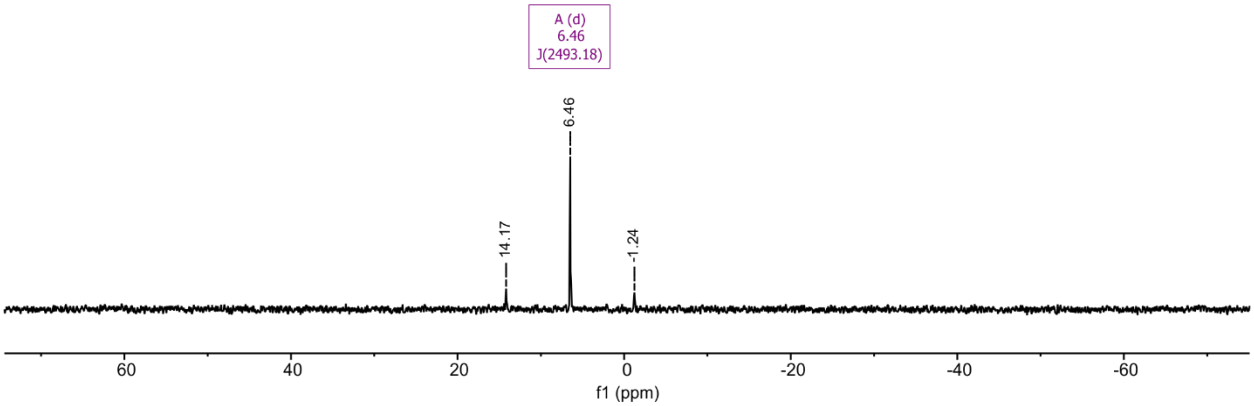

Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of **BPtSPyrSPyr** in THF-*d8*.

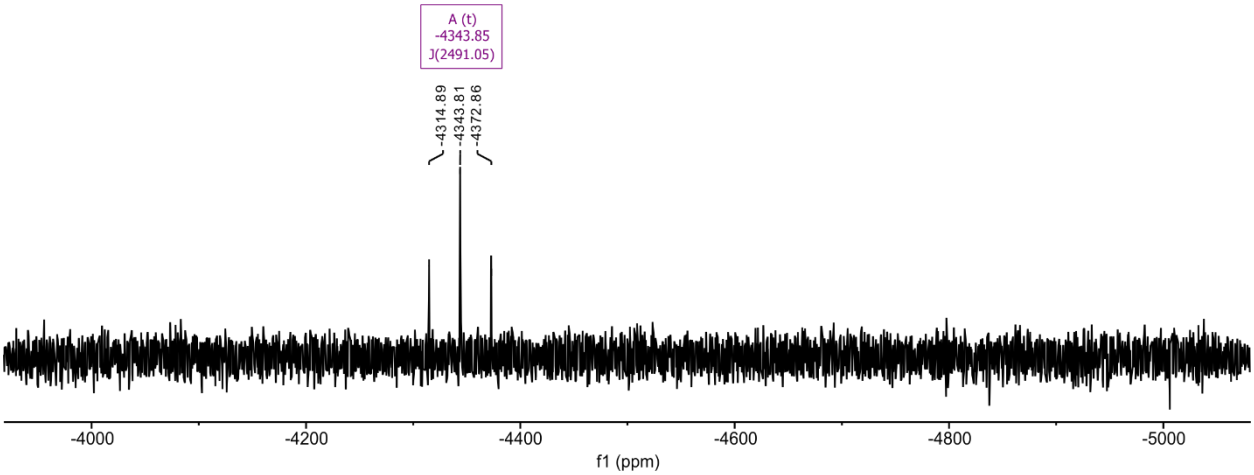

Figure S20. $^{195}Pt\{^{1}H\}$ NMR spectrum of **BPtSPyrSPyr** in THF-*d8*.

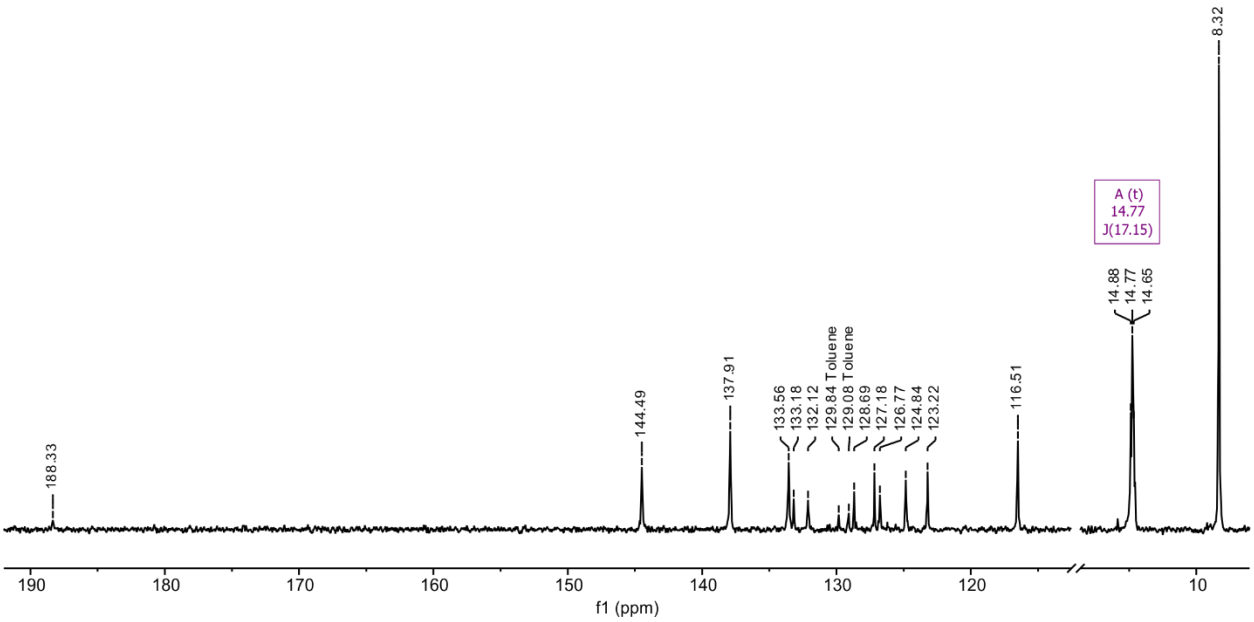

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **BPtSPyrSPyr** in THF-*d8*.

Single Crystal X-Ray Diffraction

Table S2. Crystal and refinement data of **KBPtI** and **KBPtSPyr**.

Compound	**KBPtI**	**KBPtSPyr**
Emp. formula / f. wt. (g/mol)	$C_{29}H_{52}BF_2IN_2P_2Pt$ / 861.46	$C_{98.60}H_{142}B_2Cl_{3.20}F_4N_4P_4Pt_2S_2$ / 2172.59
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	*P* 21/*n*	$P\bar{1}$
a, *b*, *c* (Å)	9.3246(5), 34.723(2), 10.3829(5)	14.1734(9), 16.7856(12), 22.6728(15)
α, *β*, *γ* (°)	90, 92.701(4), 90	78.562(5), 88.157(5), 74.328(5)
V (Å^3)	3358.0(3)	5089.1(6)
Z	4	2
D_{calcd} (Mg/m^3)	1.704	1.418
Absorption coefficient (mm^{-1})	5.225	2.987
θ range of data collection	2.049 to 27.200°	1.73 to 27.98°
Limiting Indices	$-11 \le h \le 11$, $-44 \le k \le 44$, $-13 \le l \le 13$	$-15 \le h \le 17$, $-19 \le k \le 20$, $-27 \le l \le 27$
Reflections collected / unique (> 2σ(I))	52908 / 7480 [R(int) = 0.1765]	19048 / 13599 [R(int) = 0.0889]
Data / Restraints / Parameter	7480 / 0 / 355	19048 / 668 / 1296
R (I>2σ(I))	R_1 = 0.0448, ωR_2 = 0.1126	R_1 = 0.0576, ωR_2 = 0.1401
R_W (all data)	R_1 = 0.0496, ωR_2 = 0.1153	R_1 = 0.0870, ωR_2 = 0.1505
GooF (all data)	1.005	1.052
Max. and min. res. dens. (eA^{-3})	2.574 and -2.783	1.640 and -1.747

Table S3. Selected Bond Lengths [Å] and Angles [deg] for Complexes **KBPtI**, **KBPtSPyr**, and **BPtI**.

bond parameters	**KBPtI**	**KBPtSPyr**[a]	**BPtI**
Pt1-C8	2.019(4)	2.046(8) / 2.057(8)	1.994(10)
Pt1-P1	2.3281(12)	2.332(2) / 2.308(2)	2.3206(15)
Pt1-P2	2.3300(12)	2.333(2) / 2.344(2)	2.3206(15)
Pt1-I1 / Pt1-S1	2.6914(4)	2.389(2) / 2.385(2)	2.6689(9)
C8-Pt1-P1	89.40(13)	90.5(3) / 91.7(3)	91.37(7)
C8-Pt1-P2	87.79(13)	86.8(3) / 87.8(3)	91.37(7)[b]
P1-Pt1-I1/S1	90.86(3)	93.23(8) /	88.71(7)
P2-Pt1-I1/S1	91.98(3)	89.23(8) /	88.71(7)[b]
P1-Pt1-P2	176.94(4)	176.91(8) /	176.8(3)
C8-Pt1-I1/S1	179.66(14)	172.7(3)/167.9(3)	176.03(8)
[Pyr]-[BDP][b]	n. a.	19.7 / 18.2	n. a.
[Pt]-[BDP][b]	87.0	88.8 / 88.8	90.0
[Pt]-[Pyr][b]	n. a.	70.0 / 73.2	n. a.

[a]Bond parameters for the two independent molecules in the unit cell. [b]Interplanar angle between planes defined by the central six-membered ring of the BDP unit and the carbon atoms C19-C24 of the pyrene ring, or the coordination plane of the platinum ion, respectively.

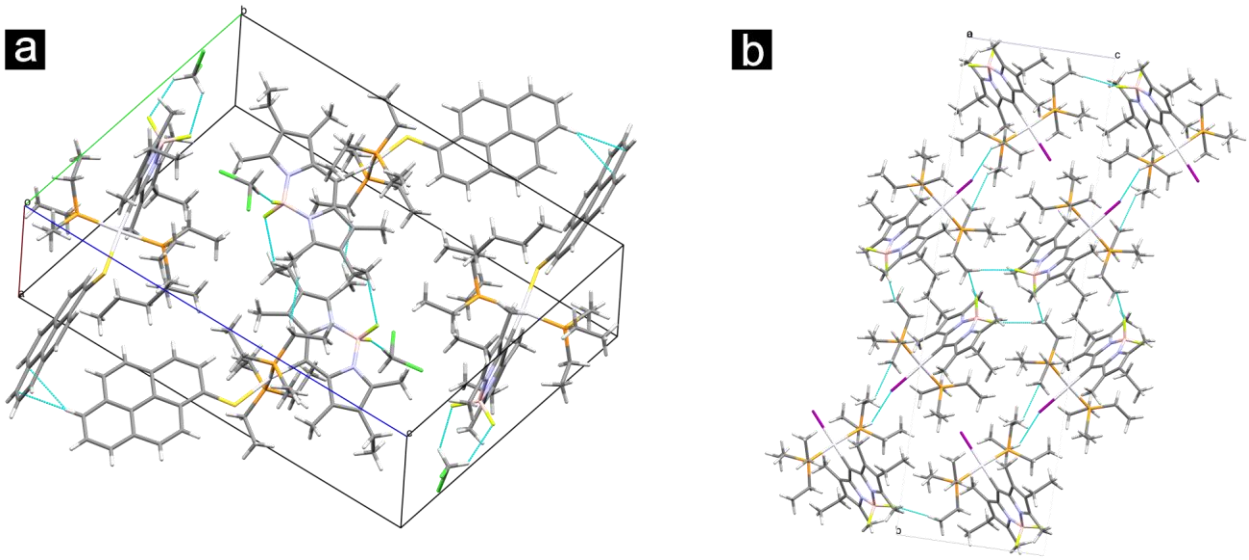

Figure S22. Packing in the crystal lattice of a) **KBPtSPyr** and b) **KBPtI**.

In the crystal lattice of complex **KBPtSPyr**, pairs of the crystallographically unique molecules pack in a centrosymmetric fashion. Molecules of type 1 form two strong hydrogen bonds of 2.423 Å and 2.431 Å with the two hydrogen atoms of a CH_2Cl_2 solvent molecule, while molecules of type 2 engage in an even stronger hydrogen bond of 2.223 Å to one H atom of another CH_2Cl_2 solvent molecule and a weaker contact of 2.618 Å to an ethyl proton of the KBDP ligand of its immediate neighbour (see Figure S22 of the Supporting Information). Molecules 1 and 2 are interconnected by CH···π hydrogen bonds between atoms C27/C28 and H77 of their pyrene substituents, which are disposed at an interplanar angle of 62.7°, as well as CH···π contacts of 2.729 and 2.770 Å to a methylene or a methyl proton of the PEt_3 ligands.

Quantum Chemical Calculations

Table S4. Calculated Mulliken parameters of BPtSPyr. Fragment contributions are given in percent.

Orbital	Pt	PEt_3	bodipy	mercaptopyrene
LUMO+1	1	0	0	99
LUMO	4	2	94	0
HOMO	3	2	1	94
HOMO-1	1	1	98	0

Table S5. Calculated Mulliken parameters of BPtSPyrSPtB. Fragment contributions are given in percent.

Orbital	bodipy(1)	Pt(1)	PEt_3(1)	SpyrS	PEt_3(2)	Pt(2)	bodipy(2)
LUMO+2	0	1	0	96	0	1	0
LUMO+1	47	2	1	0	1	2	47
LUMO	47	2	1	1	1	2	47
HOMO	0	2	1	94	1	2	0
HOMO-1	1	3	3	87	3	3	1
HOMO-2	50	1	1	0	1	1	48
HOMO-3	48	1	1	0	1	1	50

Table S6. Calculated Mulliken parameters of KBPtSPyr. Fragment contributions are given in percent.

Orbital	Pt	PEt_3	bodipy	mercaptopyrene
LUMO+1	1	0	0	98
LUMO	3	2	95	0
HOMO	4	2	1	94
HOMO-1	0	0	0	99

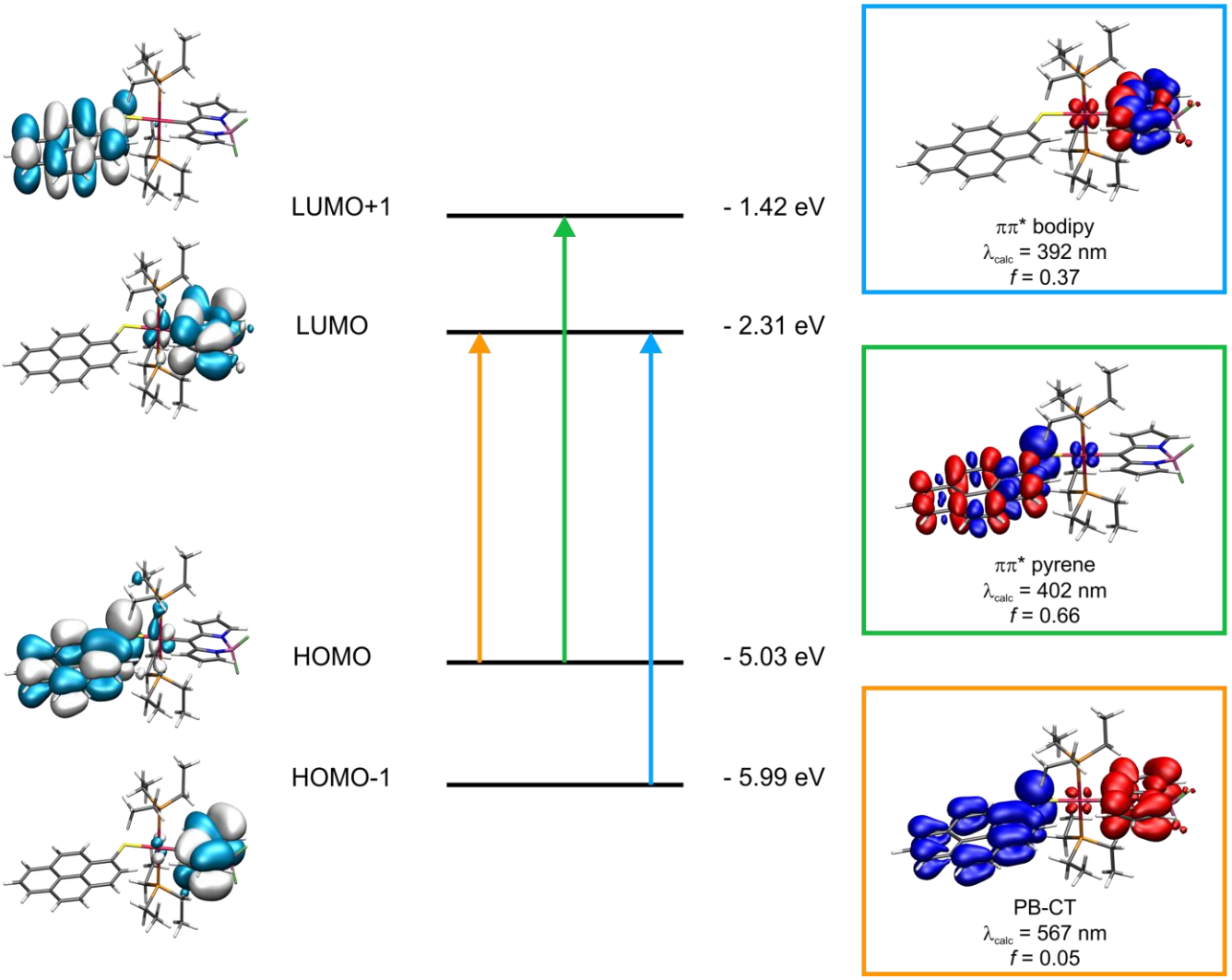

Figure S23. Graphical representation of the relevant MOs and TD-DFT energies of **BPtSPyr** as well as electron density difference maps (*blue* = electron density loss, *red* = electron density gain).

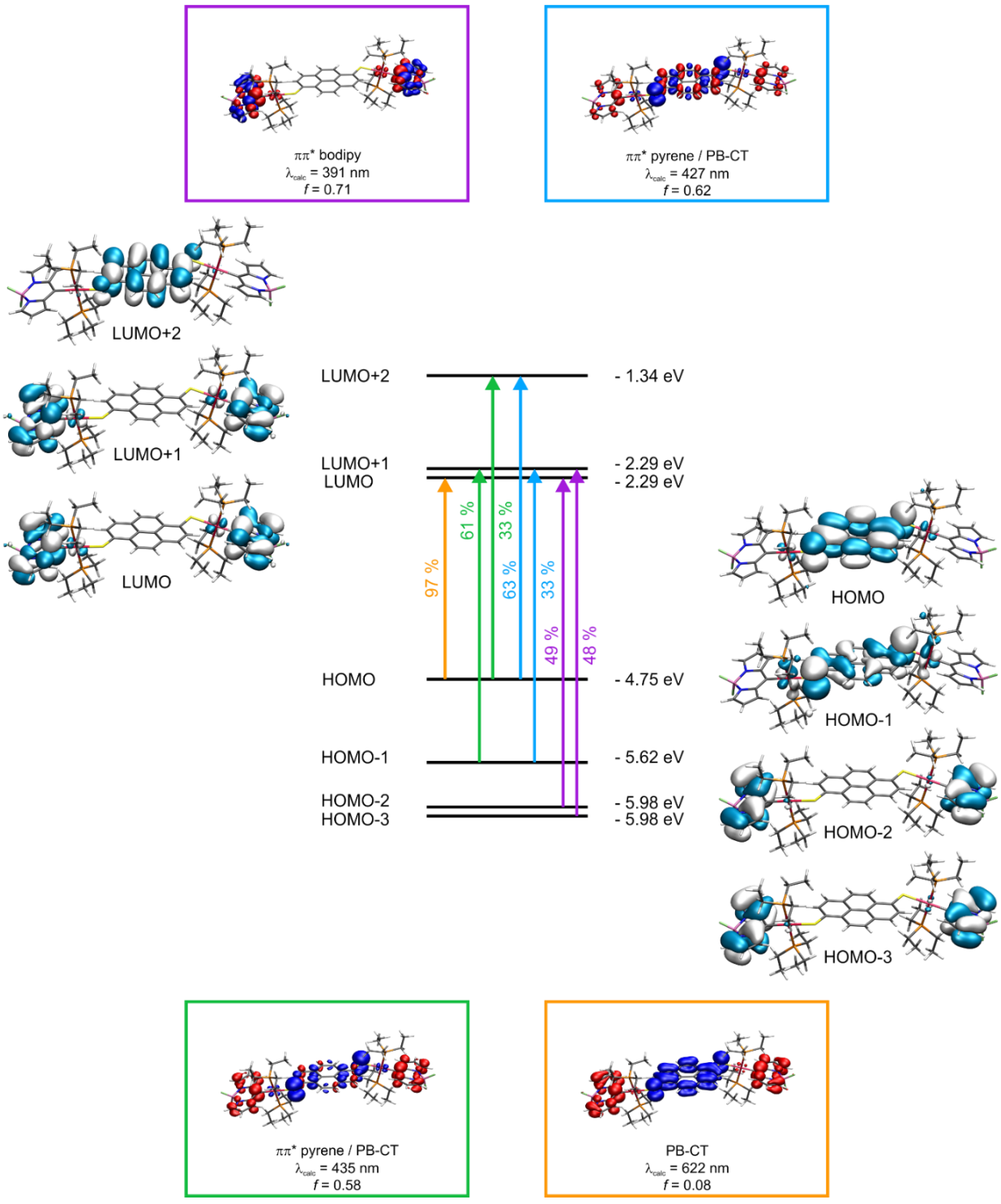

Figure S24. Graphical representation of the relevant MOs and TD-DFT energies of **BPtSPyrSPtB** as well as electron density difference maps (*blue* = electron density loss, *red* = electron density gain).

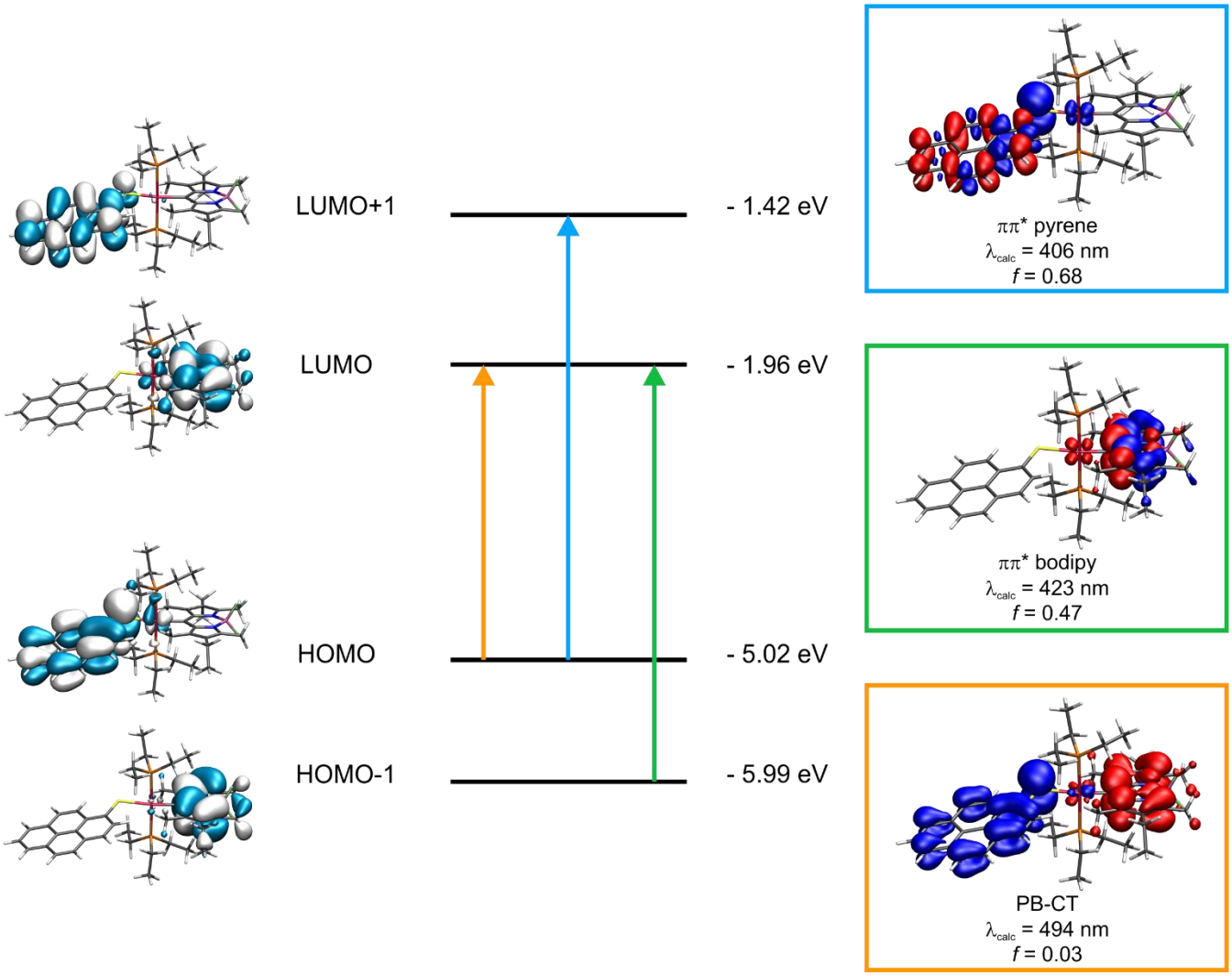

Figure S25. Graphical representation of the relevant MOs and TD-DFT energies of **KBPtSPyr** as well as electron density difference maps (blue = electron density loss, red = electron density gain).

Table S7. Calculated Mulliken parameters of the BPtSPyr radical cation. Fragment contributions are given in percent.

Orbital	Pt	PEt_3	bodipy	mercaptopyrene
LUSO+1(β)	3	2	93	2
LUSO+1(α)	2	1	31	66
LUSO(β)	2	2	1	95
LUSO(α)	1	2	63	34
HOSO(α)	1	1	93	5
HOSO(β)	1	1	98	0
HOSO-1(α)	2	2	5	90
HOSO-1(β)	6	6	1	87
HOSO-8(β)	1	0	0	99

Table S8. Calculated Mulliken parameters of BPtSPyr radical anion. Fragment contributions are given in percent.

Orbital	Pt	PEt_3	bodipy	mercaptopyrene
LUSO+11(α)	9	14	77	0
LUSO+1(β)	4	3	92	1
LUSO(β)	1	0	0	99
LUSO(α)	1	0	0	99
HOSO(α)	3	2	94	0
HOSO(β)	4	3	2	91
HOSO-1(α)	4	3	1	92
HOSO-1(β)	1	1	96	1

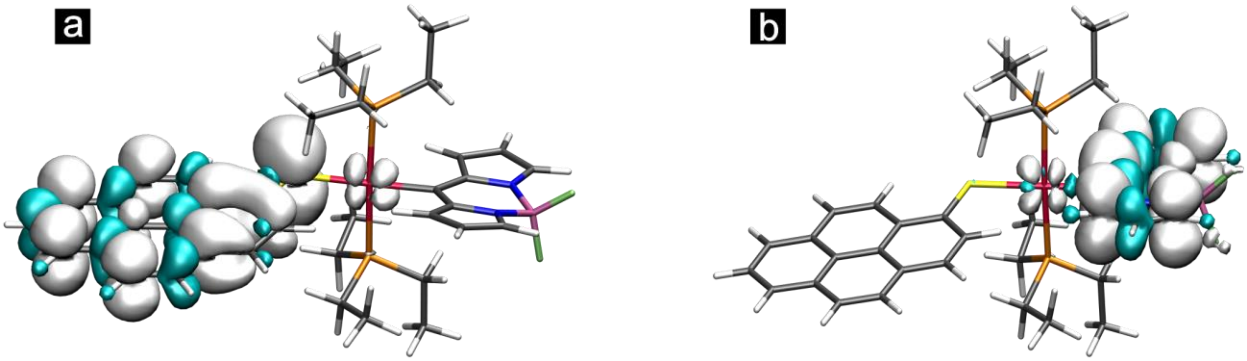

Figure S26. Calculated spin densities of the a) radical cation and b) the radical anion of **BPtSPyr**.

Table S9. Calculated spin density contributions of the respective fragments to the spin density surfaces of the radical cation and anion of BPtSPyr.

Oxidation State	cation	anion
Pt	-0.004	-0.002
PEt_3	0.023	0.017
bodipy	-0.004	0.990
mercaptopyrene	0.984	-0.006

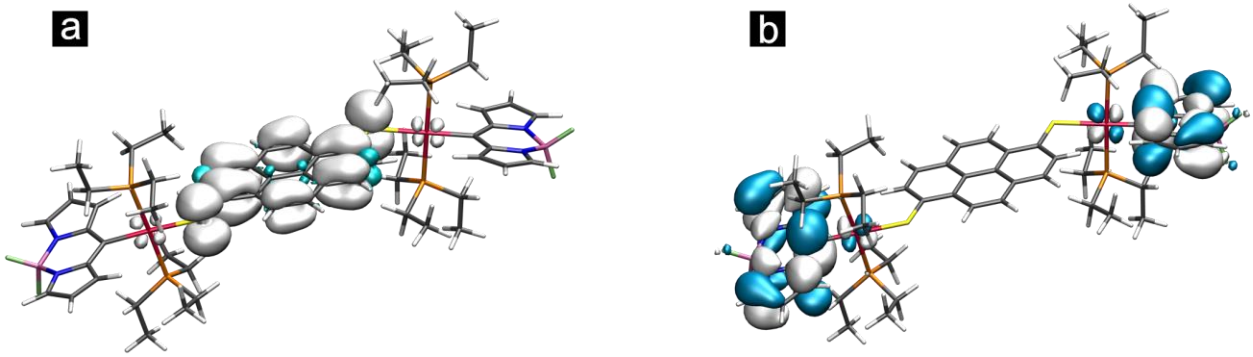

Figure S27. a) Calculated spin density of the radical cation and b) the HOMO of the two electron reduced form (open shell singlet) of **BPtSPyrSPtB**.

Table S10. Calculated spin density contributions of the respective fragments to the spin density surfaces of the radical cation of BPtSPyrSPtB.

Oxidation state	bodipy(1)	Pt(1)	PEt_3(1)	mercaptopyrene	PEt_3(2)	Pt(2)	bodipy(2)
cation	-0.001	-0.001	0.001	0.983	0.001	-0.001	-0.001

Table S11. Calculated spin density contributions of the respective fragments to the spin density surfaces of the radical cation and anion of KBPtSPyr.

Oxidation state	bodipy	Pt	PEt_3	mercaptopyrene
cation	-0.002	-0.009	0.020	0.973
anion	1.000	-0.010	0.012	-0.005

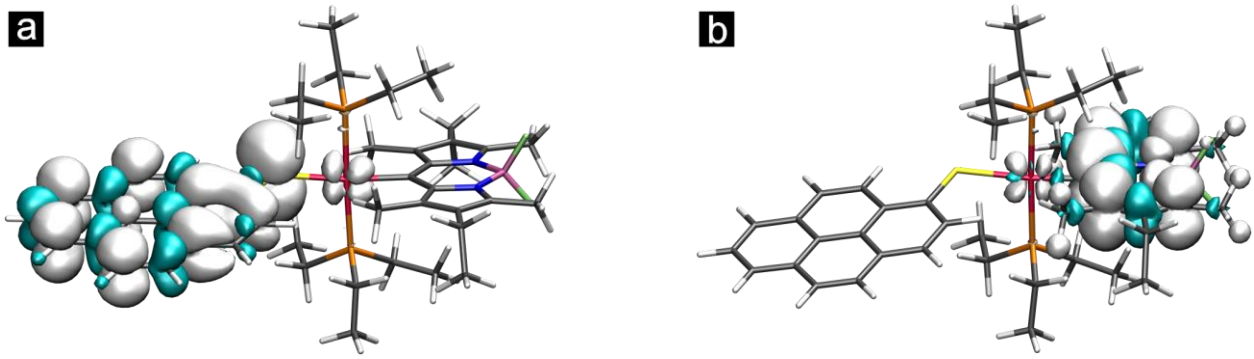

Figure S28. Calculated spin densities of a) the radical cation and b) the radical anion of **KBPtSPyr**.

Electrochemistry

Cyclic voltammograms of all complexes were recorded in the THF /0.1 M NBu_4PF_6 supporting electrolyte. Under these conditions, all BDP or KBDP containing complexes display a chemically (partially) reversible oxidation, while all complexes with a terminal mercaptopyrene or a bridging pyrene-1,6-dithiolate ligand offer a reversible oxidation. Owing to the lack of a mercaptopyrene donor ligand and the placement of the platinum complex entity outside the π-conjugated cyanine core of the bodipy ligand (note that the HOMO of a bodipy has a nodal plane at the meso position), iodo precursors **BPtI** and **KBPtI** do not exhibit any voltammetric oxidation wave within the accessible potential window of the THF/NBu_4PF_6 supporting electrolyte. BDP peralkylation has, however, the expected effect on the reduction potential as demonstrated by the cathodic shift of 370 mV between **BPtI** and **KBPtI** (see Table 4). Replacement of the iodo by the mercaptopyrene ligand leaves the potential for the BDP-centred reduction nearly unaltered (Table 4), but adds the reversible oxidation wave of the pyrS ligand to the voltammograms. The half-wave potential of this wave follows the electron richness of the (σ-aryl)$Pt(PEt_3)_2$ entity and decreases in the order **BPtSPyr** > **KBPtSPyr** > **MesPtSPyr** > **BPtSPyrSPtB** in excellent match with the positioning of the pyrene-based $^1\pi\pi^*$ absorption band. Representative voltammograms of all complexes are compiled in Figures S50 to S54 of the Supporting Information. Worthy of note and reassuring our above assignment is that the peak current of the reductive wave in the dinuclear complex **BPtSPyrSPtB** is twice that of the anodic oxidation. The computed HOMO of the corresponding dianion is consequently localized on the two bodipy ligands without any contributions of the bridging pyrene-1,6-dithiolate ligand.

As a consequence of the only minor, inductive influence of BDP peralkylation on the half-wave potential of the oxidation and a considerably larger effect on that for the BDP-centred reduction,

the half-wave potential difference $\Delta E_{1/2}$ for these processes increases by almost 300 mV (Table 4). This explains the large blue-shift of the CT absorption band and renders formation of the charge separated, excited state for **KBPtSPyr** energetically less favorable.

Table S12. Electrochemical Data for **BPtI**, **KBPtI**, **MesPtSPyr**, **BPtSPyr**, **KBPtSPyr**, and **BPtSPyrSPtB**[a]

complex	$E_{1/2}$ / mV (anodic sweep)	$E_{1/2}$ / mV (cathodic sweep)	$\Delta E_{1/2}$ / mV
BPtI	-	-1930	
KBPtI	-	-2300	
MesPtSPyr	30		
BPtSPy[b]	180	-1970	2150
KBPtSPyr	130	-2310	2440
BPtSPyrSPtB	-60	-1980	1920

[a]All potentials are referenced to the $Cp_2Fe^{0/+}$ couple ($E_{1/2}$ =0.000 V) and were measured in THF at 293 K with NBu_4PF_6 as the supporting electrolyte. [b]Data from ref. 2.

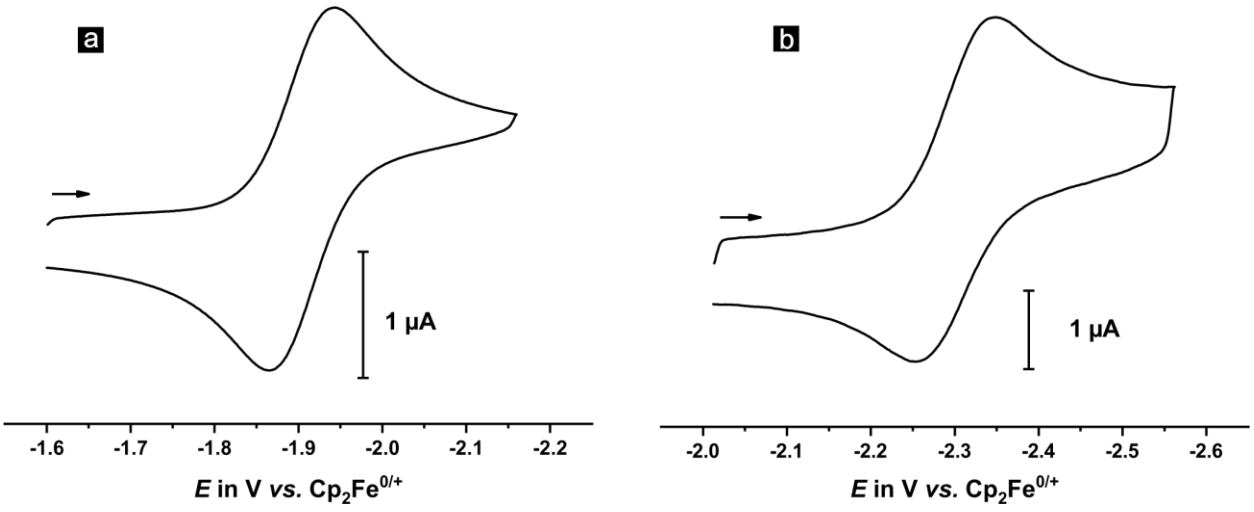

Figure S29. Cyclic voltammograms of the cathodic sweep of a) **BPtI** (ν = 200 mV/s) and b) **KBPtI** (ν = 2000 mV/s) in THF at r.t. with NBu_4PF_6 (0.1 M) as the supporting electrolyte referenced to the $Cp_2Fe^{0/+}$ couple ($E_{1/2}$ = 0.000 V).

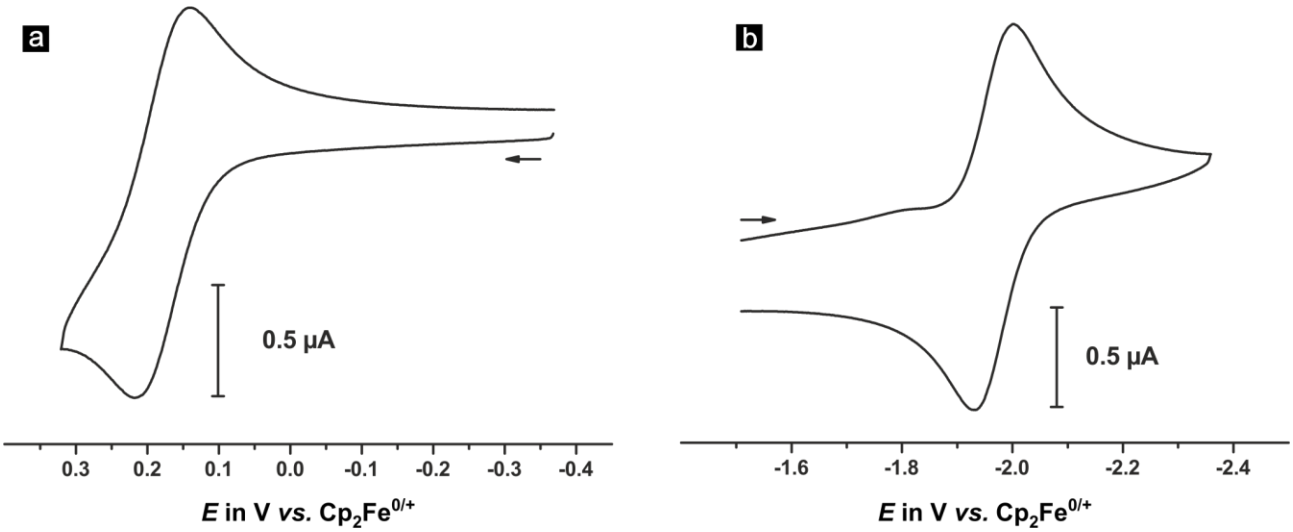

Figure S30. Cyclic voltammograms (ν = 100 mV/s) of a) the anodic and b) the cathodic sweep of **BPtSPyr** in THF at r.t. with NBu_4PF_6 (0.1 M) as the supporting electrolyte referenced to the $Cp_2Fe^{0/+}$ couple ($E_{1/2}$ =0.000 V).

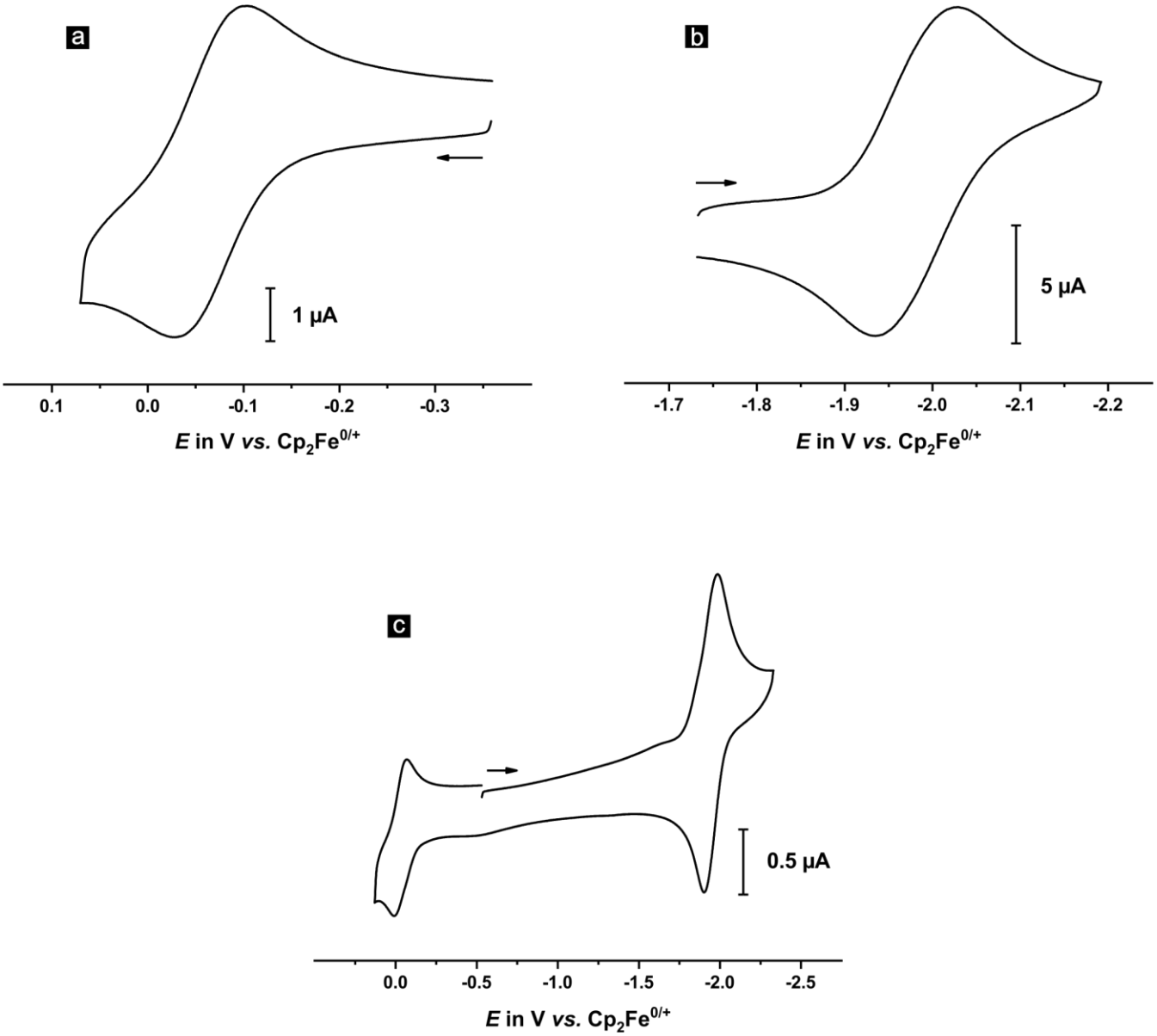

Figure S31. Cyclic voltammograms (ν = 100 mV/s) of a) the anodic and b) the cathodic sweep of **BPtSPyrSPtB** in THF at r.t. with NBu_4PF_6 (0.1 M) as the supporting electrolyte referenced to the $Cp_2Fe^{0/+}$ couple ($E_{1/2}$ =0.000 V) as well as c) the full sweep in the anodic and cathodic directions.

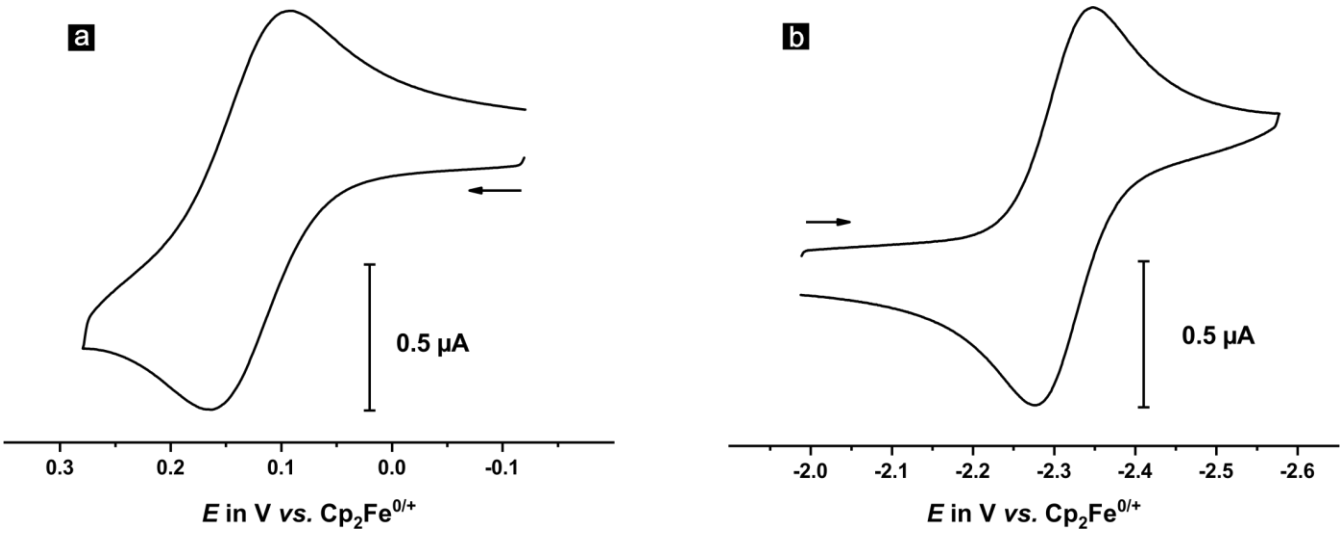

Figure S32. Cyclic voltammograms (ν = 100 mV/s) of a) the anodic and b) the cathodic sweep of **KBPtSPyr** in THF at r.t. with NBu_4PF_6 (0.1 M) as the supporting electrolyte referenced to the $Cp_2Fe^{0/+}$ couple ($E_{1/2}$ =0.000 V).

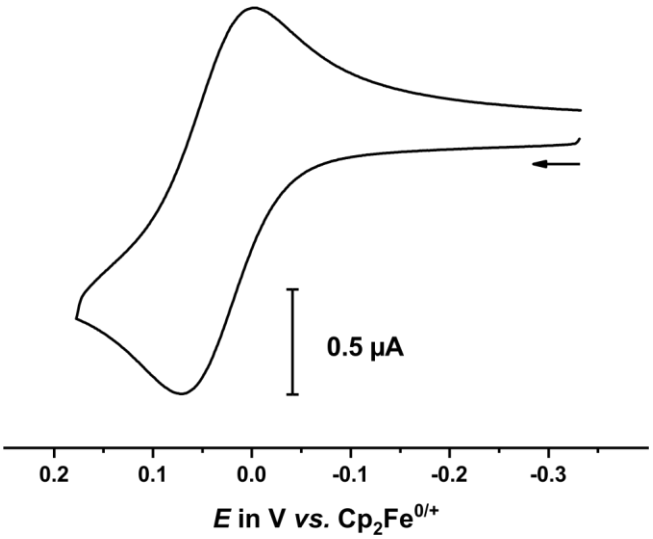

Figure S33. Cyclic voltammogram (ν = 2000 mV/s) of the anodic sweep of **MesPtSPyr** in THF at r.t. with NBu_4PF_6 (0.1 M) as the supporting electrolyte referenced to the $Cp_2Fe^{0/+}$ couple ($E_{1/2}$ = 0.000 V).

Electronic Absorption Spectroscopy

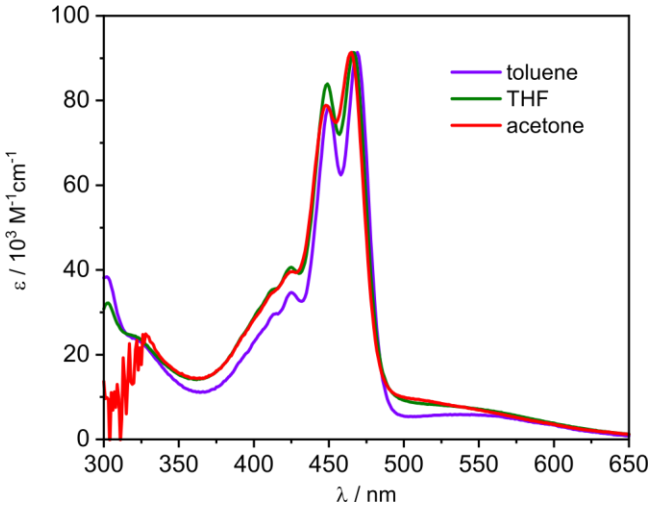

Figure S34. Electronic absorption spectra of **BPtSPyrSPyr** in different solvents. Due to the low solubility of the compound in acetone and toluene the respective spectra were normalized to that in THF.

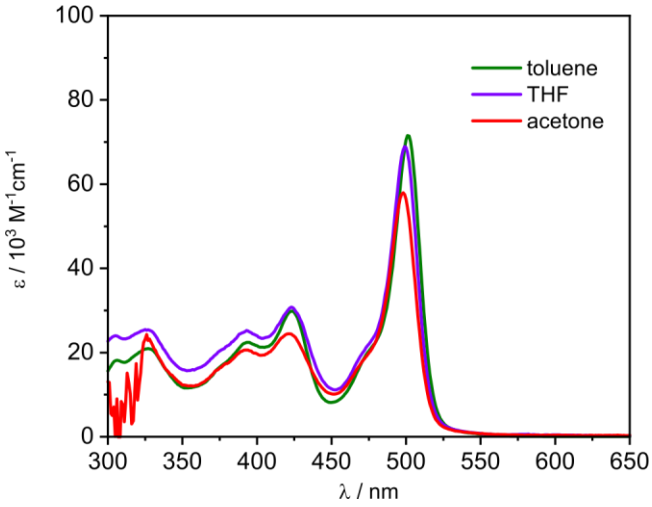

Figure S35. Electronic absorption spectra of **KBPtSPyr** in different solvents.

Luminescence Spectroscopy

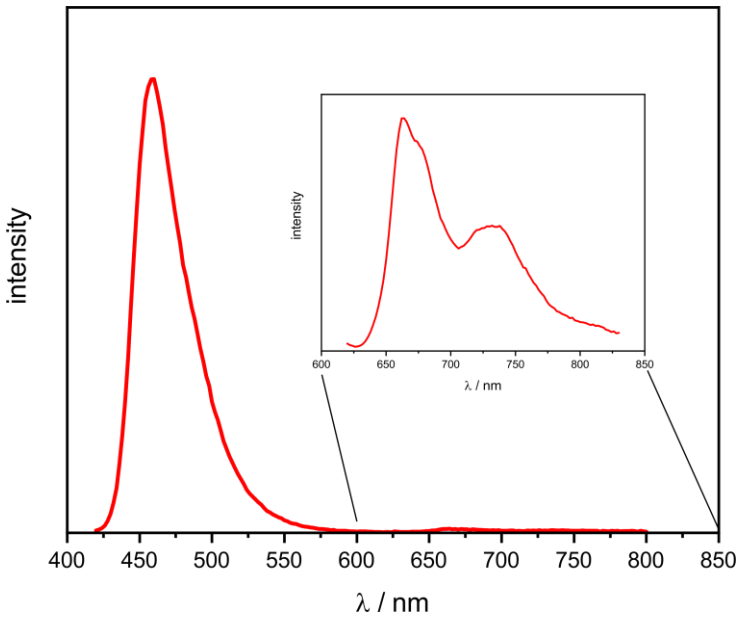

Figure S36. Emission of **MesPtSPyr** in a ca 1 μM degassed toluene solution at r.t.

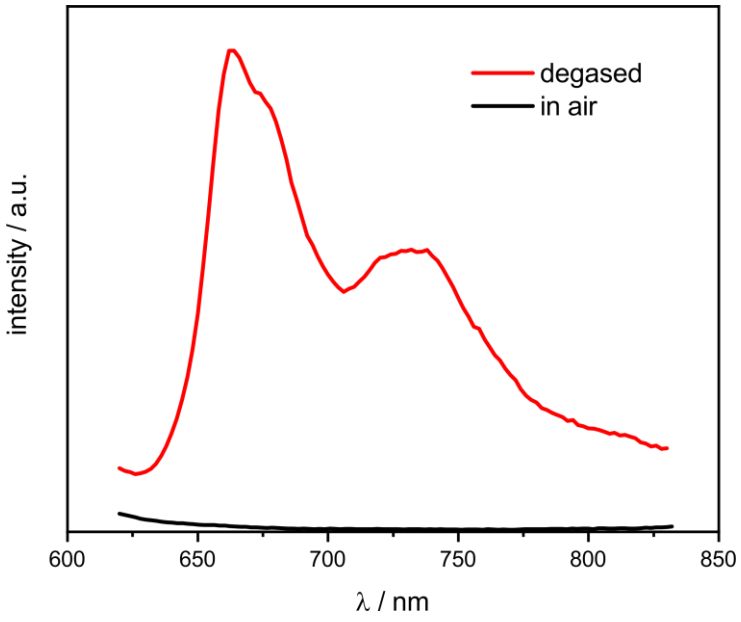

Figure S37. Phosphorescence emission of **MesPtSPyr** in a ca 1 μM toluene solution at r.t.

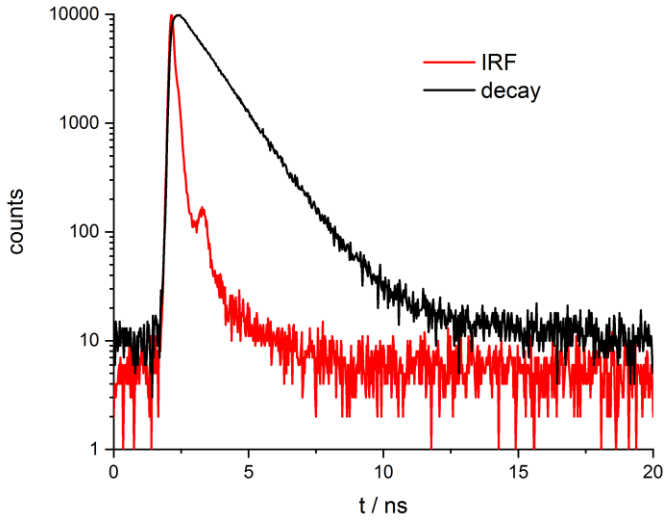

Figure S38. Fluorescence decay traces of **MesPtSPyr** in a deaerated and nitrogen-saturated 1 μM toluene solution at r.t. Decay can be fitted as a monoexponential decay with a lifetime of 1.113 ± 0.005 ns.

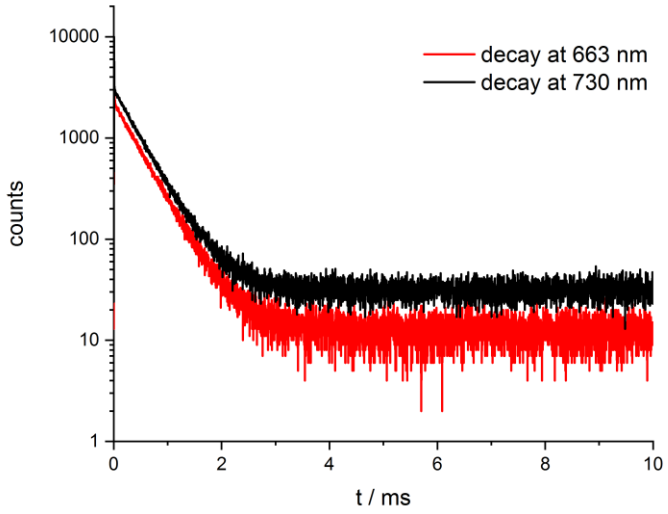

Figure S39. Phosphorescence decay traces of **MesPtSPyr** in a deaerated and nitrogen-saturated 1 μM toluene solution at r.t. Decay can be fitted as a monoexponential decay with a lifetime of 448 ± 6 μs.

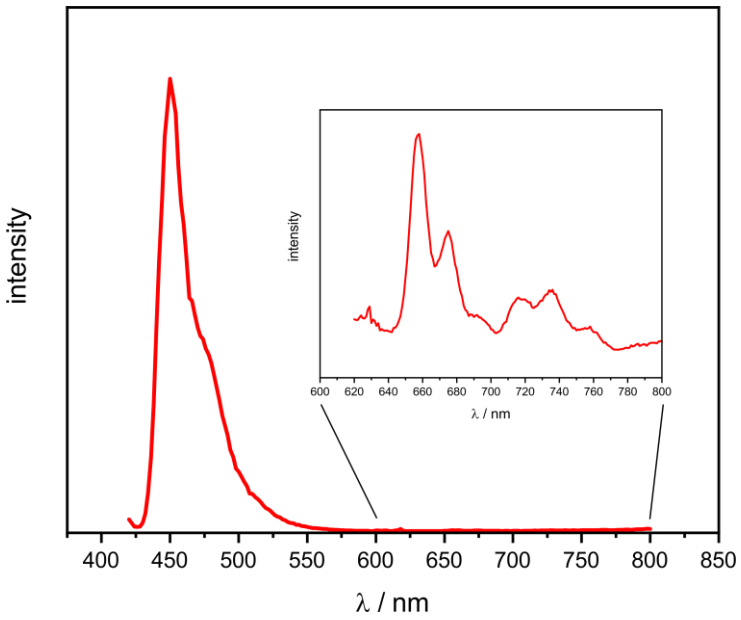

Figure S40. Emission of **MesPtSPyr** in a 2-MeTHF matrix at 77K.

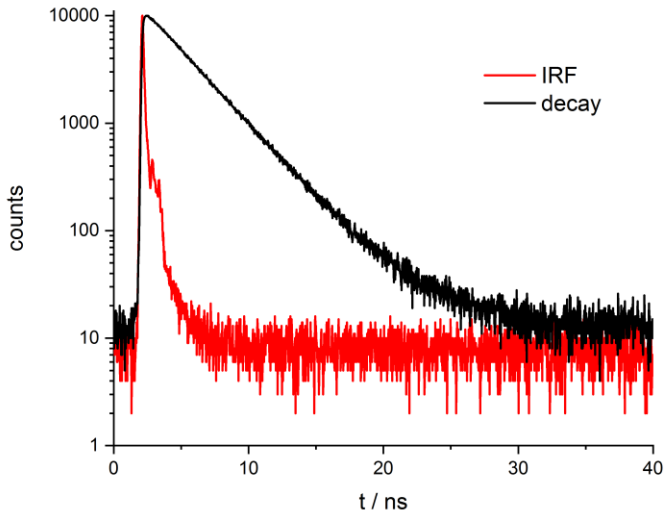

Figure S41. Fluorescence decay traces of **MesPtSPyr** in a 2-MeTHF matrix at 77 K. Decay can be fitted with a monoexponential decay with a lifetime of 3.19 ± 0.03 ns.

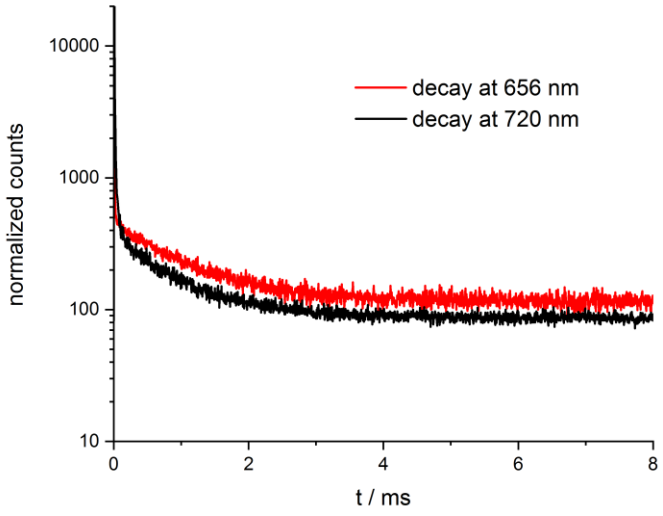

Figure S42. Phosphorescence decay traces of **MesPtSPyr** in a 2-MeTHF matrix at 77 K. Decay can be fitted with a monoexponential decay and a lifetime of 1.04 ± 0.06 ms.

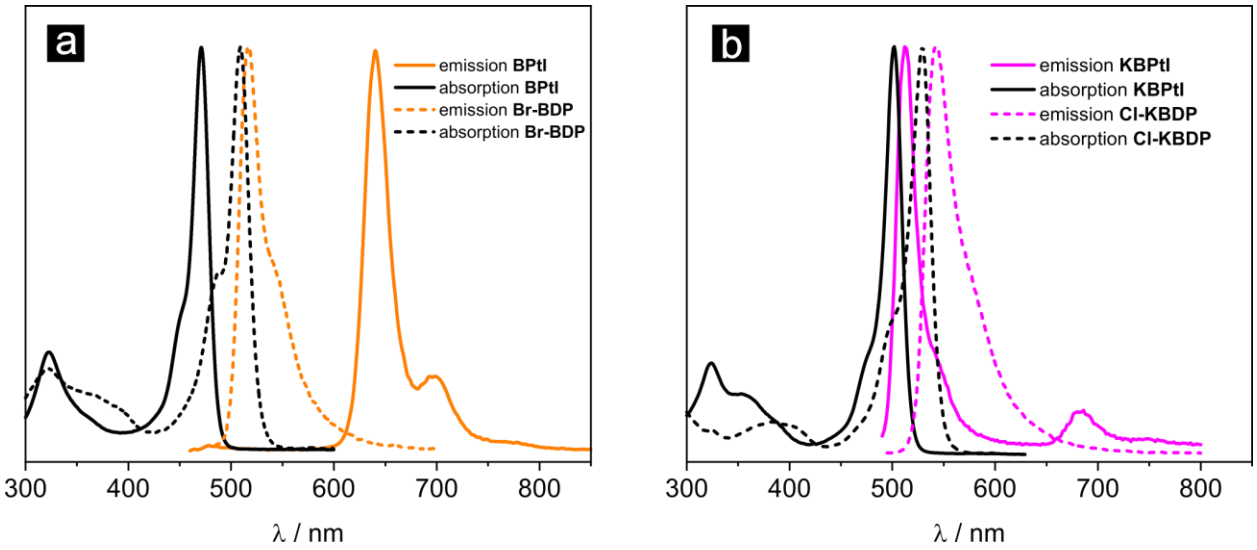

Figure S43. Absorption and emission spectra of a) **Br-BDP** and **BPtI** in CH_2Cl_2 solution at r.t. as well as b) of **Cl-KBDP** and **KBPtI** in toluene solution at r.t.

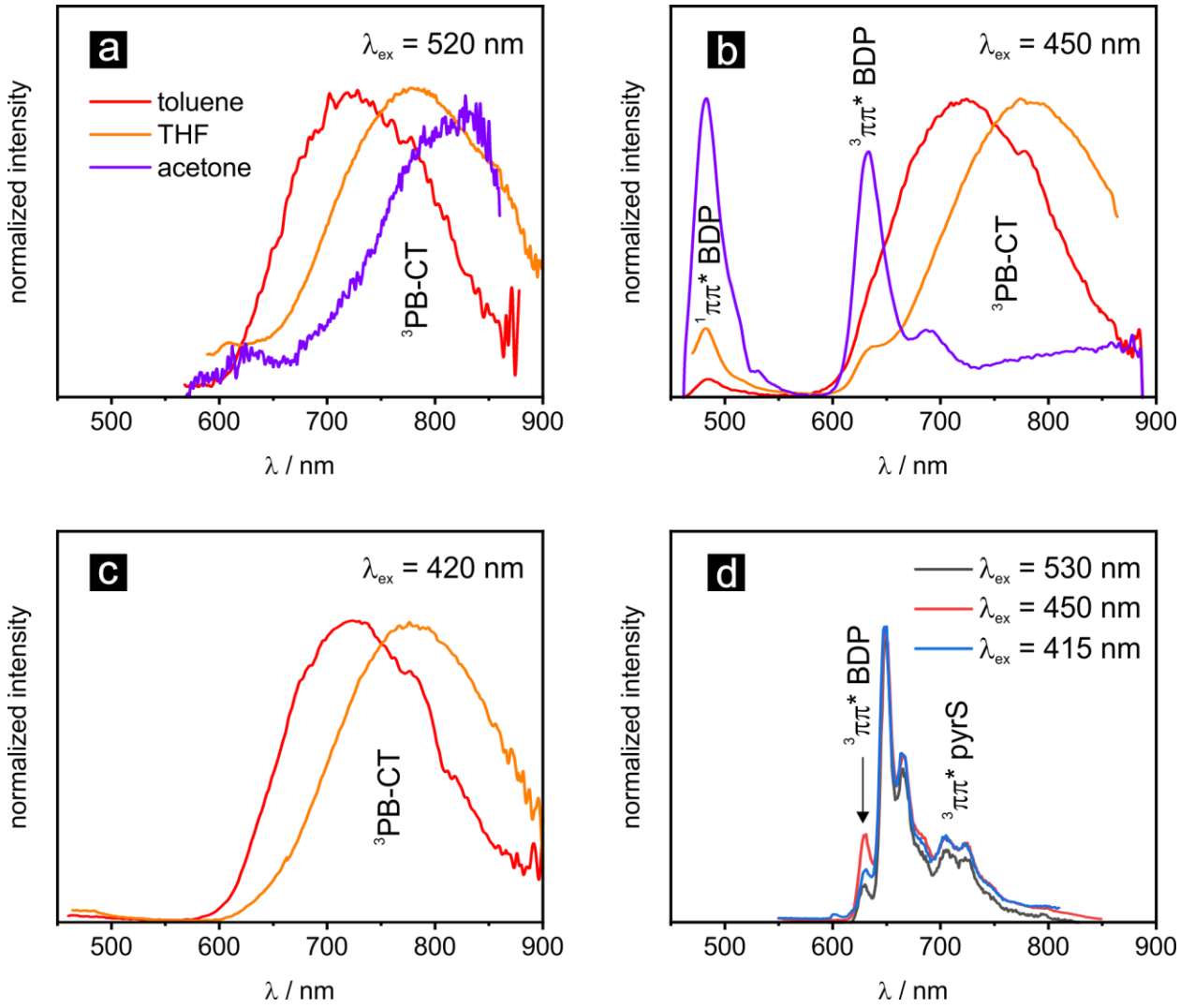

Figure S44. Emission spectra of **BPtSPyr** in *ca.* 1 μM solutions of acetone, THF or toluene at r.t. on excitation at a) 520 nm, b) 450 nm and c) 420 nm. d) Emission spectra recorded in 2-MeTHF at 77 K at different excitation wavelengths.

Table S13. Emission data of BPtI, KBPtI, MesPtSPyr, BPtSPyr, KBPtSPyr and BPtSPyrSPtB

solvent	λ_{exc}[a]	λ_{fl}[b] (assignment)	Φ_{fl}[c]	τ_{fl}[d]	λ_{ph}[b] (assignment)	Φ_{ph}[c]	τ_{ph}[d]
				BPtI *from ref.* 3			
CH_2Cl_2	467	481 (^{1}BDP)	0.002	0.48 ± 0.02 ns	641	0.364	297 ± 2 µs
				KBPtI			
toluene	485	512	0.10	0.959 ± 0.007 ns	684	0.04	239 ± 2 µs
Me-THF[e]	485	506	n.d.	1.171 ± 0.007 ns	673	n.d.	436 ± 2 µs
				MesPtSPyr *from ref.* 4			
toluene	430	460 (^{1} pyrS)	0.24	1.113 ± 0.005 ns	664 (^{3}pyrS)	<0.01	448 ± 6 µs
Me-THF[e]	430	450 (^{1} pyrS)			658 (^{3}pyrS)	n.d.	1.04 ± 0.06 ms
				BPtSPyr *from ref.* 4			
toluene	520				724 (^{3}PB-CT)	0.08	6.7 ± 0.4 µs
	470	484 (^{1}BDP)			724 (^{3}PB-CT)	0.15	6.7 ± 0.5 µs
	420				724 (^{3}PB-CT)	0.15	6.4 ± 0.3 µs
THF	520				784 (^{3}PB-CT)	n.d.	n.d.
	470	484 (^{1}BDP)		3.70 ± 0.2 ns	635 (^{3}BDP) 784 (^{3}PB-CT)	n.d.	78.0 ± 0.4 µs, 51.4 ± 0.8 ns
	420				784 (^{3}PB-CT)	n.d.	50.4 ± 0.3 ns
acetone	520				816 (^{3}PB-CT)	n.d.	n.d.
	470	484 (^{1}BDP)			635 (^{3}BDP) 816 (^{3}PB-CT)	n.d.	49.9 ± 0.3 µs 2.44 ± 0.02 ns
Me-THF[e]	530 450 415	n.o.			635 (^{3}BDP) 649 (^{3}pyrS)	n.d.	279 ± 1 µs 1.12 ± 0.02 ms
				KBPtSPyr			
toluene	485	512 (^{1}BDP)	<0.01	4.42 ± 0.07 ns	682 (^{3}BDP)	0.03	204 ± 1 µs
	405	n.o.			682 (^{3}BDP)	0.05	203.7 ± 0.9 µs
THF	485	510 (^{1}BDP)	n.d.	2.14 ± 0.07 ns	682 (^{3}BDP)	n.d.	273 ± 1 µs
Me-THF[e]	485	510 (^{1}BDP)	n.d.	2.34 ± 0.05 ns	674 (^{3}BDP)	n.d.	423 ± 2 µs
				BPtSPyrSPtB			
toluene	550				770 (^{3}PB-CT)	<0.01	32 ± 5 µs
	460	482 (^{1}BDP)	<0.01		635 (^{3}BDP) 760 (^{3}PB-CT)	0.01	178 ± 1 µs 31 ± 2 µs
	420	482 (^{1}BDP)	<0.01	5.0 ± 0.2 ns	653 (^{3}BDP) 760 (^{3}PB-CT)	<0.01	164 ± 12 µs 31 ± 1 µs
o-$C_6F_2H_4$	530	no emission observed			no emission observed		
	450	480 (^{1}BDP)	n.d.	n.d.	634 (^{3}BDP)	n.d.	82 ± 6 µs
Me-THF[e]	550				696 (^{3}pyrS)	n.d.	369 ± 6 µs
	460	480 (^{1}BDP)	n.d.	n.d.	626 (^{3}BDP) 696 (^{3}pyrS)	n.d.	499 ± 6 µs 369 ± 3 µs
	420	480 (^{1}BDP)	n.d.	4.1 ± 0.1 ns	626 (^{3}BDP) 696(^{3}pyrS)	n.d.	479 ± 12 µs 348 ± 2 µs

[a]Excitation wavelength in nm. [b]Wavelength of the fluorescence (fl) or phosphorescence (ph) emissions in nm. [c]Fluorescence (fl) or phosphorescence (ph) quantum yield. [d]Lifetime of the fluorescence (fl) or phosphorescence (ph) emissions. [e]Measured in a 2-MeTHF glass at 77 K.

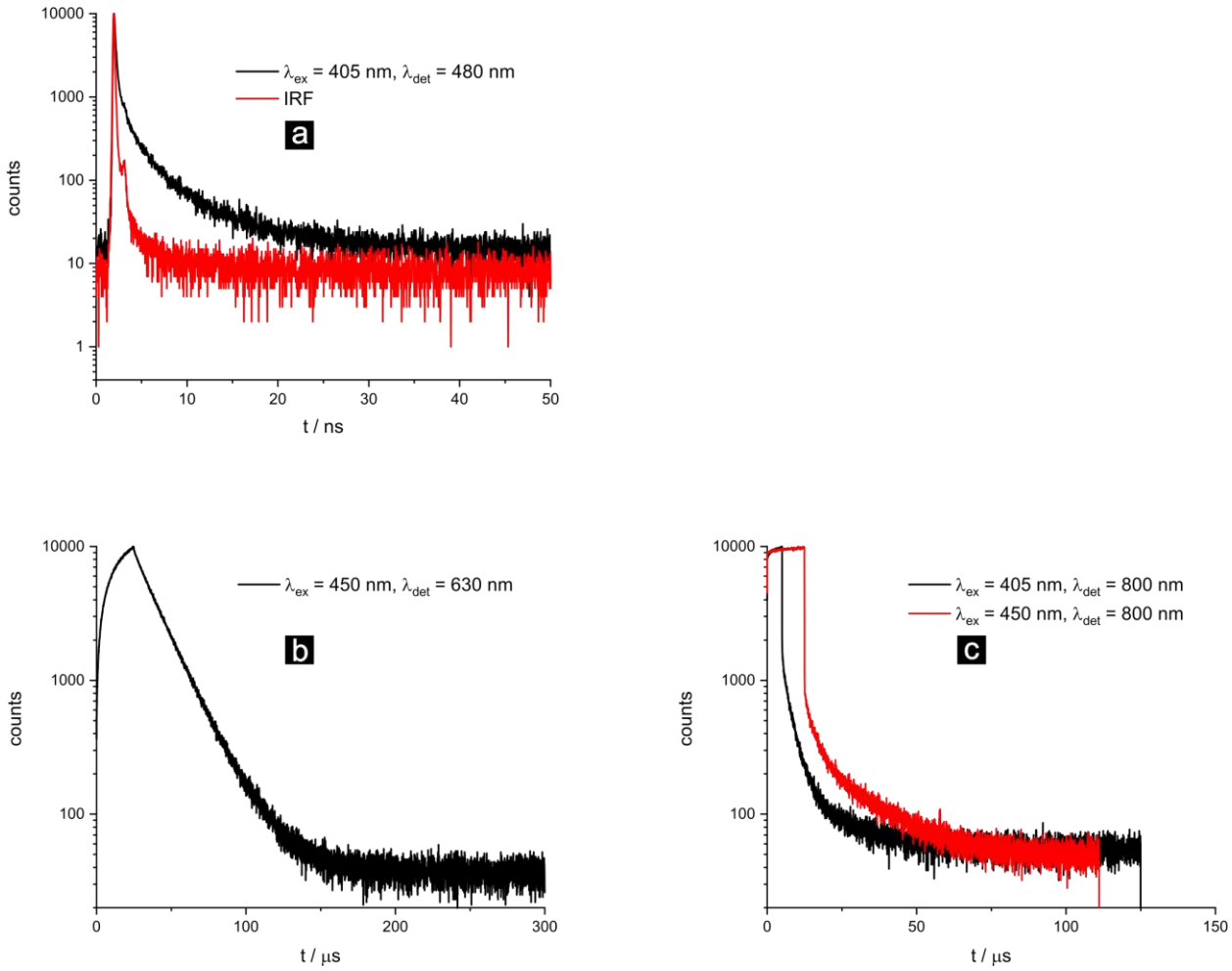

Figure S45. Emission decay traces of **BPtSPyrSPtB** in a deaerated and nitrogen-saturated 1 µM toluene solution at r.t.; a) shows the fluorescence lifetime decay with 5.0 ns; b) depicts the 178 µs component; c) depicts the 32 µs component. The rise times of 49 µs in Figure S45b and 10 or 30 µs in c) are due to foregoing excited state saturation in the "burst mode".

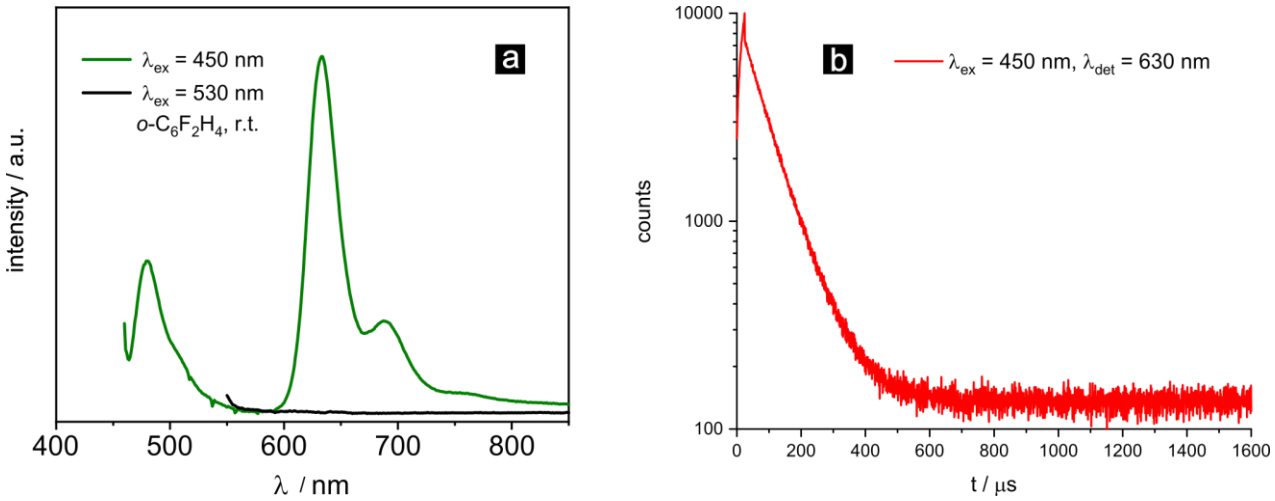

Figure S46. a) Emission spectra and b) emission decay trace of **BPtSPyrSPtB** in a ca. 1 µM o-difluorobenzene solution at r.t. (82 µs).

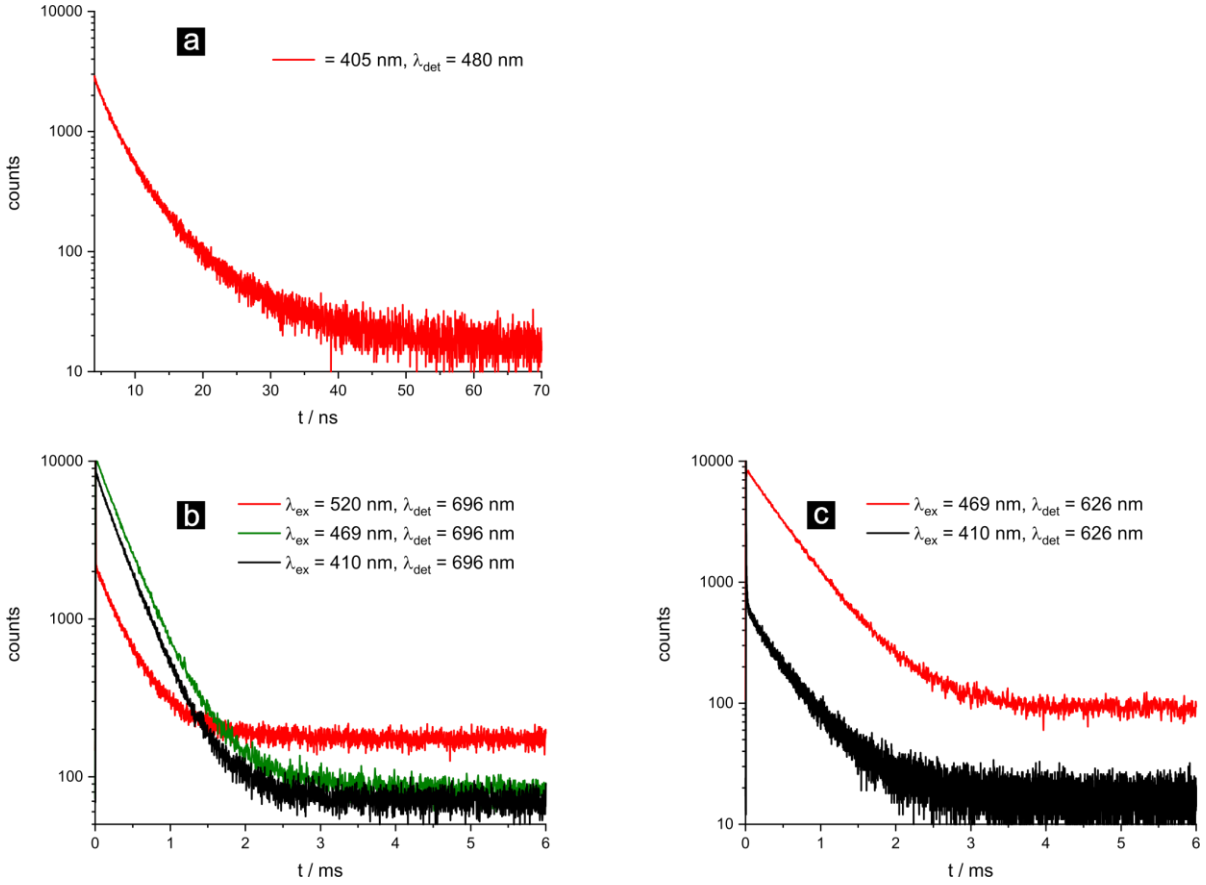

Figure S47. Emission decay traces of **BPtSPyrSPtB** in a 1 µM 2-MeTHF matrix at 77 K a) depicting the 4.1 ns component, b) depicting the 369 µs component and c) showing the 499 µs component.

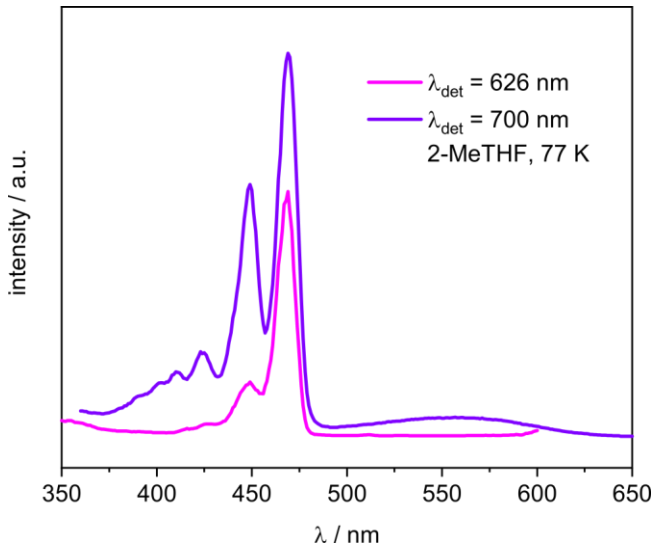

Figure S48. Excitation spectra of **BPtSPyrSPtB** recorded on a 1 mM 2-MeTHF matrix at 77 K.

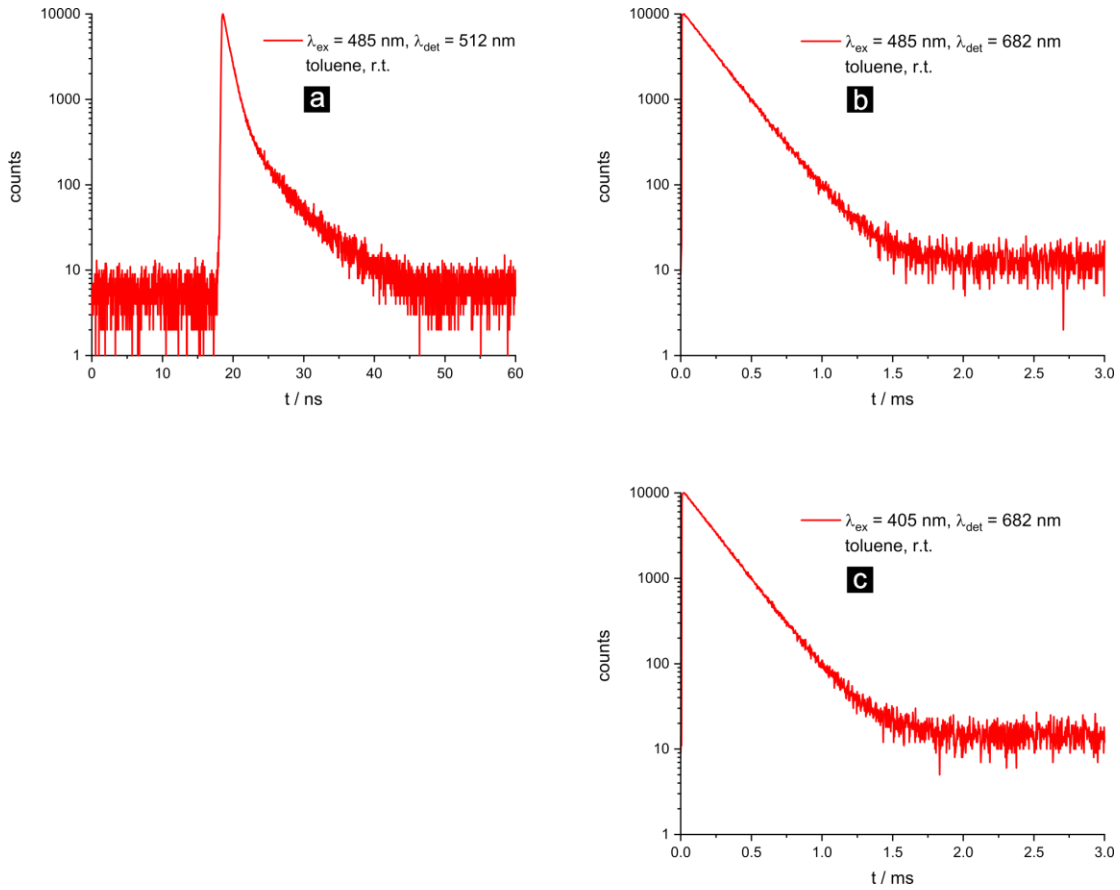

Figure S49. Emission decay traces of **KBPtSPyr** in a deaerated and nitrogen-saturated 1 µM toluene solution at r.t. a) depicting the 4.4 ns component, b) depicting the 204 µs component and c) showing the 204 µs component.

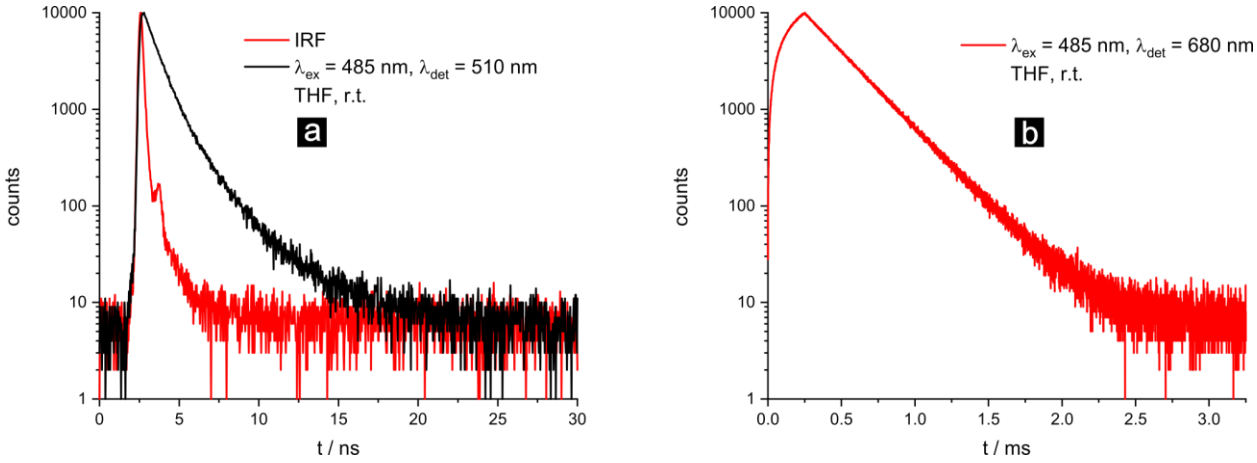

Figure S50. Emission decay traces of **KBPtSPyr** in a deaerated and nitrogen-saturated 1 µM THF solution at r.t. The rise time of 500 µs in Figure S50b is due to prior excited state saturation in the "burst mode". a) depicts the 2.1 ns component and b) shows the 273 µs component.

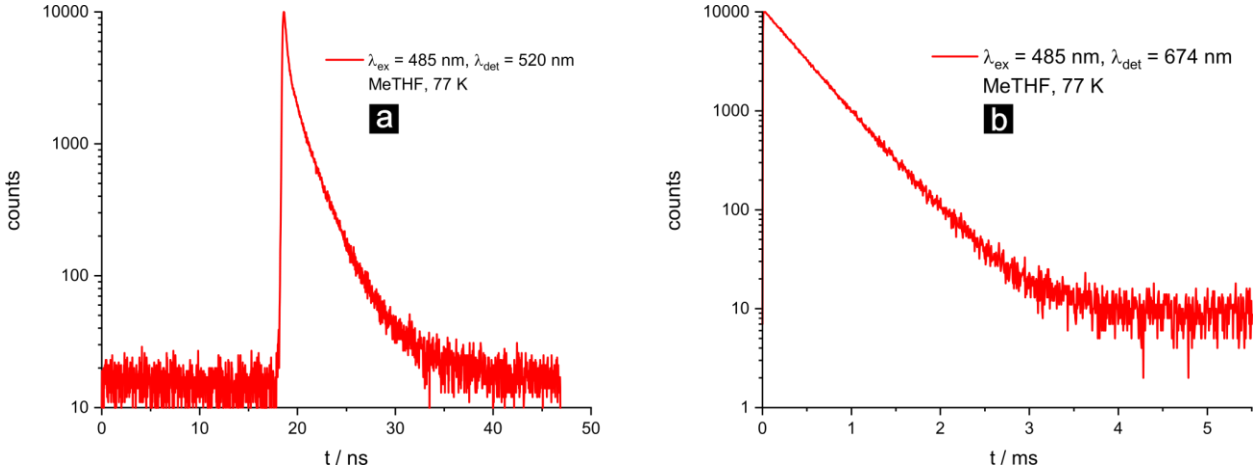

Figure S51. Emission decay traces of **KBPtSPyr** in a 1 µM 2-MeTHF matrix at 77 K a) depicting the 2.3 ns component and b) showing the 423 µs component.

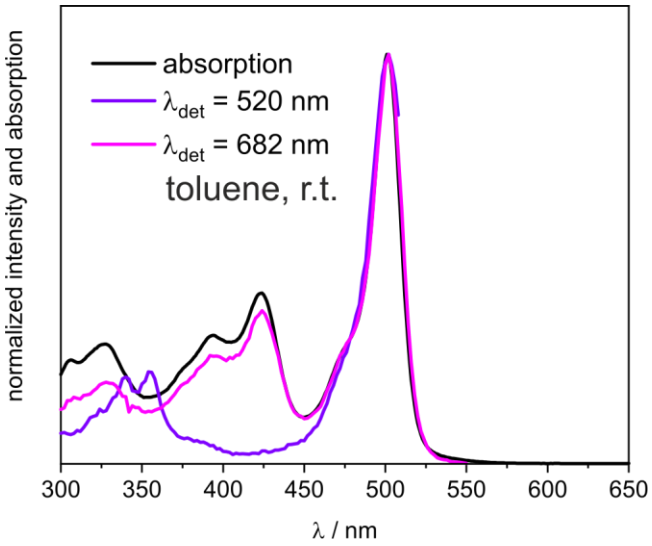

Figure S52. Comparison of the excitation spectra of **KBPtSPyr** recorded at 682 nm and 520 nm with the UV/Vis spectrum for a 1 μM toluene solution at r.t.

Table S14. Singlet Oxygen Generation Quantum Yield Φ_Δ Compared to Tetraphenylporphyrin (**TPP**) as Reference Sensitizer

sensitizer	λ_{ex} / nm	Φ_Δ[b]
TPP[a]	525	0.66 ± 0.08
	470	0.66 ± 0.08
	410	0.66 ± 0.08
BPtI	470	0.94 ± 0.11
KBPtI	470	0.65 ± 0.08
MesPtSPyr	410	0.28 ± 0.03
BPtSPyr	525	0.74 ± 0.09
	470	0.75 ± 0.09
	410	0.33 ± 0.04
KBPtSPyr	470	0.74 ± 0.09
	410	0.40 ± 0.05
BPtSPyrSPtB	525	0.11 ± 0.01
	470	0.18 ± 0.02
	410	0.07 ± 0.01

[a]Value from reference [5]. [b]Standard deviations were calculated by error propagation.

Electronic Absorption Spectroscopy and Quantum Chemical Calculations on the Oxidized and Reduced Forms

Table S15. Absorption Data for the Oxidized and Reduced Forms of BPtSPyr, KBPtSPyr, and BPtSPyrSPtB as well as TD-DFT-Calculated Band Energies and Assignments

absorption data		TD-DFT calculations[a]			
solvent	λ_{max}[b] (ε[c])	λ[b]	f[d]	m.c.[e]	assignment
radical cation of BPtSPyr					
THF[f]	322 (23), 474 (49), 518 (18), 556 (21), 755 (2), 920 (5), 1020 (9)	397	0.36	H(α) → L(α) (41%), H(β) → L+1(β) (47%)	$\pi\pi$* BDP with some BP-CT contribution
		502	0.43	H-1(α) → L(α) (20%), H-1(α) → L+1(α) (29%), H-8(β) → L(β) (14%)	$\pi\pi$* pyrS and $\pi\pi$* BDP with some PB-CT contribution
		865	0.19	H-1(β) → L(β) (92%)	$\pi\pi$* pyrS
radical anion of BPtSPyr					
THF[f]	347 (20), 395 (19), 441 (26), 519 (5)	420	0.63	H(α) → L+11(α) (12%) H-1(β) → L+1(β) (77%)	$\pi\pi$* pyrS
		432	0.06	H-1(α) → L (α) (47%), H(β) → L(β) (48%)	$\pi\pi$* BDP
radical cation of KBPtSPyr					
THF[f]	323 (24), 507 (77), 555 (26), 717 (3), 898 (6), 1008 (13)	n.d.	n.d.	n.d.	n.d.
radical anion of KBPtSPyr					
CH_2Cl_2[f]	401 (23), 437 (30), 498 (7)	n.d.	n.d.	n.d.	n.d.
radical cation of BPtSPyrSPtB					
THF[f]	319 (29), 452 (48), 470 (79), 527 (8), 600 (12), 666 (26), 1181 (6), 1383 (14)	n.d.	n.d.	n.d.	n.d.
radical anion of BPtSPyrSPtB					
CH_2Cl_2[f]	394 (41), 421 (46), 464 (66)	n.d.	n.d.	n.d.	n.d.

[a]DFT calculations on the pbe1pbe/6-31G(d) level of therory; PCM model for CH_2Cl_2. [b]λ in nm. [c]$\varepsilon \cdot 10^3$ M^{-1} cm^{-1}. [d]f = oscillator strength. [e]m.c. = major contribution. H refers to HOSO and L to LUSO. [f]With 0.1 M NBu_4PF_6 as the supporting electrolyte.

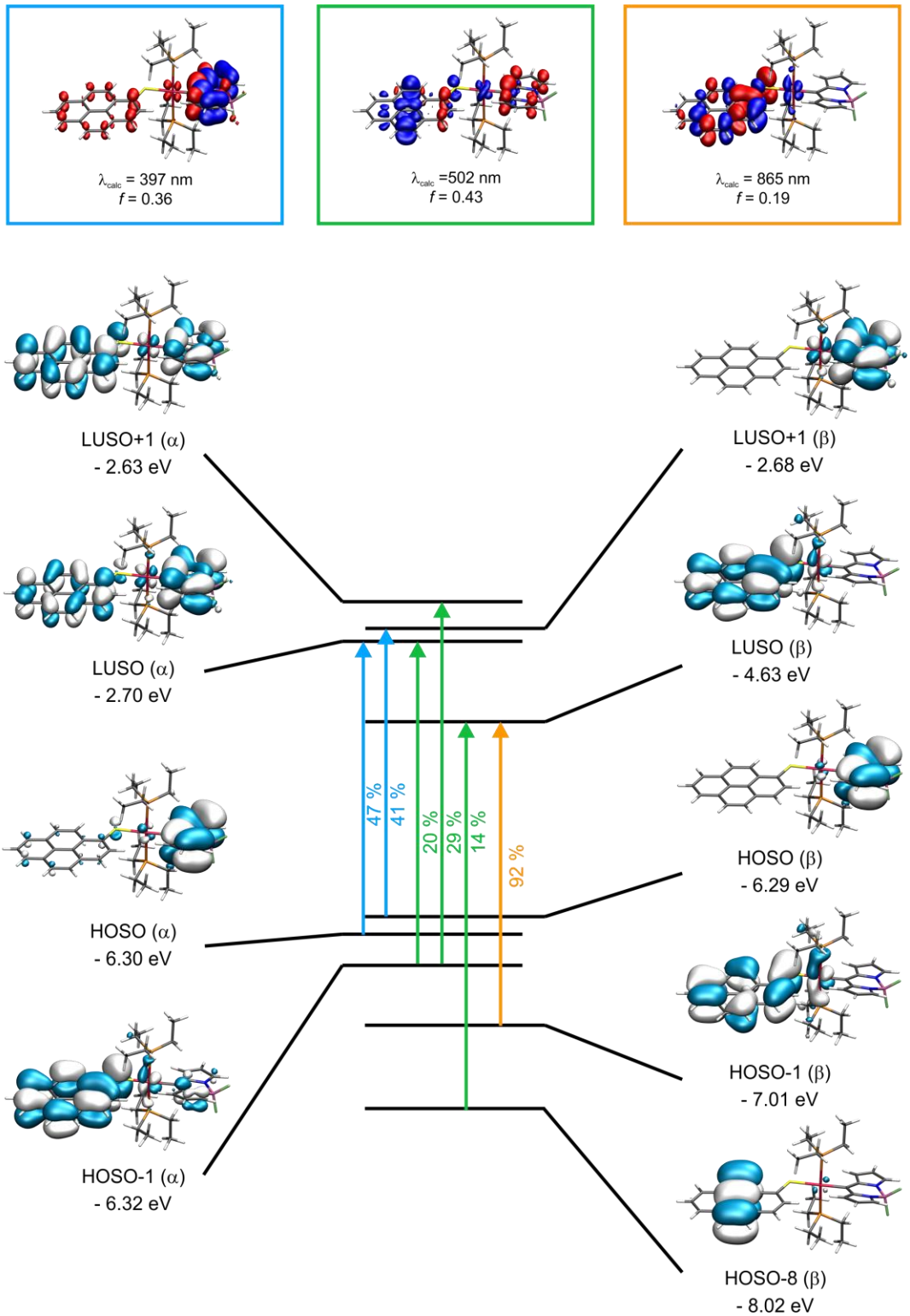

Figure S53. Graphical representations of the relevant spin orbitals and TD-DFT energies of **BPtSPyr** in the cationic form as well as electron density difference maps (*blue* = electron density loss, *red* = electron density gain).

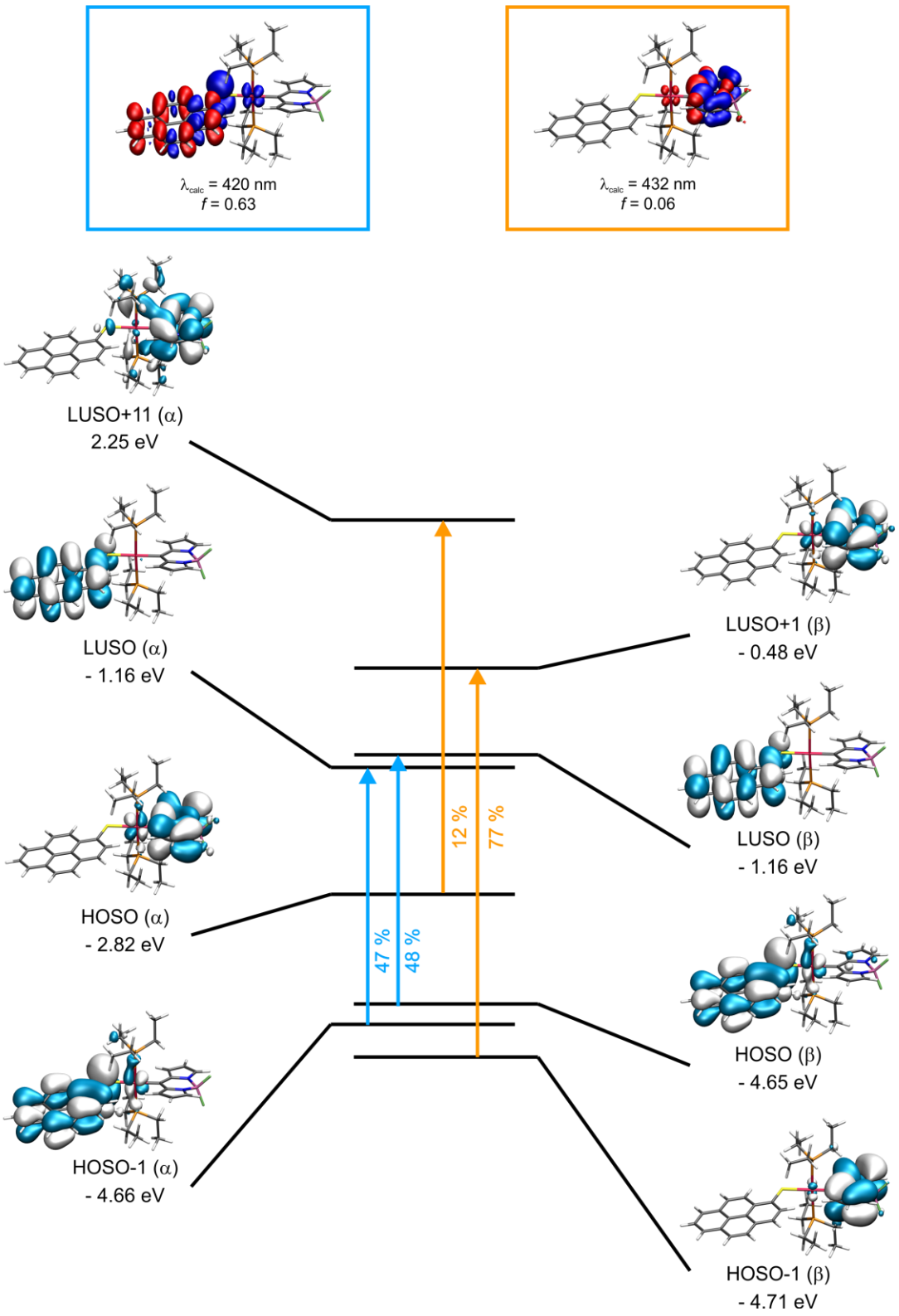

Figure S54. Graphical representations of the relevant spin orbitals and TD-DFT energies of **BPtSPyr** in the anionic form as well as electron density difference maps (*blue* = electron density loss, *red* = electron density gain).

Transient Absorption Spectroscopy

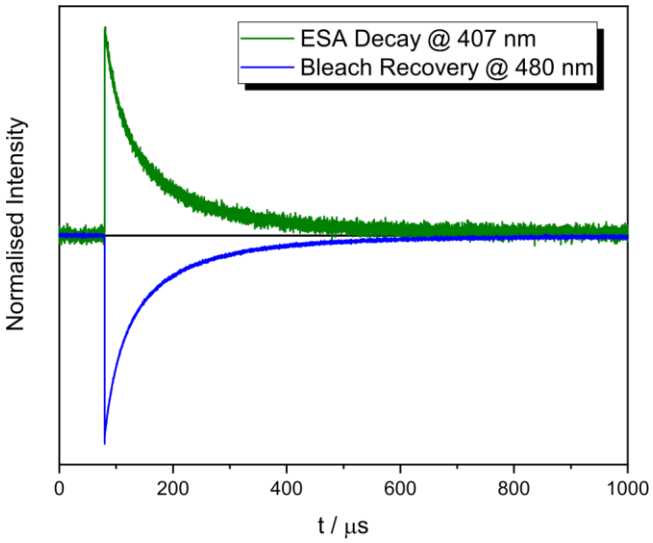

Figure S55. Single wavelength kinetics of **BPtI** recorded in 20 µM THF solution at r.t. after laser excitation at 470 nm for the different features of the transient absorption spectrum. Exponential decays can be fitted with a biexponential model with time constants of τ_1 = 30.2 µs and τ_2 = 149 µs.

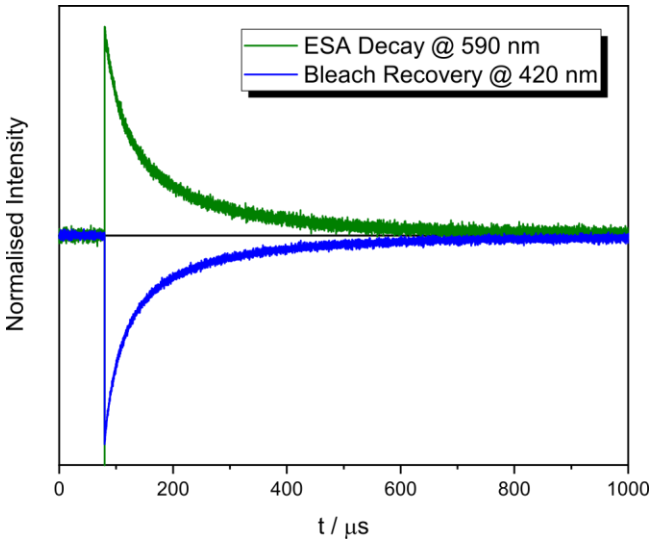

Figure S56. Single wavelength kinetics of **MesPtSPyr** recorded in 20 µM THF solution at r.t. after laser excitation at 430 nm for the different features of the transient absorption spectrum. Exponential decays can be fitted with a biexponential model with time constants of τ_1 = 34.7 µs and τ_2 = 174 µs.

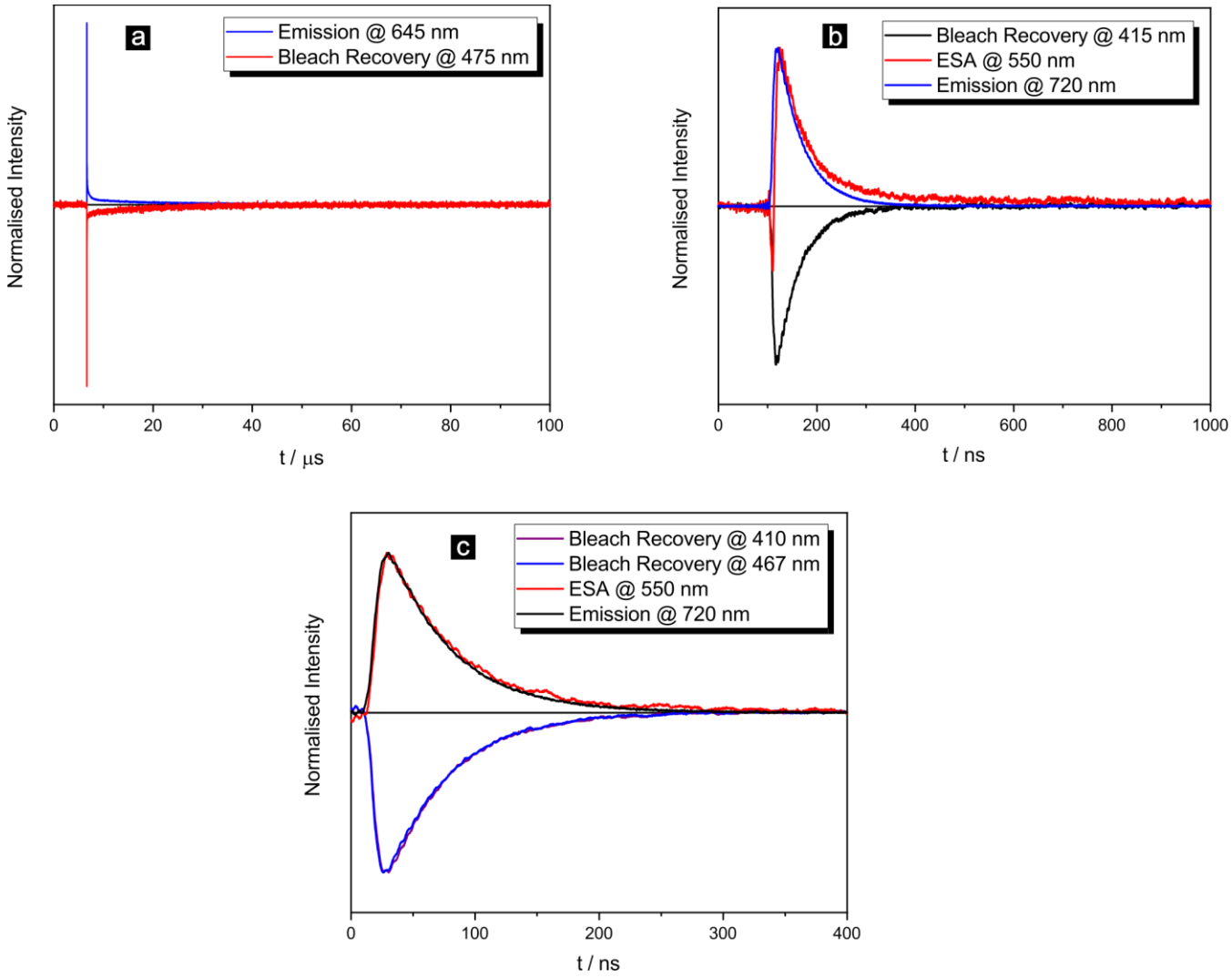

Figure S57. Single wavelength kinetics of **BPtSPyr** recorded in 20 µM THF solution at r.t. after laser excitation at a) 410 nm, b) 470 nm, or c) 532 nm for the different features of the transient absorption spectrum. The exponential decays can be fitted with a lifetime of 16.5 µs for a) and 50 ns for b) and c).

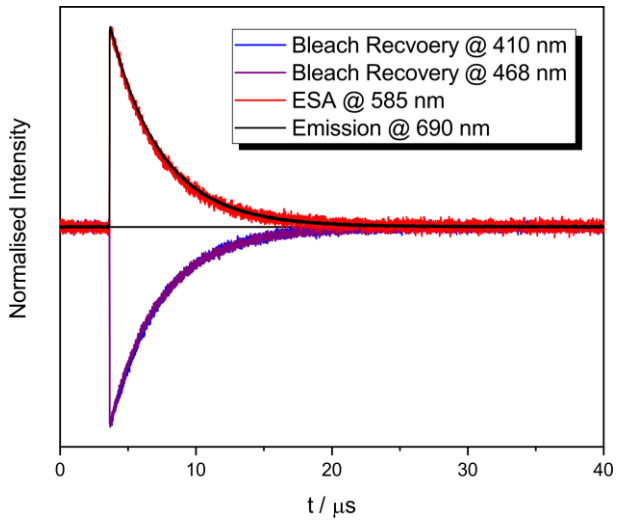

Figure S58. Single wavelength kinetics of **BPtSPyr** recorded in 20 µM toluene solution at r.t. after laser excitation at 532 nm for the different features of the transient absorption spectrum. The mono exponential decays can be fitted with a lifetime of 3.6 µs.

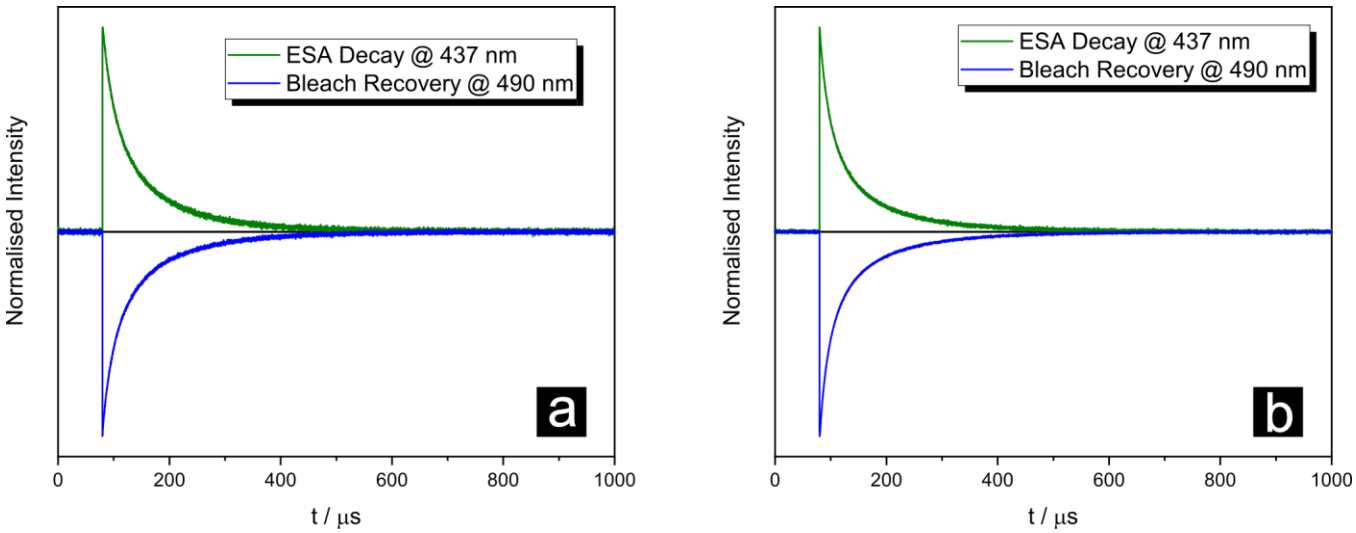

Figure S59. Single wavelength kinetics of **KBPtSPyr** recorded in 20 µM THF solution at r.t. after laser excitation at a) 420 nm and b) 500 nm for the different features of the transient absorption spectrum. Exponential decays can be fitted with a biexponential model with time constants of τ_1 = 25.0 µs and τ_2 = 104.6 µs for a) as well as τ_1 = 23.8 µs and τ_2 = 109.4 µs for b).

Molecular Structures Obtained by Quantum Chemical Calculations

Table S16. Atomic coordinates of the optimized ground state geometry of BPtSPyrSPtB in the neutral form

Atom	x	y	z
Pt	6.49556	0.14968	-0.49673
Pt	-6.49558	0.14969	0.49674
B	10.88273	-1.17254	1.63173
F	10.98538	-2.53431	1.90718
F	12.03966	-0.5154	2.02584
N	10.62253	-0.95724	0.12131
N	9.6482	-0.57878	2.35255
P	5.93046	-2.13228	-0.59855
P	7.0656	2.43209	-0.56242
P	-5.93069	-2.1323	0.59886
P	-7.06539	2.43218	0.56219
C	8.27118	-0.28686	0.34098
C	9.39499	-0.6276	-0.44204
C	9.55189	-0.65526	-1.84481
H	8.76529	-0.43201	-2.55379
C	10.87366	-0.99745	-2.1137
H	11.3466	-1.10161	-3.081
C	11.49631	-1.17749	-0.87076
H	12.51988	-1.45476	-0.65299
C	8.44168	-0.25171	1.74342
C	7.54873	0.14467	2.76301
H	6.52899	0.46844	2.59841
C	8.2257	0.05502	3.97553
H	7.84946	0.29019	4.96204
C	9.51691	-0.39776	3.67435
H	10.34378	-0.59871	4.34361
C	7.28212	-3.30345	-0.1529
H	8.12582	-3.07622	-0.81391
H	7.61448	-3.02726	0.85491
C	6.93268	-4.78698	-0.21778
H	7.80133	-5.3826	0.08277
H	6.6566	-5.09939	-1.22988
H	6.10812	-5.04761	0.45378
C	5.39938	-2.63352	-2.28781
H	5.17618	-3.7071	-2.2682
H	4.4574	-2.10465	-2.46919
C	6.40668	-2.29985	-3.38124
H	6.03778	-2.6443	-4.35328
H	7.37842	-2.77438	-3.20666
H	6.56354	-1.21745	-3.44356
C	4.50314	-2.64332	0.44484
H	3.68883	-1.94993	0.20874
H	4.18689	-3.63995	0.11217
C	4.78836	-2.6396	1.94265
H	3.87649	-2.88251	2.49811
H	5.13566	-1.65887	2.28196
H	5.55056	-3.37712	2.21559
C	8.87192	2.76253	-0.36974
H	9.13005	2.44437	0.64804
H	9.39579	2.07091	-1.03825
C	9.3344	4.1944	-0.62199
H	10.40778	4.27244	-0.41837
H	8.82823	4.9208	0.02208
H	9.17573	4.49737	-1.66201
C	6.30422	3.46499	0.76636
H	6.4002	2.88753	1.69321
H	6.93084	4.35674	0.88618
C	4.85388	3.87517	0.53335
H	4.48561	4.43087	1.40256
H	4.20308	3.00926	0.38549
H	4.75727	4.52763	-0.34012
C	6.60975	3.25186	-2.14198
H	5.52117	3.17775	-2.22647
H	6.86514	4.31565	-2.06484
C	7.27241	2.60853	-3.35546
H	6.98418	1.55492	-3.44063
H	8.36568	2.65667	-3.30356
H	6.9596	3.1185	-4.27266
S	4.3742	0.63959	-1.57842
C	3.08496	0.58787	-0.37513
C	1.72366	0.57844	-0.78702
C	3.36853	0.58407	1.00031
C	0.68764	0.57635	0.19796
C	1.34537	0.56919	-2.16893
C	2.36565	0.57064	1.95571
H	4.41076	0.58734	1.31016
C	-0.68763	0.57626	-0.19796
C	1.01548	0.57177	1.58407
C	0.03905	0.56525	-2.5473
H	2.12942	0.56249	-2.91935
H	2.62664	0.56474	3.01192
C	-1.01547	0.57144	-1.58407
C	-1.72365	0.57843	0.78702
C	-0.03904	0.56566	2.5473
H	-0.22592	0.55626	-3.60238
C	-2.36564	0.57013	-1.95571
C	-3.08495	0.58769	0.37513
C	-1.34536	0.56944	2.16893
H	0.22594	0.55687	3.60239
C	-3.36852	0.58365	-1.00031
H	-2.62663	0.56405	-3.01191
H	-2.12941	0.5628	2.91936
H	-4.41075	0.58678	-1.31017
S	-4.37419	0.63953	1.57841
C	-8.2712	-0.28679	-0.34101
C	-7.28246	-3.30339	0.15332
C	-5.3997	-2.63339	2.28818
C	-4.50339	-2.6436	-0.44445
C	-8.87168	2.76279	0.36955
C	-6.30394	3.46484	-0.76673
C	-6.60939	3.25208	2.14164
C	-9.3951	-0.62728	0.44199
C	-8.44158	-0.25193	-1.74347
H	-8.12615	-3.07599	0.81429
H	-7.61477	-3.02728	-0.85453
C	-6.93319	-4.78695	0.21838
H	-5.17663	-3.70701	2.26869
H	-4.45764	-2.10463	2.46951
C	-6.40696	-2.29948	3.38156
H	-3.68901	-1.95029	-0.20837
H	-4.18728	-3.64025	-0.11168
C	-4.78856	-2.63995	-1.94226
H	-9.1299	2.44452	-0.64817
H	-9.39559	2.07131	1.03819
C	-9.33399	4.19474	0.62163
H	-6.40001	2.88728	-1.69351
H	-6.93047	4.35664	-0.88664
C	-4.85355	3.87489	-0.5338
H	-5.52082	3.17783	2.22611
H	-6.86465	4.31589	2.06438
C	-7.2721	2.60897	3.35521
N	-10.62262	-0.95693	-0.12139

C	-9.5521	-0.65468	1.84475	H	-6.98401	1.55533	3.44049
N	-9.64808	-0.579	-2.35263	H	-8.36537	2.65727	3.30335
C	-7.54849	0.1441	-2.76308	H	-6.95918	3.11901	4.27234
H	-7.8019	-5.38251	-0.0821	B	-10.88273	-1.1725	-1.63178
H	-6.65713	-5.09927	1.23051	C	-11.4965	-1.17689	0.87066
H	-6.10867	-5.04775	-0.45317	H	-8.76553	-0.43138	2.55375
H	-6.03812	-2.64389	4.35364	C	-10.87393	-0.99667	2.11361
H	-7.37876	-2.77389	3.20702	C	-9.51667	-0.39828	-3.67446
H	-6.56367	-1.21705	3.44378	H	-6.52872	0.46776	-2.59846
H	-3.87671	-2.88304	-2.49767	C	-8.22539	0.0543	-3.97563
H	-5.13569	-1.65919	-2.28166	F	-10.9855	-2.53431	-1.90697
H	-5.55087	-3.37737	-2.21518	F	-12.03956	-0.51532	-2.02611
H	-10.40738	4.27287	0.41807	H	-12.52008	-1.4541	0.65286
H	-8.82778	4.921	-0.02258	H	-11.34695	-1.10059	3.08089
H	-9.17523	4.49784	1.6616	H	-10.34351	-0.59927	-4.34374
H	-4.48524	4.43044	-1.40308	H	-7.84904	0.28923	-4.96216
H	-4.20284	3.00893	-0.38583				
H	-4.75687	4.52746	0.33959				

Table S17. Atomic coordinates of the optimized ground state geometry of BPtSPyrSPtB in the mono cationic form

Atom	x	y	z
Pt	-6.51214	0.14825	0.46749
Pt	6.51213	0.14801	-0.46746
B	-10.98114	-1.08606	-1.50195
F	-11.07643	-2.45733	-1.72205
F	-12.14898	-0.44944	-1.88894
N	-10.68055	-0.81448	-0.00653
N	-9.76615	-0.51332	-2.27512
P	-6.08167	-2.17409	0.60274
P	-7.0156	2.45621	0.46323
P	6.08206	-2.17441	-0.6026
P	7.01513	2.45607	-0.46342
C	-8.32259	-0.23006	-0.31779
C	-9.42688	-0.5103	0.51043
C	-9.54087	-0.48939	1.91871
H	-8.72715	-0.26743	2.59777
C	-10.86366	-0.77736	2.2357
H	-11.31137	-0.83378	3.21868
C	-11.52966	-0.97466	1.01653
H	-12.56785	-1.22401	0.83812
C	-8.53012	-0.21359	-1.71323
C	-7.66279	0.14745	-2.76889
H	-6.62989	0.44783	-2.64719
C	-8.38529	0.0649	-3.95406
H	-8.0395	0.28124	-4.95578
C	-9.67742	-0.34999	-3.60168
H	-10.53248	-0.53621	-4.23884
C	-7.53174	-3.26609	0.29481
H	-8.29307	-2.99019	1.03275
H	-7.94579	-2.97683	-0.67812
C	-7.25589	-4.76569	0.3402
H	-8.18404	-5.31187	0.14217
H	-6.88996	-5.08801	1.32013
H	-6.52618	-5.0751	-0.41486
C	-5.45109	-2.66442	2.26184
H	-5.29652	-3.75005	2.25326
H	-4.46315	-2.20088	2.36177
C	-6.3482	-2.24935	3.42209
H	-5.91482	-2.58526	4.36991
H	-7.35064	-2.6835	3.34402
H	-6.45229	-1.1598	3.46744
C	-4.7679	-2.78981	-0.529
H	-3.87897	-2.17904	-0.33666
H	-4.52138	-3.81326	-0.22005
C	-5.13841	-2.747	-2.00722
H	-4.2904	-3.07882	-2.61503
H	-5.40635	-1.73514	-2.32598
H	-5.98591	-3.40187	-2.23457
C	-8.81804	2.83115	0.35702
H	-9.14579	2.47206	-0.62617
H	-9.32213	2.19295	1.09048
C	-9.21745	4.28955	0.56144
H	-10.29911	4.3904	0.42392
H	-8.73503	4.9641	-0.15307
H	-8.98182	4.64078	1.57115
C	-6.29003	3.40757	-0.94207
H	-6.45925	2.80503	-1.84183
H	-6.8862	4.31992	-1.05835
C	-4.81479	3.76484	-0.79681
H	-4.4667	4.26638	-1.70585
H	-4.19173	2.87943	-0.64421
H	-4.64705	4.4479	0.04152
C	-6.44722	3.31452	1.98537
H	-5.35861	3.20432	2.02576
H	-6.66183	4.38448	1.87507
C	-7.08089	2.753	3.25429
H	-6.85219	1.68769	3.37034
H	-8.17036	2.86471	3.25279
H	-6.69358	3.27811	4.13338
S	-4.36736	0.54635	1.51411
C	-3.09626	0.45586	0.35468
C	-1.72083	0.45244	0.78203
C	-3.3715	0.41164	-1.03488
C	-0.68356	0.44415	-0.19953
C	-1.35539	0.44441	2.14881
C	-2.36769	0.40166	-1.97024
H	-4.41229	0.39859	-1.34705
C	0.68346	0.44396	0.1995
C	-1.00494	0.42878	-1.58411
C	-0.03681	0.4304	2.53605
H	-2.13555	0.44007	2.90279
H	-2.61367	0.37907	-3.02885
C	1.00483	0.42836	1.58408
C	1.72073	0.45214	-0.78205
C	0.0367	0.43072	-2.53608
H	0.21744	0.41659	3.59244
C	2.36758	0.40089	1.9702
C	3.09616	0.45521	-0.3547
C	1.35529	0.44437	-2.14884
H	-0.21755	0.4171	-3.59247
C	3.37139	0.41076	1.03485
H	2.61356	0.37812	3.02881
H	2.13545	0.43995	-2.90281
H	4.41216	0.39739	1.34704
S	4.36728	0.54563	-1.51413
C	8.32266	-0.22988	0.31783
C	7.53231	-3.26615	-0.29465
C	5.45151	-2.66493	-2.26166
C	4.76843	-2.79033	0.52918
C	8.81749	2.83142	-0.35721
C	6.28929	3.4074	0.94177
C	6.44659	3.31408	-1.98566
C	9.42701	-0.50992	-0.51038
C	8.5302	-0.21325	1.71326
H	8.29357	-2.99019	-1.03264
H	7.94635	-2.97674	0.67824
C	7.2567	-4.7658	-0.33988
H	5.2972	-3.7506	-2.25303
H	4.46345	-2.20164	-2.36155
C	6.34846	-2.24969	-3.42198
H	3.8794	-2.17969	0.33686
H	4.52207	-3.81382	0.22026
C	5.13898	-2.74745	2.00739
H	9.14526	2.4726	0.62608
H	9.32175	2.19318	-1.09051
C	9.21658	4.28986	-0.56192
H	6.4587	2.80502	1.84161
H	6.88518	4.31994	1.05793
C	4.81393	3.76418	0.79648
H	5.358	3.20369	-2.02603
H	6.66103	4.38409	-1.87551
C	7.08035	2.75248	-3.2545
N	10.68076	-0.81373	0.00659
C	9.54099	-0.48911	-1.91866
N	9.76631	-0.51261	2.27517
C	7.66279	0.14766	2.76889

H	8.18496	-5.31181	-0.14185	H	8.1698	2.86443	-3.25305
H	6.89076	-5.08828	-1.31976	H	6.69289	3.27733	-4.13367
H	6.52709	-5.07524	0.41525	B	10.98147	-1.08506	1.50204
H	5.91515	-2.58583	-4.36975	C	11.5299	-0.97381	-1.01646
H	7.35104	-2.68351	-3.3439	H	8.7272	-0.26742	-2.59774
H	6.4522	-1.16011	-3.46743	C	10.86384	-0.7768	-2.23564
H	4.29104	-3.07941	2.61523	C	9.67754	-0.34923	3.60172
H	5.40674	-1.73555	2.32613	H	6.62982	0.44778	2.64717
H	5.9866	-3.40217	2.23472	C	8.3853	0.06536	3.95408
H	10.29818	4.39101	-0.42424	F	11.07719	-2.45627	1.72228
H	8.73388	4.96448	0.15232	F	12.14911	-0.44803	1.88894
H	8.98102	4.64078	-1.57177	H	12.56815	-1.2229	-0.83804
H	4.46571	4.26578	1.70544	H	11.31154	-0.83321	-3.21862
H	4.19114	2.87857	0.64403	H	10.53264	-0.5352	4.23889
H	4.64596	4.44705	-0.04197	H	8.03946	0.28166	4.95578
H	6.85188	1.68709	-3.37035				

Table S18. Atomic coordinates of the optimized ground state geometry of BPtSPyrSPtB in the dianionic form (open shell singlet).

Atom	x	y	z
Pt	-6.53504	-0.102	-0.53716
Pt	6.53501	-0.10209	0.53714
B	-10.96606	0.77625	1.70658
F	-11.10188	2.11383	2.14663
F	-12.14399	0.0926	2.05495
N	-10.73246	0.73155	0.19453
N	-9.74409	0.12153	2.35551
P	-6.15803	2.20358	-0.42564
P	-7.06593	-2.36339	-0.77764
P	6.15791	2.20354	0.4254
P	7.06597	-2.3634	0.7777
C	-8.35209	0.16067	0.33672
C	-9.49555	0.53089	-0.41178
C	-9.67585	0.72681	-1.79918
H	-8.89244	0.6277	-2.54108
C	-11.03372	1.04553	-2.01142
H	-11.51882	1.24568	-2.95972
C	-11.64808	1.04218	-0.76898
H	-12.67823	1.24173	-0.50261
C	-8.51805	-0.07335	1.7251
C	-7.61897	-0.54946	2.70627
H	-6.58259	-0.80645	2.52155
C	-8.32319	-0.63516	3.92538
H	-7.93902	-0.97328	4.88063
C	-9.61885	-0.21343	3.67275
H	-10.46534	-0.12775	4.34202
C	-7.61079	3.23483	0.04595
H	-8.4038	2.98893	-0.66909
H	-7.96403	2.8456	1.00765
C	-7.37509	4.73976	0.11506
H	-8.29968	5.2468	0.41302
H	-7.07242	5.15497	-0.85243
H	-6.60636	5.00417	0.84946
C	-5.57771	2.90833	-2.02597
H	-5.43577	3.98839	-1.89642
H	-4.59131	2.46454	-2.20232
C	-6.5011	2.61261	-3.20149
H	-6.10521	3.0586	-4.12089
H	-7.50899	3.01114	-3.0418
H	-6.58967	1.53181	-3.35588
C	-4.82479	2.73695	0.73005
H	-3.94209	2.14316	0.46875
H	-4.58369	3.78638	0.51748
C	-5.17521	2.55095	2.20261
H	-4.30482	2.76953	2.83111
H	-5.49744	1.52514	2.41179
H	-5.98609	3.21909	2.51286
C	-8.87298	-2.72818	-0.71623
H	-9.18432	-2.50021	0.31008
H	-9.36264	-1.97173	-1.33962
C	-9.30418	-4.13354	-1.12259
H	-10.3861	-4.24111	-0.98585
H	-8.8224	-4.91245	-0.52167
H	-9.08607	-4.33971	-2.17591
C	-6.3771	-3.50238	0.50397
H	-6.66037	-3.06717	1.47011
H	-6.9064	-4.45981	0.41856
C	-4.87085	-3.7289	0.43094
H	-4.54526	-4.35483	1.26952
H	-4.31638	-2.78695	0.47528
H	-4.58567	-4.2421	-0.49348
C	-6.50807	-3.09255	-2.37405
H	-5.41766	-2.99834	-2.39543
H	-6.7495	-4.16303	-2.3727
C	-7.11191	-2.39115	-3.58632
H	-6.84459	-1.32845	-3.58977
H	-8.20551	-2.4607	-3.59855
H	-6.73806	-2.83774	-4.51434
S	-4.3624	-0.41164	-1.6306
C	-3.08413	-0.3804	-0.4207
C	-1.71408	-0.37701	-0.81054
C	-3.38484	-0.38008	0.95303
C	-0.6909	-0.37722	0.18818
C	-1.31558	-0.37105	-2.18613
C	-2.3947	-0.3734	1.92153
H	-4.43316	-0.3765	1.24538
C	0.6909	-0.37726	-0.18827
C	-1.03802	-0.37456	1.57017
C	-0.00329	-0.3703	-2.54682
H	-2.09074	-0.36564	-2.94592
H	-2.6702	-0.36884	2.97452
C	1.03803	-0.37476	-1.57026
C	1.71408	-0.37698	0.81045
C	0.00329	-0.36998	2.54673
H	0.27648	-0.36485	-3.59854
C	2.39471	-0.37365	-1.92162
C	3.08413	-0.38049	0.42062
C	1.31559	-0.37081	2.18604
H	-0.27648	-0.36436	3.59844
C	3.38484	-0.38027	-0.95312
H	2.67021	-0.3692	-2.97461
H	2.09075	-0.36531	2.94582
H	4.43316	-0.37674	-1.24547
S	4.36238	-0.41179	1.63055
C	8.35208	0.16071	-0.33667
C	7.61072	3.23484	-0.04591
C	5.57721	2.90834	2.02559
C	4.82486	2.73678	-0.73058
C	8.87303	-2.72809	0.71616
C	6.37709	-3.50242	-0.50386
C	6.50829	-3.09267	2.37412
C	9.49545	0.53105	0.41194
C	8.5182	-0.07333	-1.72502
H	8.40358	2.98905	0.66933
H	7.96422	2.84558	-1.0075
C	7.37495	4.73976	-0.11517
H	5.43515	3.98837	1.8959
H	4.59086	2.46442	2.20183
C	6.50045	2.61285	3.20128
H	3.94214	2.14297	-0.46939
H	4.58369	3.78621	-0.51814
C	5.17554	2.55065	-2.20306
H	9.18425	-2.50006	-0.31018
H	9.36269	-1.97162	1.33952
C	9.3044	-4.13341	1.12244
H	6.66028	-3.06718	-1.47001
H	6.90643	-4.45983	-0.4185
C	4.87086	-3.72905	-0.43073
H	5.41784	-2.99896	2.39546
H	6.75016	-4.16305	2.37277
C	7.11181	-2.39103	3.58639
N	10.73241	0.73176	-0.19423
C	9.67556	0.72708	1.79935
N	9.74429	0.12165	-2.3553
C	7.61926	-0.5495	-2.70628

H	8.29956	5.24682	-0.41301	H	8.20546	-2.45998	3.59854
H	7.07211	5.15502	0.85226	H	6.73828	-2.83789	4.51441
H	6.60633	5.00409	-0.8497	B	10.96624	0.77628	-1.70625
H	6.10432	3.05881	4.12058	C	11.64788	1.04256	0.76937
H	7.5083	3.01154	3.04176	H	8.89204	0.62797	2.54114
H	6.58916	1.53206	3.35575	C	11.03336	1.04596	2.01173
H	4.30528	2.7693	-2.83173	C	9.61922	-0.21331	-3.67255
H	5.49767	1.52479	-2.41212	H	6.58288	-0.80656	-2.52167
H	5.98656	3.21866	-2.51321	C	8.32361	-0.63515	-3.92531
H	10.38629	-4.24092	0.98545	F	11.10232	2.1138	-2.1464
H	8.82252	-4.91236	0.52165	F	12.14414	0.09244	-2.05438
H	9.08657	-4.33957	2.17582	H	12.67804	1.24218	0.50311
H	4.54525	-4.35489	-1.26938	H	11.51834	1.2462	2.96007
H	4.3163	-2.78715	-0.47486	H	10.46577	-0.12755	-4.34174
H	4.58581	-4.24242	0.49363	H	7.93957	-0.97328	-4.88062
H	6.84392	-1.32847	3.58993				

Table S19. Atomic coordinates of the optimized ground state geometry of KBPtSPyr in the neutral form.

Atom	x	y	z
Pt	-0.2733	-0.3559	0.30649
P	0.0962	-0.14906	-2.01813
P	-0.56161	-0.5621	2.64025
S	1.95422	-1.25618	0.6719
C	-2.04865	0.20239	3.43146
H	-1.7952	0.36064	4.48774
H	-2.16693	1.19427	2.98067
C	-2.24306	0.08702	0.0405
F	-5.91295	0.96461	-1.47464
F	-6.10132	0.65198	0.77971
C	3.23363	-0.09127	0.34638
C	-2.74169	1.41159	0.12095
C	-2.98465	-2.37159	-0.40169
N	-4.51798	-0.70371	-0.43391
C	0.80832	0.11013	3.67693
H	0.61904	-0.23378	4.70104
H	1.72607	-0.373	3.32665
C	-0.62703	-2.34828	3.09578
H	-1.52241	-2.74898	2.60641
H	0.23107	-2.81726	2.59959
N	-4.09776	1.6929	-0.0666
C	4.57609	-0.53169	0.17543
C	-0.66013	2.93523	0.64208
H	-0.53901	3.45277	1.6021
H	-0.21174	3.57807	-0.1259
H	-0.08832	2.00091	0.6835
C	3.97296	2.21576	0.04165
H	3.72415	3.274	-0.00468
C	2.97204	1.28572	0.27318
H	1.9496	1.6202	0.41335
C	5.60836	0.42762	-0.05145
C	7.29	-1.38227	-0.14739
C	4.94388	-1.91636	0.22352
H	4.15937	-2.64954	0.38266
C	-2.09668	2.66214	0.36012
C	6.96105	0.00185	-0.21238
C	-4.29865	3.01891	0.04375
C	-1.74741	-3.20162	-0.31223
H	-1.47886	-3.62539	-1.28881
H	-1.89494	-4.05038	0.36779
H	-0.88705	-2.62352	0.04439
C	-3.15749	-0.96222	-0.24321
C	5.30508	1.81769	-0.12264
C	-5.16077	-1.85683	-0.69515
C	-4.2414	-2.91882	-0.68478
C	6.36001	2.75695	-0.35256
H	6.10622	3.81347	-0.40268
C	7.64837	2.34994	-0.50363
H	8.44154	3.07335	-0.67652
C	7.99371	0.96	-0.43846
C	-3.07619	3.65877	0.31098
C	6.23311	-2.3225	0.07212
H	6.48204	-3.38047	0.11221
C	8.62528	-1.78045	-0.30495
H	8.87107	-2.83852	-0.25454
C	-0.63199	-2.67705	4.58625
H	-0.79519	-3.75103	4.72671
H	-1.42658	-2.14934	5.12453
H	0.32159	-2.42602	5.05997
C	9.31463	0.5165	-0.59066
H	10.10018	1.24841	-0.76299
C	0.96106	1.62664	3.66269
H	0.04297	2.13654	3.97407
H	1.23571	1.99439	2.67112
H	1.75454	1.92246	4.3573
C	9.62433	-0.83839	-0.52369
H	10.65468	-1.16238	-0.64384
B	-5.21021	0.66167	-0.30468
C	-2.85978	5.13244	0.47085
H	-3.72731	5.58721	0.96604
H	-2.00773	5.30366	1.14077
C	-5.6442	3.6381	-0.11538
H	-5.96972	3.60555	-1.16132
H	-5.62844	4.68216	0.2069
H	-6.39281	3.09696	0.47054
C	-2.60703	5.85236	-0.85717
H	-3.46109	5.7363	-1.53388
H	-1.72514	5.44337	-1.36319
H	-2.44141	6.92434	-0.70016
C	-6.62682	-1.91135	-0.95443
H	-7.17698	-1.35138	-0.19255
H	-6.97988	-2.94543	-0.95836
H	-6.87041	-1.45998	-1.92277
C	1.48269	-1.15568	-2.69613
H	1.62092	-0.84586	-3.73902
H	2.38719	-0.87883	-2.14481
C	-1.28995	-0.61525	-3.15676
H	-0.82492	-0.90249	-4.10882
H	-1.75088	-1.51867	-2.74343
C	-4.54562	-4.35708	-0.97336
H	-5.54892	-4.60858	-0.60664
H	-3.85216	-4.99655	-0.41281
C	0.51019	1.58671	-2.48723
H	-0.37846	2.17743	-2.23526
H	1.30299	1.91451	-1.80689
C	-3.35431	-0.57947	3.32062
H	-3.29209	-1.54964	3.82413
H	-3.64009	-0.75394	2.2811
H	-4.16096	-0.01215	3.79717
C	1.25579	-2.66165	-2.62019
H	0.36884	-2.97098	-3.18385
H	1.14203	-2.98659	-1.58216
H	2.11674	-3.1882	-3.04634
C	0.93151	1.81887	-3.93609
H	0.20581	1.42101	-4.65294
H	1.90255	1.36283	-4.15108
H	1.02569	2.89382	-4.12479
C	-2.36338	0.44141	-3.40362
H	-3.12997	0.02932	-4.06891
H	-1.95647	1.33515	-3.8867
H	-2.85808	0.75009	-2.48045
C	-4.45496	-4.70443	-2.46238
H	-4.66993	-5.76526	-2.63442
H	-3.45324	-4.49385	-2.854
H	-5.17019	-4.11389	-3.04588

Table S20. Atomic coordinates of the optimized ground state geometry of KBPtSPyr in the mono cationic form.

Atom	x	y	z
Pt	-0.24062	-0.34303	0.1185
P	-0.20528	0.04748	-2.22592
P	-0.36163	-0.68054	2.46928
S	1.9887	-1.2131	0.17979
C	-1.6726	0.21137	3.41957
H	-1.28617	0.31359	4.44177
H	-1.73816	1.22165	3.00119
C	-2.23089	0.06151	0.10259
F	-6.01189	0.93337	-1.00543
F	-6.00404	0.55516	1.24852
C	3.26734	-0.09106	0.01511
C	-2.72154	1.37312	0.29885
C	-2.97499	-2.39255	-0.36418
N	-4.52452	-0.75158	-0.13637
C	1.16793	-0.21649	3.38882
H	1.0125	-0.52507	4.42953
H	1.98823	-0.82482	2.99167
C	-0.58999	-2.47069	2.83657
H	-1.56663	-2.74288	2.4191
H	0.15766	-3.0065	2.23941
N	-4.09126	1.64189	0.26455
C	4.63463	-0.55689	0.02915
C	-0.61042	2.90054	0.69849
H	-0.39718	3.29987	1.69842
H	-0.25842	3.64666	-0.02414
H	-0.01578	1.98821	0.56924
C	4.04134	2.2018	-0.26358
H	3.81923	3.25988	-0.37307
C	3.02033	1.29789	-0.1345
H	1.98943	1.63407	-0.13433
C	5.68486	0.39539	-0.10423
C	7.35211	-1.41037	0.05251
C	4.97696	-1.92697	0.16986
H	4.18518	-2.6616	0.26958
C	-2.06463	2.62062	0.53198
C	7.0394	-0.0327	-0.09142
C	-4.29132	2.95866	0.45133
C	-1.72227	-3.19704	-0.4744
H	-1.57261	-3.56428	-1.49807
H	-1.76493	-4.08139	0.1733
H	-0.83275	-2.61911	-0.19823
C	-3.14863	-0.99368	-0.11998
C	5.39569	1.7826	-0.25184
C	-5.17701	-1.90378	-0.37159
C	-4.24757	-2.94951	-0.51886
C	6.45735	2.71056	-0.38209
H	6.21972	3.76452	-0.4941
C	7.76423	2.2941	-0.3678
H	8.56986	3.01621	-0.46856
C	8.09168	0.91687	-0.22257
C	-3.05248	3.60359	0.62462
C	6.28403	-2.33853	0.18139
H	6.51738	-3.394	0.29109
C	8.70167	-1.81509	0.06334
H	8.9344	-2.87084	0.17345
C	-0.48969	-2.87638	4.30509
H	-0.75277	-3.93399	4.41117
H	-1.16943	-2.30189	4.94256
H	0.52574	-2.74977	4.69151
C	9.42472	0.46931	-0.20524
H	10.22564	1.19697	-0.3041
C	1.52101	1.26486	3.3305
H	0.72448	1.8907	3.74616
H	1.71098	1.59243	2.30473
H	2.4277	1.45276	3.9147
C	9.7234	-0.88287	-0.0638
H	10.75858	-1.20924	-0.05299
B	-5.21473	0.60499	0.09231
C	-2.83713	5.07146	0.83169
H	-3.65139	5.48618	1.4393
H	-1.91988	5.22626	1.41333
C	-5.65038	3.56695	0.44853
H	-6.06683	3.58578	-0.56508
H	-5.61525	4.5923	0.82422
H	-6.33803	2.98407	1.0676
C	-2.74123	5.85631	-0.48009
H	-3.66079	5.7519	-1.0665
H	-1.91131	5.49193	-1.09638
H	-2.57924	6.92314	-0.28948
C	-6.66161	-1.97494	-0.46207
H	-7.12672	-1.45405	0.37971
H	-6.99927	-3.01391	-0.46887
H	-7.01907	-1.48897	-1.37688
C	1.15458	-0.81422	-3.12368
H	1.14449	-0.43812	-4.15357
H	2.10354	-0.49876	-2.67589
C	-1.68984	-0.45764	-3.21043
H	-1.31769	-0.67174	-4.22066
H	-2.04474	-1.40713	-2.79704
C	-4.56896	-4.3784	-0.83316
H	-5.50287	-4.66883	-0.3357
H	-3.79094	-5.02843	-0.41415
C	0.03598	1.83483	-2.60727
H	-0.84545	2.34716	-2.20311
H	0.88812	2.17767	-2.01158
C	-3.05745	-0.42935	3.45002
H	-3.03965	-1.42251	3.90913
H	-3.49345	-0.52166	2.45369
H	-3.72769	0.19706	4.04788
C	1.03683	-2.33515	-3.12458
H	0.12088	-2.66939	-3.62269
H	1.041	-2.74228	-2.10873
H	1.88387	-2.7719	-3.66351
C	0.25459	2.19015	-4.07649
H	-0.53774	1.80377	-4.72509
H	1.21106	1.80939	-4.44658
H	0.26937	3.27935	-4.18869
C	-2.84471	0.53763	-3.28543
H	-3.6427	0.11035	-3.9018
H	-2.54476	1.48295	-3.74732
H	-3.26845	0.7578	-2.30404
C	-4.69605	-4.6495	-2.33525
H	-4.92192	-5.70448	-2.52681
H	-3.76634	-4.40118	-2.85978
H	-5.49735	-4.04556	-2.77547

Table S21. Atomic coordinates of the optimized ground state geometry of KBPtSPyr in the mono anionic form.

Atom	x	y	z
Pt	-0.24696	-0.38864	0.26415
P	-4.9E-4	-0.12303	-2.05273
P	-0.56574	-0.59201	2.5762
S	2.0053	-1.31351	0.5796
C	-2.01668	0.24421	3.36215
H	-1.75418	0.41674	4.41456
H	-2.09789	1.22436	2.87832
C	-2.23336	0.0855	0.03248
F	-5.9498	1.02268	-1.3643
F	-6.08176	0.67499	0.88672
C	3.28241	-0.14902	0.27935
C	-2.72006	1.42647	0.14888
C	-3.03295	-2.36312	-0.41913
N	-4.53263	-0.67609	-0.38893
C	0.83184	2.8E-4	3.62859
H	0.62597	-0.32208	4.65677
H	1.72099	-0.53559	3.27921
C	-0.71226	-2.37395	3.04152
H	-1.61281	-2.74186	2.53577
H	0.13459	-2.87805	2.55944
N	-4.0798	1.70994	0.00401
C	4.64077	-0.56473	0.16238
C	-0.62632	2.93228	0.6427
H	-0.45988	3.42181	1.6135
H	-0.17594	3.58719	-0.11819
H	-0.06371	1.98925	0.64792
C	3.99266	2.16524	-0.05933
H	3.72668	3.21754	-0.1405
C	3.00155	1.22398	0.16236
H	1.96708	1.53816	0.25952
C	5.66253	0.40674	-0.05829
C	7.3784	-1.37437	-0.06095
C	5.03204	-1.93949	0.25791
H	4.25452	-2.68068	0.41546
C	-2.0726	2.66583	0.38965
C	7.0272	0.00206	-0.16946
C	-4.28584	3.05772	0.14558
C	-1.80347	-3.21271	-0.37784
H	-1.51272	-3.58671	-1.37154
H	-1.94761	-4.10108	0.25457
H	-0.9425	-2.65586	0.01614
C	-3.17328	-0.96091	-0.24536
C	5.33763	1.78918	-0.17297
C	-5.22191	-1.83385	-0.6385
C	-4.32746	-2.89341	-0.66594
C	6.38193	2.74054	-0.39485
H	6.11121	3.79093	-0.47888
C	7.68214	2.35443	-0.499
H	8.46703	3.08807	-0.66709
C	8.0497	0.97323	-0.38993
C	-3.06804	3.67742	0.38476
C	6.33205	-2.32732	0.15362
H	6.59791	-3.37934	0.22945
C	8.72482	-1.75192	-0.17119
H	8.98742	-2.80396	-0.08761
C	-0.75331	-2.7031	4.53132
H	-0.95947	-3.77007	4.67252
H	-1.53533	-2.14411	5.05646
H	0.20089	-2.48692	5.02147
C	9.38228	0.54974	-0.49386
H	10.15964	1.29159	-0.66176
C	1.07407	1.50479	3.59551
H	0.1956	2.06932	3.92746
H	1.33319	1.84522	2.58982
H	1.90474	1.76391	4.26163
C	9.7131	-0.79744	-0.38515
H	10.75208	-1.10572	-0.46848
B	-5.1874	0.68881	-0.21732
C	-2.82405	5.14568	0.56466
H	-3.7128	5.62738	0.99428
H	-2.01856	5.29832	1.29709
C	-5.64552	3.6639	0.04524
H	-6.0726	3.54274	-0.95774
H	-5.60603	4.73358	0.27358
H	-6.34726	3.18692	0.73984
C	-2.4516	5.86958	-0.7333
H	-3.25615	5.7778	-1.47208
H	-1.54657	5.43882	-1.17743
H	-2.26769	6.93765	-0.56112
C	-6.7029	-1.84421	-0.81984
H	-7.21051	-1.39285	0.04101
H	-7.06915	-2.86835	-0.94109
H	-7.00952	-1.26324	-1.69786
C	1.38316	-1.07699	-2.81627
H	1.49241	-0.73695	-3.85328
H	2.29634	-0.80407	-2.27625
C	-1.41992	-0.58878	-3.15061
H	-0.98685	-0.88809	-4.11458
H	-1.87388	-1.47975	-2.70456
C	-4.64781	-4.33128	-0.94451
H	-5.68856	-4.54547	-0.66734
H	-4.03024	-4.97989	-0.30675
C	0.36393	1.63095	-2.50259
H	-0.52912	2.19481	-2.20805
H	1.16722	1.96482	-1.83771
C	-3.35304	-0.48479	3.26277
H	-3.33002	-1.45385	3.77292
H	-3.64048	-0.64847	2.22213
H	-4.13551	0.11872	3.73655
C	1.18108	-2.58794	-2.77575
H	0.28854	-2.89432	-3.33245
H	1.08182	-2.93715	-1.74413
H	2.04208	-3.09574	-3.22524
C	0.73913	1.90608	-3.95653
H	0.00473	1.50309	-4.66195
H	1.71487	1.47904	-4.2085
H	0.80088	2.98684	-4.12741
C	-2.4972	0.47054	-3.3671
H	-3.29007	0.0568	-4.00087
H	-2.1057	1.36019	-3.87118
H	-2.95031	0.78083	-2.42338
C	-4.43407	-4.73578	-2.40661
H	-4.66585	-5.79588	-2.56974
H	-3.39488	-4.56712	-2.71243
H	-5.07347	-4.14151	-3.06966

References

1. M. A. Cairns, K. R. Dixon and G. A. Rivett, *J. Organomet. Chem.*, 1979, **171**, 373-385.
2. P. Irmler, F. S. Gogesch, C. B. Larsen, O. S. Wenger and R. F. Winter, *Dalton Trans.*, 2019, **48**, 1171-1174.
3. P. Irmler and R. F. Winter, *Dalton Trans.*, 2016, **45**, 10420-10434.
4. P. Irmler, F. S. Gogesch, C. B. Larsen, O. S. Wenger and R. F. Winter, *Dalton Trans.*, 2019, **48**, 1171-1174.
5. F. Wilkinson, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1993, **22**, 113-262.