Supplementary Information

Figure S1. View of the asymmetric unit in the molecular structure of [{Pt(pq)(μ−C≡C^{t}Bu)}$_2$(μ-bpe)]·4CHCl$_3$ (**4a**·4CHCl$_3$)

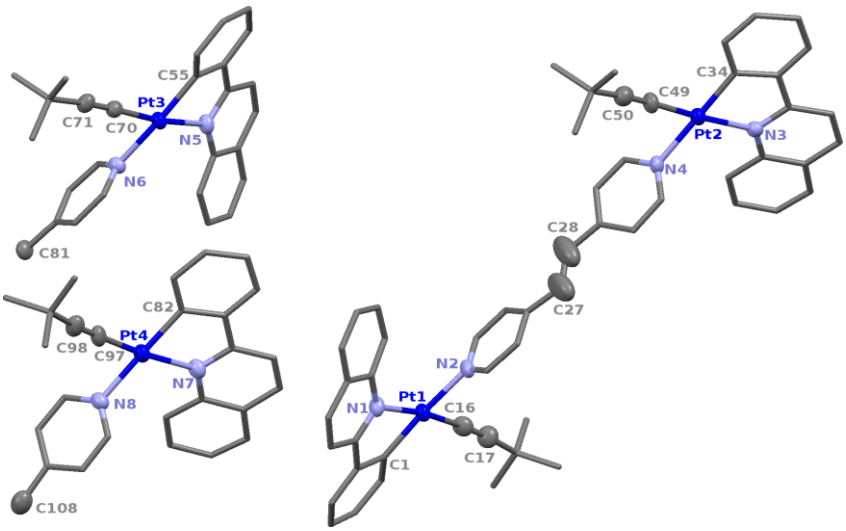
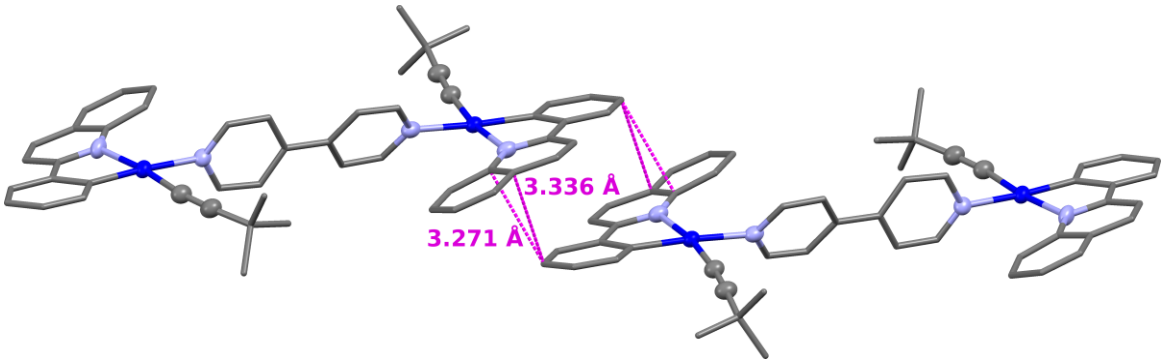
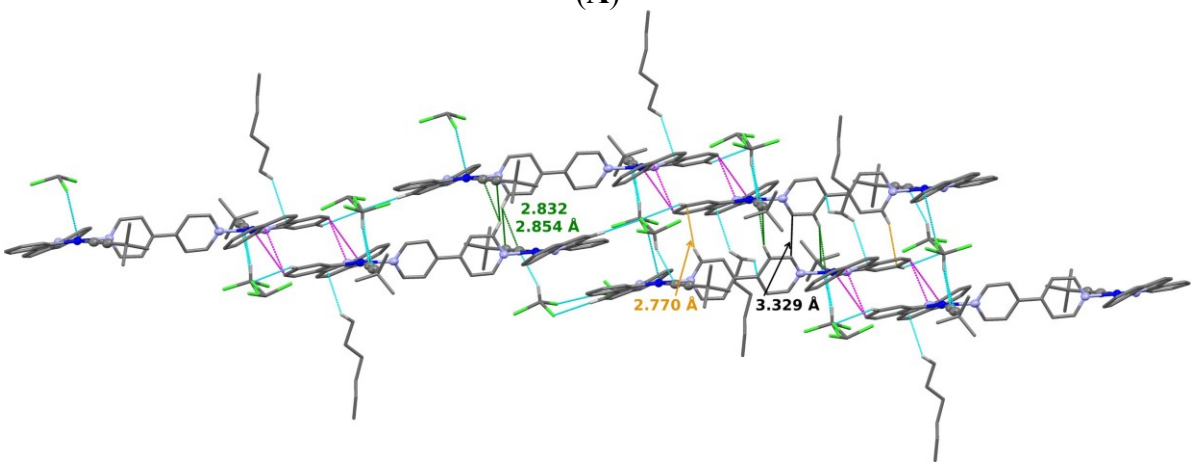


Figure S2. Packing of the complex [{Pt(pq)(μ−C≡C^{t}Bu)}$_2$(μ-4,4'-bpy)]·2CHCl$_3$·C$_6$H$_{14}$ (**2a**·2CHCl$_3$·C$_6$H$_{14}$) showing (**A**) the disposition of the dimers and (**B**) the interactions through secondary interactions with the crystallization solvents (CHCl$_3$, *n*-hexane) and with other dimers (H$_{py}$···π$_{C\equiv C}$/C$_{pq}$).



(**A**)



(**B**)

Figure S3. Packing of [{Pt(pq)(μ–C≡C^{t}Bu)}$_2$(μ-bpe)]·4CHCl$_3$ (**4a**·4CHCl$_3$) showing the interactions through secondary contacts between the molecules [C-H$_{py}$···C-H$_{py}$ (C···C 3.353 Å, C···H 2.897 Å, C-C-H 53.42°) (green), Hpy···Cpq (2.735 Å) (green), C$_{py}$···H^{t}Bu (2.881 Å) (black), H$_{pq}$···C$_{pq}$ (2.856, 2.885 Å) (orange) C$_{C≡C}$···H$_{C=C}$ (2.872 Å) (violet)] and between the crystallization solvents and the molecules (blue) (Cl···C^{t}Bu 3.430 Å, Cl···H^{t}Bu 2.940 Å, Cl···H$_{pq}$ 2.892–2.949 Å, Cl···C$_{pq}$ 3.376, 3.426 Å, Cl···H$_{py}$ 2.933 Å, Cl···C$_{py}$ 3.403 Å, HCHCl$_3$···C$_{C=C}$ 2.458–2.824 Å, HCHCl$_3$···Pt 2.737, 2.888 Å, HCHCl$_3$···C$_{pq}$ 2.896 Å, HCHCl$_3$···N$_{pq}$ 2.724 Å).

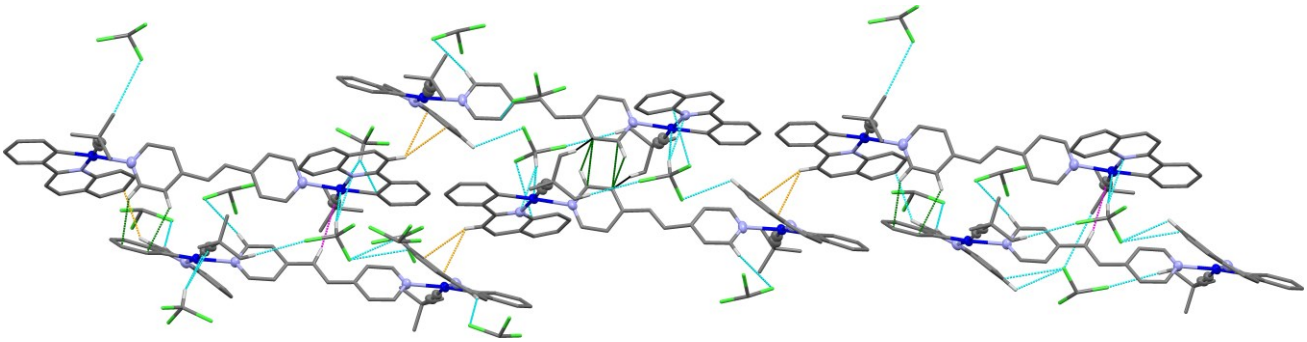


Figure S4. ^{1}H NMR spectra at 298 K and at 218 K of a sample of recently dissolved solid **2a** in CDCl3 (3×10^{-3} M).

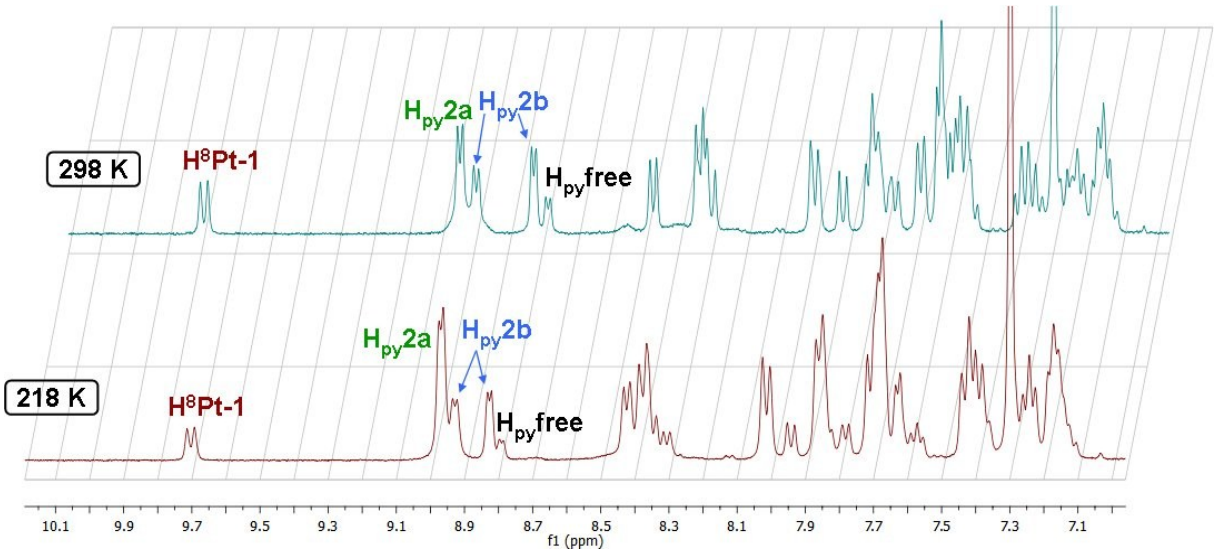


Figure S5. ^{1}H NMR spectra at 298 K in CD_3COCD_3 (3×10^{-3} M) of a sample of recently dissolved solid **2a**.

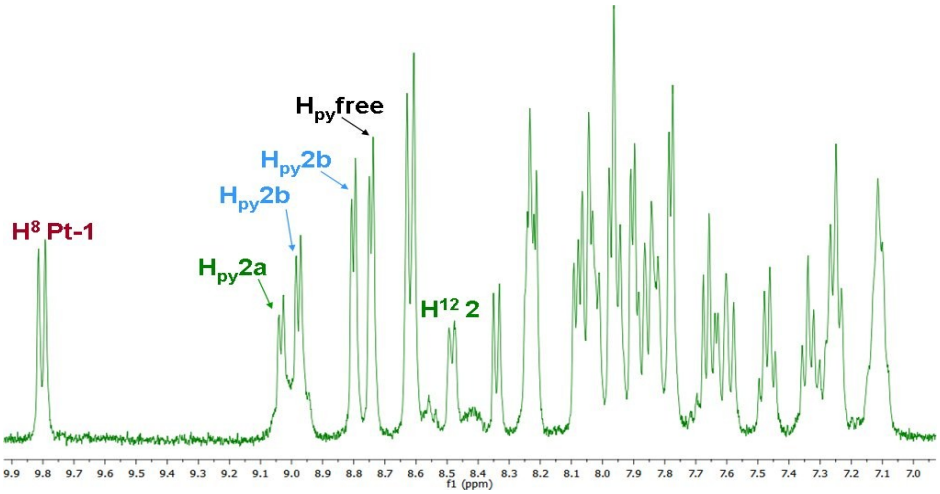


Figure S6. Normalized absorption spectra calculated from their reflectance spectra of **1a**–**6a**.

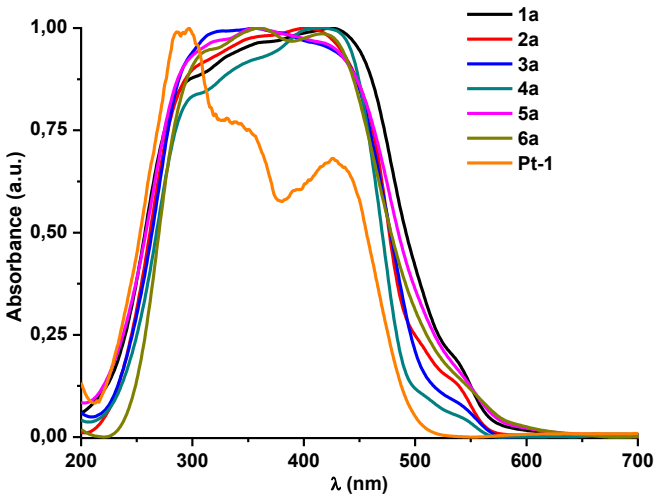
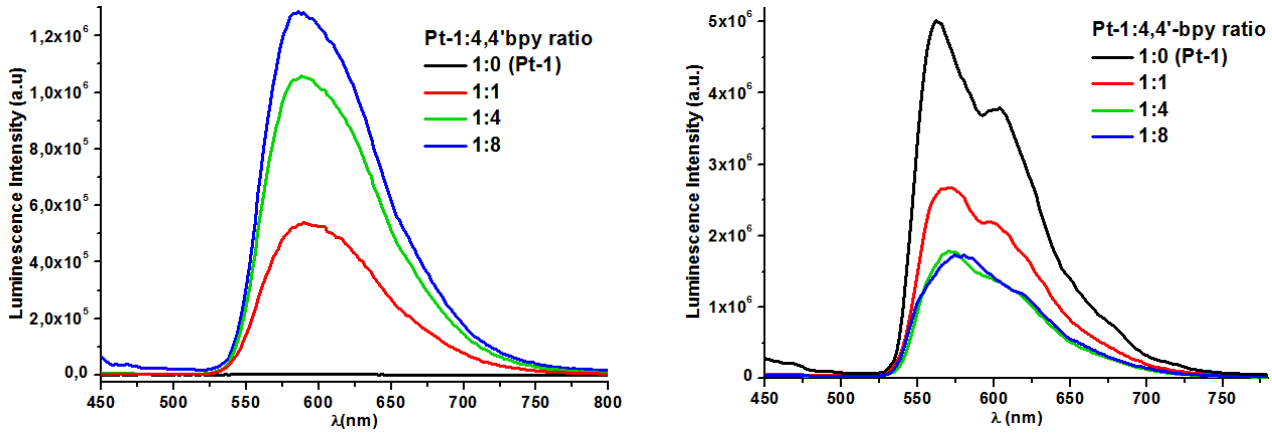


Figure S7. Comparative emission spectra in CH2Cl2 5×10^{-5} M of the starting material and successive additions of 1, 4 and 8 equiv. of the 4,4'-bpy (**A**) at 298 K; (**B**) at 77 K.



(**A**) (**B**)

Figure S8. Spin density plot for the computed T_1 state of **2a**.

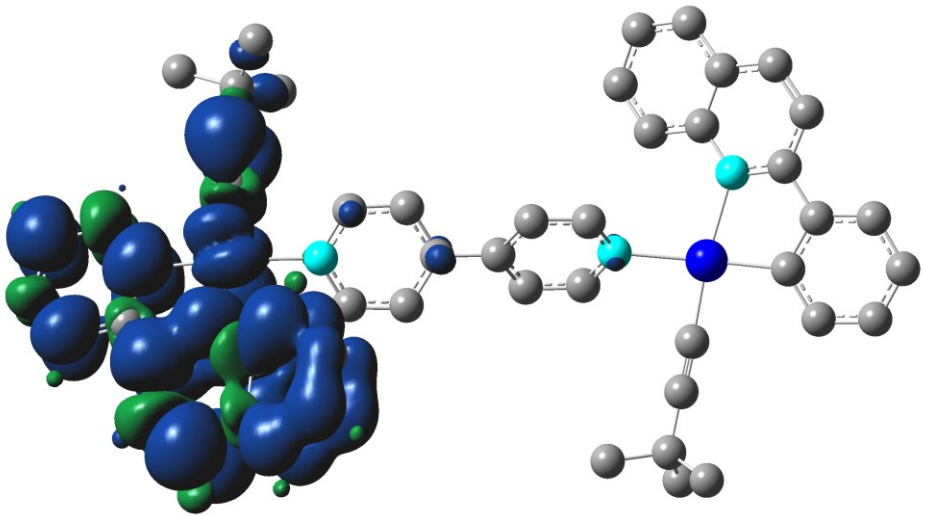


Table S1. Selected bond lengths and angles for complex [{Pt(pq)(C≡C^{t}Bu)}$_2$(μ-bpe)]·4CHCl$_3$ (**4a**·4CHCl$_3$).

Distances (Å)			
Pt(1)-C(1)	1.972(9)	Pt(3)-C(55)	1.988(9)
Pt(1)-N(1)	2.096(7)	Pt(3)-N(5)	2.091(7)
Pt(1)-C(16)	1.949(9)	Pt(3)-C(70)	1.959(9)
Pt(1)-N(2)	2.130(7)	Pt(3)-N(6)	2.114(7)
C(16)-C(17)	1.209(12)	C(70)-C(71)	1.195(12)
Pt(2)-C(34)	1.979(8)	Pt(4)-C(82)	1.993(9)
Pt(2)-N(3)	2.136(7)	Pt(4)-N(7)	2.146(7)
Pt(2)-C(49)	1.956(9)	Pt(4)-C(97)	1.954(9)
Pt(2)-N(4)	2.145(7)	Pt(4)-N(8)	2.125(7)
C(49)-C(50)	1.195(12)	C(97)-C(98)	1.205(12)
C(27)-C(28)	1.290(9)	C(81)-C(81)#1	1.334(17)
-	-	C(108)-C(108)#2	1.240(19)
Angles (°)			
N(1)-Pt(1)-C(1)	80.3(3)	N(5)-Pt(3)-C(55)	79.4(3)
C(16)-Pt(1)-C(1)	92.1(4)	C(70)-Pt(3)-C(55)	94.9(4)
C(16)-Pt(1)-N(2)	87.8(3)	C(70)-Pt(3)-N(6)	86.0(3)
N(1)-Pt(1)-N(2)	99.4(3)	N(5)-Pt(3)-N(6)	99.2(3)
Pt(1)-C(16)-C(17)	176.3(9)	Pt(3)-C(70)-C(71)	177.4(8)
C(16)-C(17)-C(18)	175.4(11)	C(70)-C(71)-C(72)	175.9(10)
N(3)-Pt(2)-C(34)	80.9(3)	N(7)-Pt(4)-C(82)	79.7(4)
C(49)-Pt(2)-C(34)	93.0(4)	C(97)-Pt(4)-C(82)	92.2(4)
C(49)-Pt(2)-N(4)	83.9(3)	C(97)-Pt(4)-N(8)	86.6(3)
N(3)-Pt(2)-N(4)	102.0(3)	N(7)-Pt(4)-N(8)	101.1(3)
Pt(2)-C(49)-C(50)	174.7(9)	Pt(4)-C(97)-C(98)	173.1(8)
C(49)-C(50)-C(51)	174.6(11)	C(97)-C(98)-C(99)	173.7(11)
C(24)-C(27)-C(28)	121.4(14)	C(78)-C(81)-C(81)#1	123.6(10)
C(27)-C(28)-C(31)	126.5(14)	C(105)-C(108)-C(108)#2	124.2(15)

Table S2. Absorption data for the ligands at 298 K (5×10^{-5} M CH_2Cl_2 Solutions).

Compound	λ_{abs}/nm (10^3 ε M^{-1} cm^{-1})
pyz	219 (20.9), 261 (11.4), 315 (3.5)
bpy	214 (21.3), 239 (23.5), 269 (10.6), tail to 300 nm
bpa	218 (11.3), 256 (7.3), 265 (4.6), 298 (1)
bpe	219 (24.9), 288 (48.6), 298 (47.3), 313 (28.0)
bpac	218 (19.9), 262 (16.7), 276 (20.7), 285 (17.6), 292 (17.4), 322 (5.0)
tpab	218 (37.9), 269 (48.2), 284 (67.8), 302 (66.7), 327 (11.2)

Table S3. Photophysical data for the ligands in dichloromethane solutions.

Compound	Medium (T [a]/K)	λ_{em}/nm (λ_{exc}/nm)
pyz	5×10^{-5} M (298)	360_{max}, 450_{sh} (300)
	5×10^{-5} M (77K)	375_{max}, 390, 480_{sh} (250–270)
4,4'-bipy	5×10^{-5} M (298)	365 (230–300) [(a)]
	5×10^{-5} M (77K)	400_{max}, 430, 460, 490_{sh} (250–270)
bpa	5×10^{-5} M (298)	380 (300), 380, 575 (340), 575 (365) [(a)]
	5×10^{-5} M (77K)	490_{max}, 520, 560_{sh} (300–365)
bpe	5×10^{-5} M (298)	400 (280–300)
	5×10^{-5} M (77K)	400 (300)
bpac	5×10^{-5} M (298)	380_{max}, (300–320),420 (365) [(a)]
	5×10^{-5} M (77K)	410_{max}, 510, (365) [(a)]
tpab	5×10^{-5} M (298)	350_{max}, 360, 380_{sh} (270–300), 380 (330), 420 (365)
	5×10^{-5} M (77K)	405 (230–365)

[a] Weak.

Table S4. DFT optimized geometries for ground state and triplet state of complex **2a**.

Distances (Å)			
Parameters	**X-ray**	**S_0**	**T_1**
Pt(1)-C(1)	1.994(5)	1.99156	1.99066
Pt(1)-N(1)	2.115(4)	2.18658	2.18541
Pt(1)-C(16)	1.967(5)	1.95948	1.95941
Pt(1)-N(2)	2.113(4)	2.23148	2.23056
C(16)-C(17)	1.197(7)	1.22337	1.22336
Pt(2)-C(32)	1.980(5)	1.99088	1.99972
Pt(2)-N(3)	2.127(4)	2.18572	2.05012
Pt(2)-C(47)	1.961(5)	1.95953	1.96122
Pt(2)-N(4)	2.125(4)	2.23261	2.24171
C(47)-C(48)	1.209(7)	1.22337	1.22968
Angles (°)			
N(1)-Pt(1)-C(1)	80.9(2)	76.65	79.65
C(16)-Pt(1)-C(1)	91.7(2)	94.03	94.00
C(16)-Pt(1)-N(2)	88.50(19)	84.40	84.55
N(1)-Pt(1)-N(2)	98.56(16)	101.82	101.68
Pt(1)-C(16)-C(17)	175.2(5)	177.81	177.91
C(16)-C(17)-C(18)	176.6(8)	179.36	179.23
N(3)-Pt(2)-C(32)	80.6(2)	79.64	81.37
C(47)-Pt(2)-C(32)	95.8(2)	94.04	94.05
C(47)-Pt(2)-N(4)	81.36(19)	84.61	87.44
N(3)-Pt(2)-N(4)	101.96(16)	101.61	97.48
Pt(2)-C(47)-C(48)	167.6(5)	177.74	178.14
C(47)-C(48)-C(49)	172.7(6)	179.41	178.96

Table S5. Composition of frontier molecular orbitals in the ground-state for **2a**.

MO	**Energy**	**Pt(1)**	**pq(1)**	**C≡C^{t}Bu(1)**	**bpy**	**Pt(2)**	**pq(2)**	**C≡C^{t}Bu(2)**
LUMO+4	−1.08	1	14	0	79	0	5	0
LUMO+3	−1.22	1	4	0	93	0	2	0
LUMO+2	−2.02	0	1	0	2	3	93	0
LUMO+1	−2.04	3	93	1	2	0	1	0
LUMO	−2.51	1	2	0	94	1	1	0
HOMO	−5.15	0	0	0	0	32	7	61
HOMO−1	−5.15	35	8	57	0	0	0	0
HOMO−2	−5.38	0	0	0	1	24	27	48
HOMO−3	−5.39	0	0	0	2	27	43	28
HOMO−4	−5.49	30	55	13	1	0	0	0

Table S6. Selected vertical excitation energies singlets (S_0) computed by TD-DFT in gas phase with the orbitals involved for complex **2a** ($f^a > 0.01$).

State	λ_{exc} (calc.)/nm	f^a	Transition (Percentage Contribution)
S_1	494.3	0.1217	H−4→LUMO (93%)
S_2	482.8	0.0929	H−1→L+1 (52%), H−1→L+2 (14%), HOMO→L+2 (14%)
S_3	481.7	0.0178	H−5→LUMO (14%), HOMO→L+1 (17%), HOMO→L+2 (46%), H−1→L+1 (9%)
S_4	459.3	0.0277	H−6→LUMO (93%)
S_5	450.8	0.0107	H−2→L+1 (24%), H−2→L+2 (68%)
S_6	436.2	0.0201	H−5→L+1 (21%), H−5→L+2 (25%), H−4→L+1 (36%)
S_7	435.1	0.0855	H−5→L+1 (25%), H−4→L+2 (47%)

[a] Oscillator Strength.

Table S7. Selected vertical excitation energies singlets (S_0) computed by TD-DFT in CH_2Cl_2 with the orbitals involved for complex **2a** ($f^a > 0.01$).

State	λ_{exc} (calc.)/nm	f^a	Transition (Percentage Contribution)
S_1	434.6	0.0153	H−2→LUMO (41%), HOMO→L+1 (25%), HOMO→L+2 (20%)
S_2	430.8	0.0114	H−2→LUMO (49%), HOMO→L+1 (19%), HOMO→L+2 (15%)
S_3	428.3	0.0113	H−3→LUMO (36%), H−1→L+1 (19%), H−1→L+2 (22%), H−5→LUMO (7%)
S_4	419.0	0.2736	H−4→LUMO (62%), H−5→L+1 (6%)
S_5	414.7	0.0179	H−5→LUMO (56%), H−4→L+1 (9%)
S_6	406.7	0.0155	H−2→L+1 (45%), H−2→L+2 (39%), H−4→LUMO (5%)
S_7	404.3	0.0143	H−3→L+1 (37%), H−3→L+2 (47%), H−5→LUMO (6%),
S_8	396.6	0.0869	H−5→L+1 (11%), H−4→LUMO (12%), H−4→L+1 (26%), H−4→L+2 (28%)
S_9	394.1	0.0829	H−5→LUMO (14%), H−5→L+1 (21%), H−5→L+2 (30%), H−4→L+2 (12%), H−4→L+1 (9%)
S_{10}	378.8	0.0196	H−6→LUMO (69%), H−6→L+1 (21%), H−6→L+2 (6%)
S_{11}	376.3	0.0133	H−7→LUMO (70%), H−7→L+1 (17%), H−7→L+2 (9%)

[a] Oscillator Strength.

Table S8. Cartesian coordinates for the computed singlet state (S_0, Charge = 0; Multiplicity = 1) first triplet state (T_1, Charge = 0; Multiplicity = 3) for complex **2a**.

Atom	S_0			T_1		
	***x*-axis**	***y*-axis**	***z*-axis**	***x*-axis**	***y*-axis**	***z*-axis**
C	6.962	4.866	–0.954	7.72513	0.45963	0.23484
C	8.082	5.416	–1.624	8.45539	1.61131	0.56478
H	8.934	5.104	–1.417	7.94655	2.56717	0.58687
C	7.94	6.392	–2.564	9.81241	1.53833	0.87734
H	8.691	6.754	–2.975	10.35474	2.44676	1.12762
C	6.651	6.855	–2.915	10.48139	0.30956	0.87781
H	6.55	7.488	–3.59	11.53738	0.25704	1.12518
C	5.553	6.368	–2.259	9.78455	–0.84592	0.55032
H	4.709	6.69	–2.48	10.31486	–1.79329	0.53547
C	5.676	5.392	–1.258	8.41776	–0.78035	0.22222
C	4.577	4.895	–0.438	7.65214	–1.94405	–0.21993
C	3.212	5.217	–0.656	8.17728	–3.26694	–0.23044
H	2.98	5.795	–1.346	9.16499	–3.44744	0.17371
C	2.263	4.701	0.117	7.43259	–4.30158	–0.72339
H	1.37	4.873	–0.081	7.81568	–5.31844	–0.71242
C	2.587	3.886	1.245	6.15922	–4.04315	–1.29149
C	1.633	3.41	2.173	5.3783	–5.05322	–1.90429
H	0.727	3.537	2.009	5.75459	–6.07265	–1.90231
C	2.027	2.771	3.3	4.17953	–4.74678	–2.50949
H	1.391	2.444	3.895	3.58941	–5.52396	–2.98469
C	3.404	2.598	3.571	3.733	–3.40702	–2.53184
H	3.673	2.175	4.355	2.80842	–3.15929	–3.0449
C	4.335	3.05	2.688	4.46009	–2.40517	–1.92283
H	5.237	2.953	2.893	4.13407	–1.37577	–1.96844
C	3.974	3.658	1.48	5.67972	–2.69572	–1.26303
C	8.735	2.795	–0.16	5.40859	2.17687	0.42943
C	9.798	2.441	–0.584	5.14017	3.32765	0.74611
C	11.096	2.051	–1.147	4.82737	4.71474	1.1387
C	11.048	0.599	–1.617	3.75383	4.7109	2.25294
H	11.892	0.362	–2.009	3.50905	5.73591	2.55641
H	10.353	0.499	–2.272	4.11041	4.1666	3.13232
H	10.869	0.027	–0.87	2.83567	4.22617	1.90632
C	12.2	2.172	–0.17	4.29044	5.49533	–0.08483
H	12.198	3.053	0.208	5.02913	5.50853	–0.89174
H	13.038	2.015	–0.612	4.05997	6.53173	0.18955
H	12.081	1.523	0.529	3.37624	5.03302	–0.47114
C	11.383	2.907	–2.393	6.10394	5.41233	1.66497
H	11.472	3.828	–2.135	6.87715	5.44201	0.89123
H	10.659	2.817	–3.016	6.50948	4.87762	2.5289
H	12.199	2.61	–2.804	5.88226	6.44233	1.96906
C	7.532	1.641	2.774	2.80384	1.08667	–0.81874

Table S8. *Cont.*

Atom	S_0			T_1		
	***x*-axis**	***y*-axis**	***z*-axis**	***x*-axis**	***y*-axis**	***z*-axis**
H	8.153	2.312	2.948	3.35844	1.85813	–1.33839
C	7.386	0.629	3.695	1.41522	1.09722	–0.7646
H	7.874	0.644	4.487	0.8729	1.89005	–1.2679
C	6.505	–0.413	3.441	0.73779	0.11574	–0.02748
C	5.797	–0.37	2.24	1.52337	–0.84631	0.62451
H	5.211	–1.057	2.017	1.06676	–1.64519	1.19794
C	5.965	0.684	1.399	2.90604	–0.79917	0.50557
H	5.461	0.701	0.617	3.53492	–1.53919	0.98739
C	6.34	–1.542	4.4	–0.74078	0.09527	0.06221
C	5.747	–2.732	3.993	–1.39852	–0.31183	1.23142
H	5.444	–2.836	3.12	–0.83903	–0.59678	2.11553
C	5.616	–3.767	4.912	–2.78734	–0.3329	1.27241
H	5.181	–4.541	4.64	–3.32402	–0.67494	2.14851
C	6.634	–2.54	6.567	–2.92852	0.43945	–0.89655
H	6.933	–2.467	7.444	–3.57403	0.72464	–1.71967
C	6.772	–1.449	5.719	–1.54605	0.47561	–1.02174
H	7.151	–0.66	6.032	–1.10643	0.77239	–1.96748
C	5.256	–6.593	8.912	–7.68739	–0.72212	0.03858
C	4.005	–6.921	9.514	–8.34153	–1.90513	0.41411
H	3.245	–6.457	9.243	–7.77911	–2.67423	0.9292
C	3.873	–7.898	10.48	–9.69	–2.10615	0.12171
H	3.034	–8.094	10.83	–10.1728	–3.03147	0.42615
C	4.988	–8.589	10.93	–10.4262	–1.13308	–0.56278
H	4.898	–9.231	11.6	–11.4753	–1.29504	–0.79127
C	6.229	–8.328	10.39	–9.80559	0.04971	–0.94193
H	6.975	–8.793	10.69	–10.3883	0.80759	–1.45674
C	6.363	–7.356	9.39	–8.44807	0.26613	–0.6409
C	7.635	–7.068	8.74	–7.76217	1.52369	–0.93108
C	8.866	–7.596	9.167	–8.36051	2.58854	–1.66191
H	8.892	–8.175	9.894	–9.3446	2.44885	–2.09024
C	10.012	–7.27	8.528	–7.68936	3.76545	–1.84138
H	10.828	–7.582	8.849	–8.12826	4.57469	–2.41877
C	9.973	–6.458	7.374	–6.42025	3.95028	–1.23614
C	11.117	–6.122	6.624	–5.71507	5.17661	–1.30331
H	11.952	–6.378	6.943	–6.14778	5.99291	–1.87539
C	11.049	–5.44	5.456	–4.51954	5.33918	–0.63886
H	11.82	–5.208	4.993	–3.98872	6.28474	–0.68636
C	9.76	–5.089	4.955	–3.9998	4.27445	0.12994
H	9.688	–4.666	4.13	–3.07917	4.41633	0.68835
C	8.617	–5.367	5.68	–4.65135	3.0601	0.19454
H	7.786	–5.128	5.336	–4.26901	2.25765	0.80914

Table S8. *Cont.*

Atom	S_0			T_1		
	***x*-axis**	***y*-axis**	***z*-axis**	***x*-axis**	***y*-axis**	***z*-axis**
C	8.694	–6.003	6.92	–5.86588	2.85266	–0.50504
C	3.933	–4.342	7.662	–5.27705	–2.1013	0.83745
C	3.01	–3.584	7.573	–4.93753	–3.21272	1.2197
C	1.953	–2.551	7.366	–4.54207	–4.55897	1.67452
C	1.439	–2.049	8.758	–5.35831	–5.62904	0.91117
H	0.774	–1.368	8.628	–5.07005	–6.63623	1.23553
H	2.173	–1.686	9.259	–5.18848	–5.55102	–0.16675
H	1.054	–2.783	9.241	–6.42975	–5.50338	1.09309
C	0.834	–3.058	6.516	–4.81186	–4.69818	3.19176
H	0.178	–2.365	6.404	–4.52542	–5.69649	3.54372
H	0.426	–3.816	6.943	–5.87222	–4.54575	3.41313
H	1.175	–3.317	5.658	–4.24079	–3.95671	3.75919
C	2.618	–1.314	6.615	–3.03541	–4.78216	1.40216
H	1.962	–0.627	6.486	–2.72519	–5.77882	1.73807
H	2.954	–1.601	5.762	–2.43057	–4.03902	1.93176
H	3.342	–0.972	7.144	–2.81781	–4.69595	0.33322
N	4.93	4.064	0.572	6.40068	–1.69256	–0.65423
N	7.575	–6.236	7.664	–6.5123	1.63827	–0.43822
N	6.816	1.706	1.622	3.54595	0.1452	–0.20715
N	6.076	–3.715	6.162	–3.54938	0.04622	0.22987
Pt	6.92	3.37	0.345	5.76898	0.32823	–0.11131
Pt	5.678	–5.256	7.559	–5.7546	–0.29462	0.24806

Table S9. Composition of frontier molecular orbitals in the first triple-state for **2a**.

	2a						
	C≡C(1)	C≡C(2)	pq(1)	pq(2)	Pt(1)	Pt(2)	bpy
SOMO	1	0	92	0	4	0	3
SOMO−1	16	0	58	0	26	0	0

Table S10. Some selected crystal data and structure refinement details for **2a**·2$CHCl_3$·C_6H_{14} and **4a**·4$CHCl_3$.

	2a·2$CHCl_3$·C_6H_{14}	**4a**·4$CHCl_3$
empirical formula	$C_{60}H_{62}Cl_6N_4Pt_2$	$C_{116}H_{104}Cl_{24}N_8Pt_4$
*F*w	1442.02	3241.23
T (K)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073
crystal system	Triclinic	Triclinic
space group	P−1	P−1
crystal size (mm^3)	0.25 × 0.25 × 0.15	0.4 × 0.2 × 0.1
a (Å)	13.1180(3)	16.1460(5)
b (Å)	13.8089(5)	19.1590(6)
c (Å)	17.1915(6)	23.2760(6)
α (°)	103.738(2)	69.0100(10)
β (°)	94.528(2)	79.852(2)
γ (°)	103.049(2)	69.8410(10)
V ($Å^3$)	2917.89(16)	6299.2(3)
Z	2	2
D_{calc} (Mg/m^3)	1.641	1.709
Absorption coeficient (mm^{-1})	5.105	4.986
F(000)	1416	3152
θ range (°)	1.72 to 25.68	0.94 to 26.37
index ranges	$0 \le h \le 15$, $-16 \le k \le 16$, $-20 \le l \le 20$	$0 \le h \le 20$, $-22 \le k \le 23$, $-28 \le l \le 29$
no. of data/restraints/params	11041/0/631	2571/3/1369
GOF of F^2	1.059	1.105
final R indixes [I› 2σ(I)][a]	R1 = 0.0334, wR2 = 0.0762	R1 = 0.0577, wR2 = 0.1185
R indixes (all data)[a]	R1 = 0.0415, wR2 = 0.0808	R1 = 0.1064, wR2 = 0.1403
Largest diff. peak and hole (e A^{-3})	3.088 and −1.337	1.588 and −1.067