Electronic Supplementary Information

Modulation of luminescent properties for [cyclometalated]-Pt^{II}(isocyanide) complexes upon co-crystallisation with halosubstituted perfluorinated arenes

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S1. Materials and instrumentation

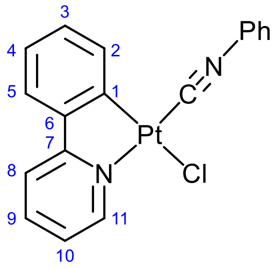
Reagents and materials used. Solvents, $K_2[PtCl_4]$, 2-phenylpyridine, formic acid and anilines were obtained from commercial sources (Aldrich) and used as received, apart from CH_2Cl_2, which was purified by the conventional distillation over $CaCl_2$. Phenyl isocyanide was synthesized by the modified literature procedures [*Angew. Chem. Int. Ed.*, 2018, 39, 12785–12789]. Complex $[Pt(ppy)(\mu\text{-}Cl)]_2$ was prepared by the known method, that includes heating of $K_2[PtCl_4]$ with 2-phenylpyridine in a glacial AcOH [*Z. Kristallogr. - Cryst. Mater.*, 2018, 11, 795–802].

Instrumentation and methods. The high-resolution mass spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source and MeOH was used as the solvent. The instrument was operated at positive ion mode using *m/z* range of 50–3000. The most intensive peak in the isotopic pattern is reported. Infrared spectra (4000–400 cm^{-1}) were recorded on Shimadzu IRAffinity-1 FTIR spectrophotometer in KBr pellets. NMR spectra were recorded on Bruker AVANCE III 400 spectrometers in $CDCl_3$ at ambient temperature (at 400, 100, and 86 MHz for ^1H, ^{13}C, and ^{195}Pt NMR, respectively). Chemical shifts are given in δ-values [ppm] referenced to the residual signals of undeuterated solvent ($CHCl_3$): δ 7.26 (^1H) and 77.2 (^{13}C). ^1H and ^{13}C NMR data assignment for **1** was achieved by using 2D ($^1H,^1H$-COSY, $^1H,^1H$-NOESY, $^1H,^{13}C$-HMQC/HSQC and $^1H,^{13}C$-HMBC) NMR correlation experiments.The luminescence spectra were recorded on a Fliorolog-3 instrument at RT. Quantum luminescence yields were determined on the same instrument with the help of direct measurement using an integrating sphere.

X-ray Structure Determinations. Single-crystal X-ray diffraction experiments were carried out on Agilent Technologies «Xcalibur» and «SuperNova» diffractometers with monochromated MoKα or CuKα radiation, respectively. Crystals were kept at 100(2) K during data collection. Structures have been solved by the Superflip [*J. Appl. Cryst.*, 2007, 786–790, *J. Appl. Cryst.*, 2012, 45, 575–580] structure solution program using Charge Flipping and refined by means of the ShelXL [*Acta Crystallog. C, Struc. Chem.*, 2015, **71**, 3–8] program incorporated in the OLEX2 program package [*J. Appl. Cryst.*, 2009, 339–341]. Empirical absorption correction was applied in CrysAlisPro (Agilent Technologies, 2012) program complex using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm. CCDC numbers 2042269–2042273 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

S2. Synthetic work and characterization

Synthesis of 1. A solution of CNPh (27 mg, 0.26 mmol) in MeCN (4 mL) was added dropwise to a suspension of $[PtCl(ppy)]_2$ (100 mg, 0.13 mmol) in MeCN (2 mL) at RT. The reaction mixture was stirred at RT for approximately 2.5 h; during this period, it turns to a pale-yellow homogeneous solution. Next, small amount of undissolved material was separated by filtration, Et_2O (3 mL) was added to the filtrate and the mixture left to stand without stirring for 3 d at RT. The formed yellow crystals were separated by centrifugation, washed with three 3-mL portions of Et_2O and dried in air at RT. Yield: 108 mg, 85%.



Yellow solid. HR-MS ESI$^+$ *m/z*: calcd. for $C_{18}H_{13}N_2Pt^+$ 452.0722, found 452.0695 $[M-Cl]^+$. IR (KBr, selected bands, cm^{-1}): 2187 (C≡N). ^{1}H NMR (400.13 MHz, $CDCl_3$, δ): 7.12 (td, $J_{H,H}$ = 7.4, 1.4 Hz, 1H, H^3), 7.17 (td, $J_{H,H}$ = 7.5, 1.3 Hz, 1H, H^4), 7.30 (ddd, $J_{H,H}$ =7.3, 5.8, 1.4 Hz, 1H, H^{10}), 7.53–7.66 (m, 7H, H^2, H^5 and 5H from Ph), 7.74–7.76 (m, 1H, H^8), 7.89 (td, $J_{H,H}$ = 8.0, 1.7 Hz, 1H, H^9), 9.56 (d with Pt satellites, $J_{H,H}$ = 5.3 Hz, $J_{H,Pt}$ = 28.6 Hz, 1H, H^{11}). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$, δ): 118.57 (C^8), 122.23 (C^{10}), 124.23 (C^5), 124.41 (C from Ph), 124.70 (C^4), 126.52 (CH from Ph), 129.77 (CH from Ph), 130.10 (CH from Ph), 131.45 (C^3), 136.14 (C^2), 140.27 (C^9), 141.32 (C^1), 144.02 (C^6), 148.98 (C^{11}), 166.37 (C^7); the $C_{isocyanide}$ resonances were not detected. ^{195}Pt{^{1}H} NMR (80.015 MHz, $CDCl_3$, δ): –3893.

Synthesis of 2. Complex **2** was synthesized by the published procedure [*Russ. J. Gen. Chem.*, 2020, 4, 648-654].

Crystal Growth. The single crystals of supramolecular adducts **1**·(IC_6F_5), **1**·(*o*-$Br_2C_6F_4$), **2**·(BrC_6F_5), and **2**·(*o*-$Br_2C_6F_4$ were prepared by slow evaporation of a CH_2Cl_2 solution of a mixture of the corresponding isocyanide complex and X-^{F}arenes taken in a 1:1 molar ratio at 20–25° C.

S3. X-ray diffraction studies

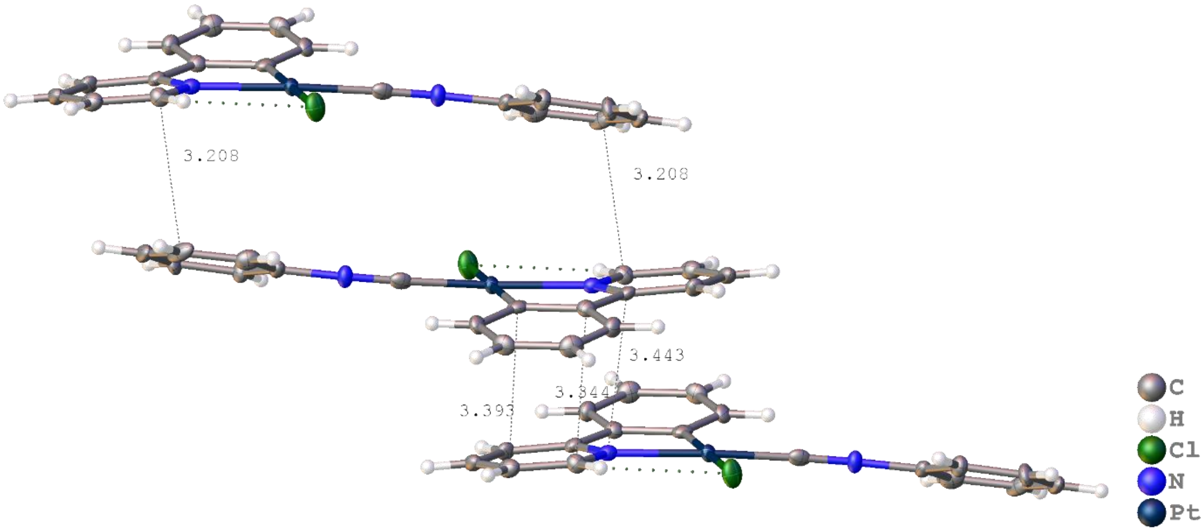


Figure S1. A fragment of the layer-type crystal packing of **1** with week π···π stacking interactions between neighboring molecules.

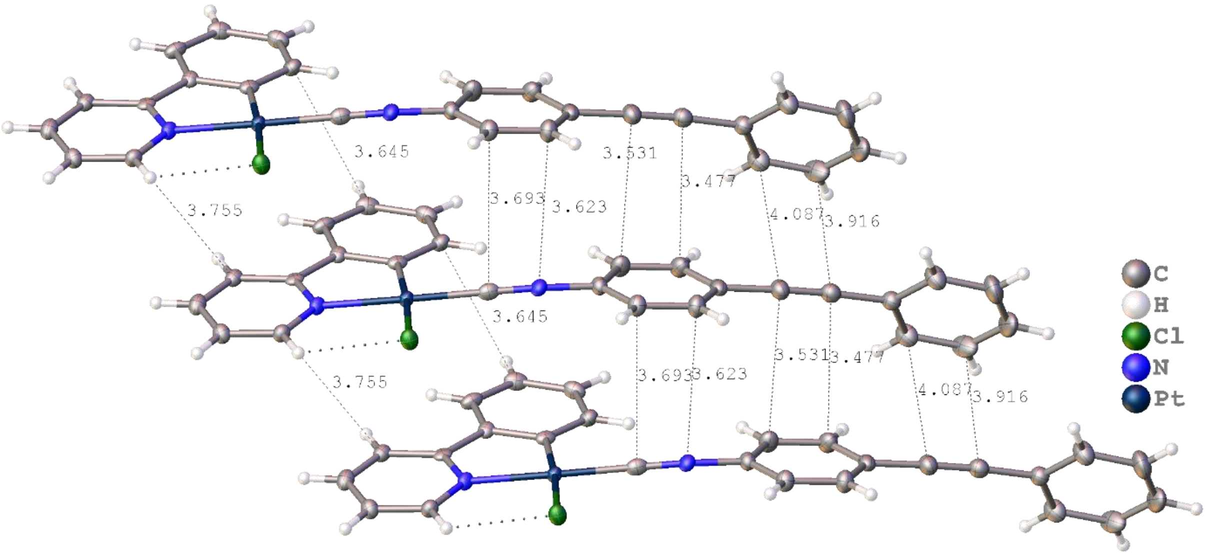


Figure S2. A fragment of the layer-type crystal packing of **2** week π···π stacking interactions between neighboring molecules (CCDC 1956173, ref [*Russ. J. Gen. Chem.*, 2020, 4, 648-654]).

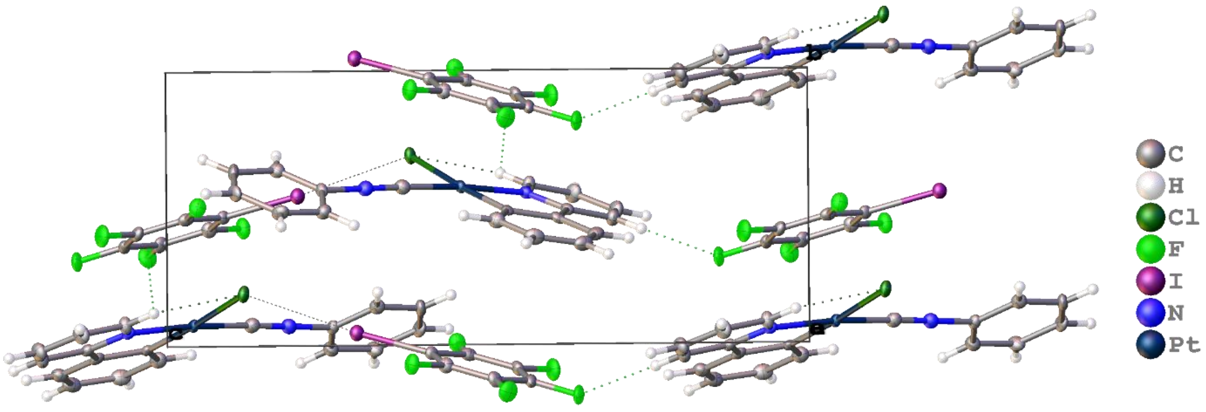


Figure S3. A fragment of the crystal packing of **1**·(IC_6F_5).

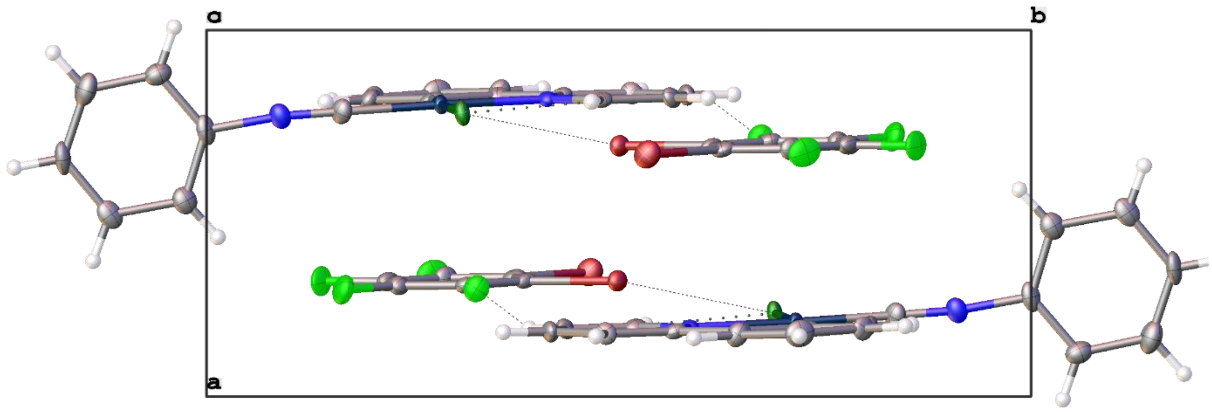


Figure S4. A fragment of the crystal packing of **1**·(*o*-$Br_2C_6F_4$).

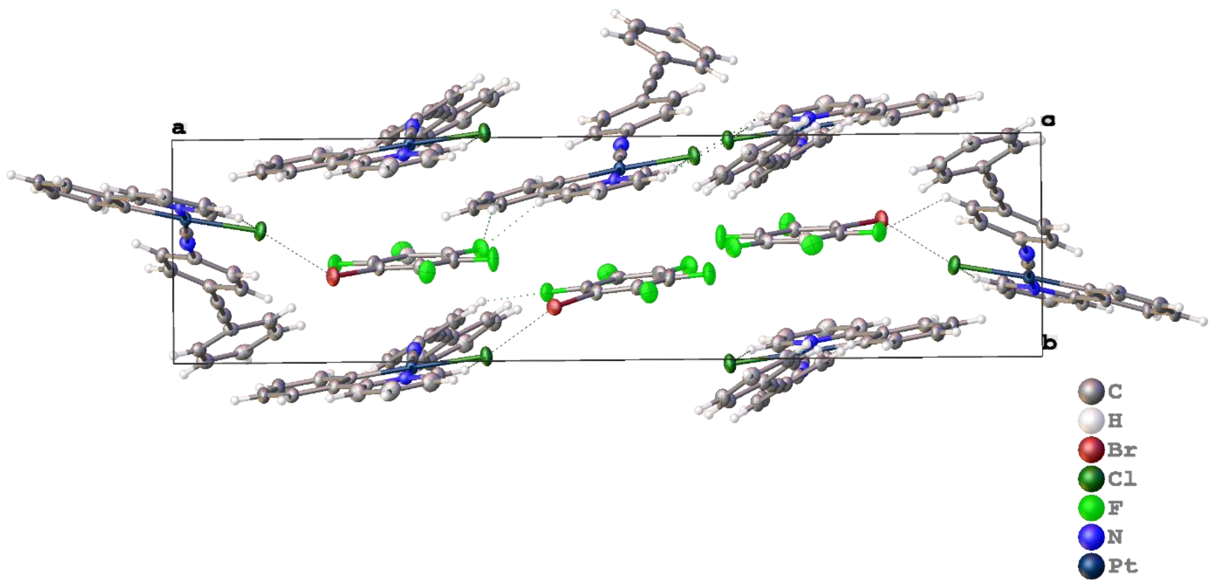


Figure S5. A fragment of the crystal packing of **2**·(BrC_6F_5).

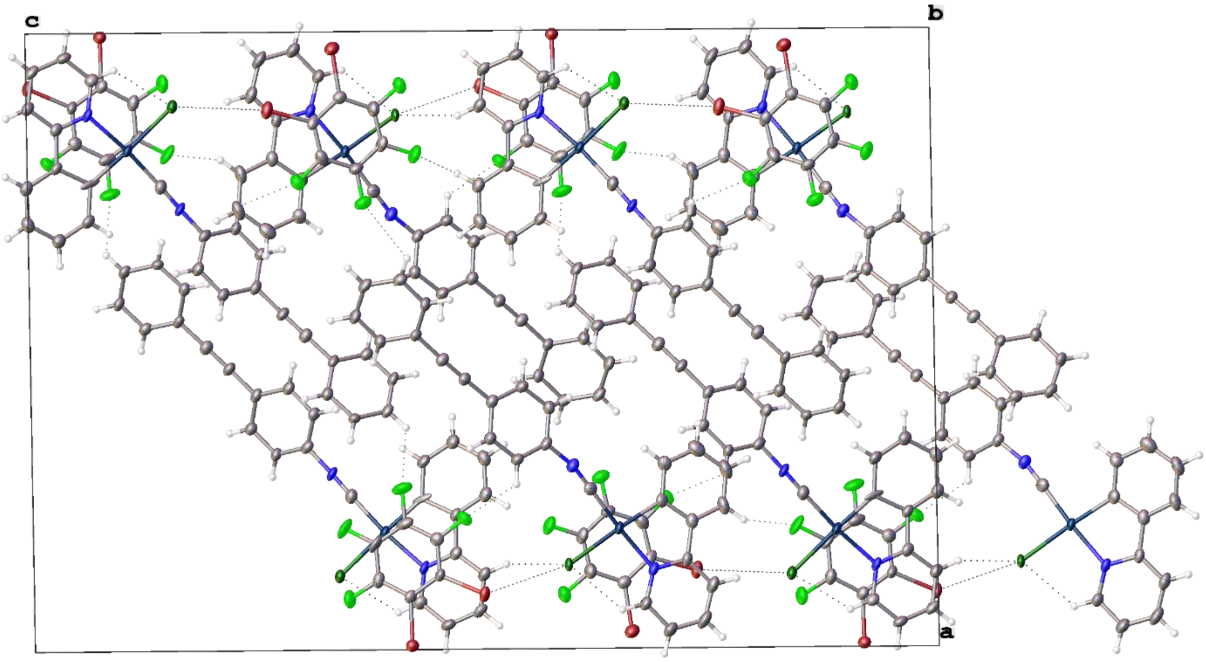


Figure S6. A fragment of the crystal packing of **2**·(*o*-$Br_2C_6F_4$).

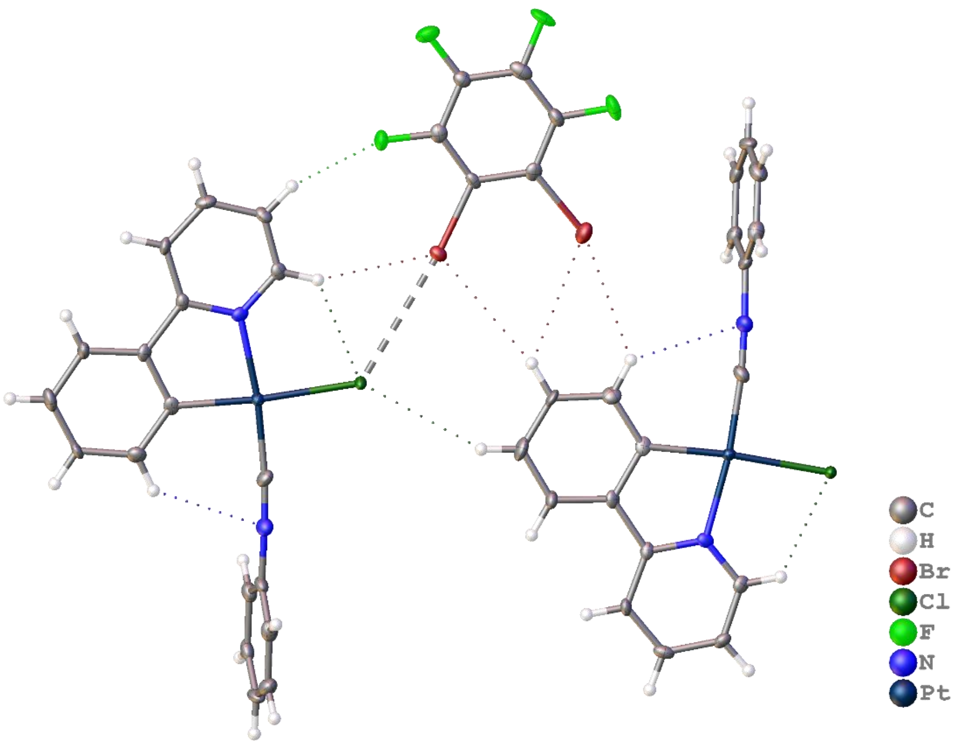


Figure S7. The closest supramolecular environment of the *o*-$Br_2C_6F_4$ in **1**·(*o*-$Br_2C_6F_4$). The dashed line denotes the XB contact. The dotted lines denote a H-bond contacts.

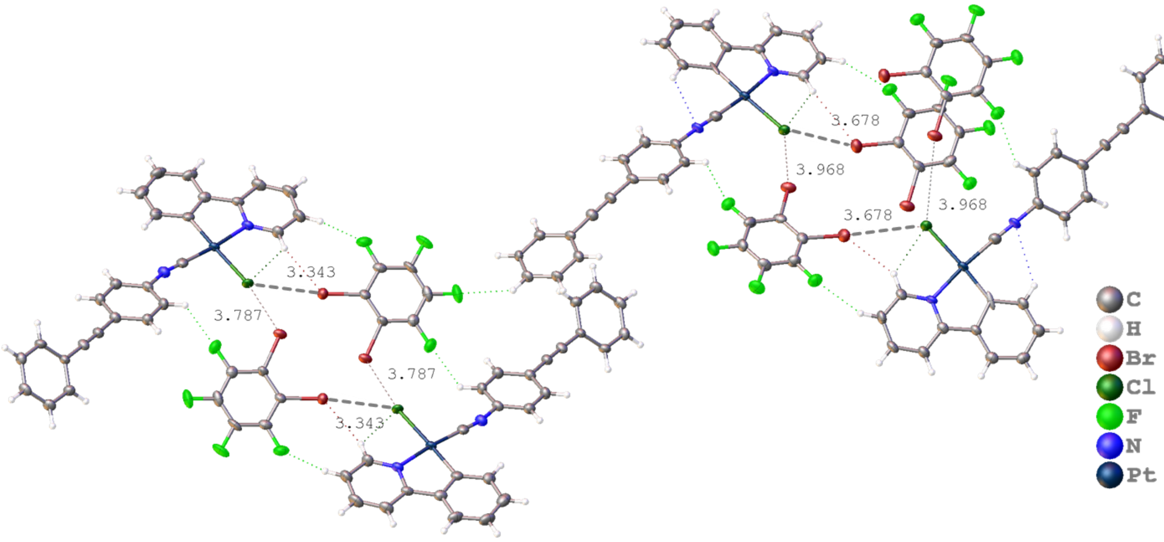


Figure S8. A fragment of the crystal packing of **2**·(*o*-$Br_2C_6F_4$). The dashed lines denote the XB contacts.

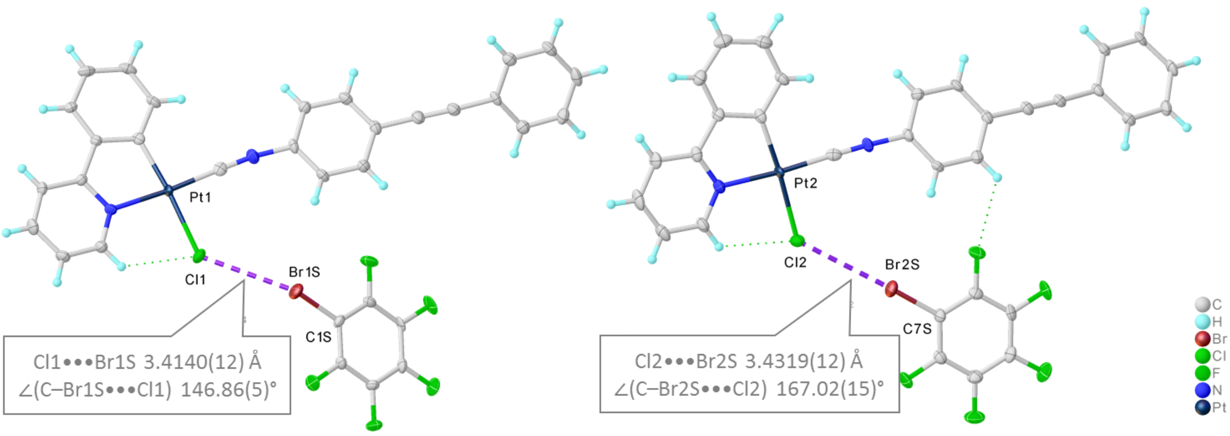


Figure S9. Two types of crystallography independent isocyanide complexes and two types of crystallography independent X-^{F}Arenes in **2**·(BrC_6F_5). The dashed lines denote the XB contacts.

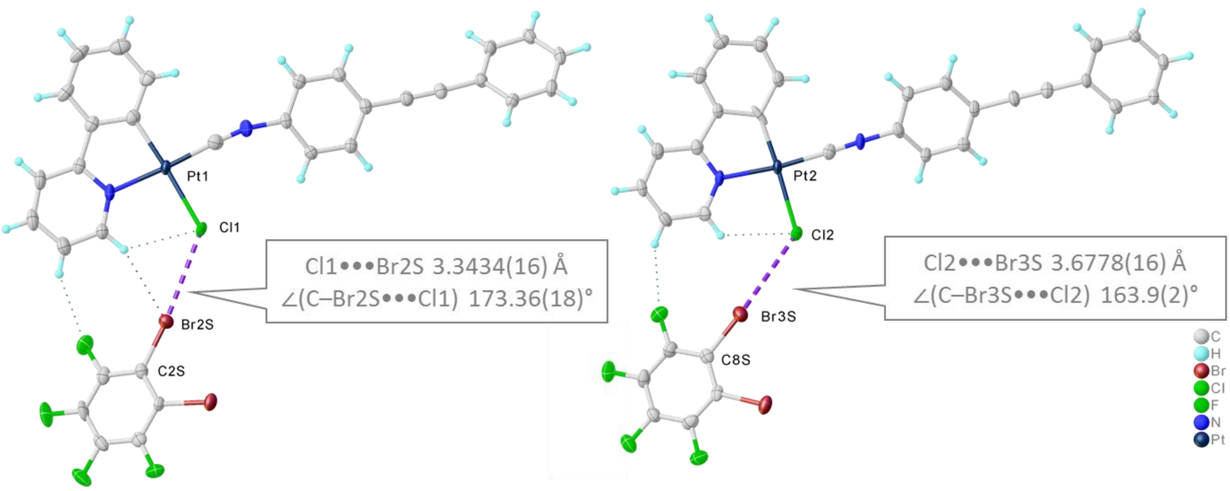


Figure S10. Two types of crystallography independent isocyanide complexes and two types of crystallography independent X-^{F}Arenes in **2** (*o*-$Br_2C_6F_4$). The dashed lines denote the XB contacts.

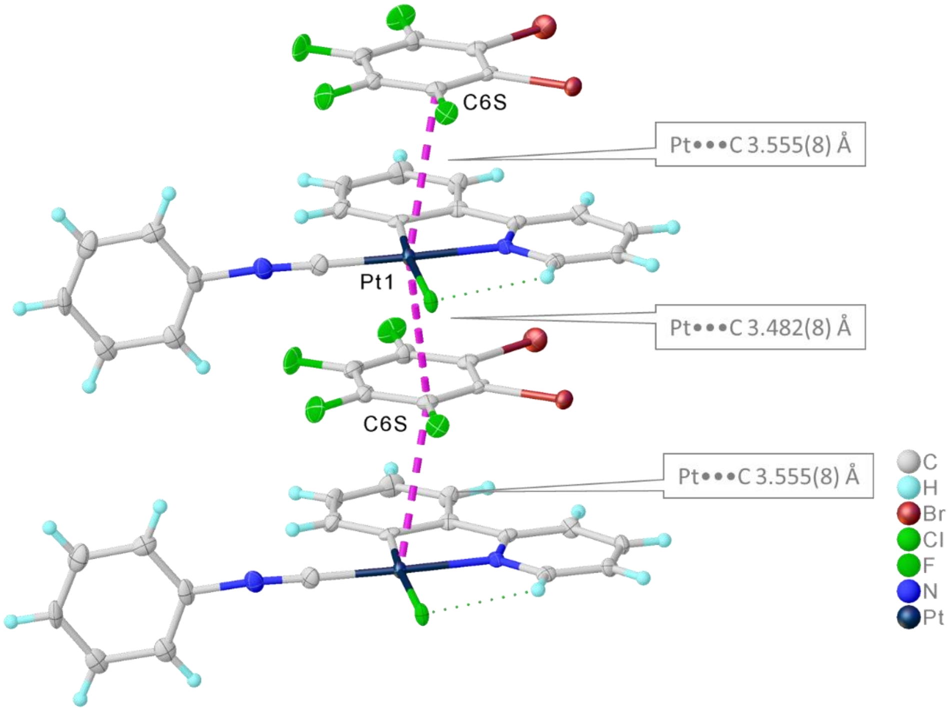


Figure S11. Molecular structure of **1**·(*o*-$Br_2C_6F_4$) with dashed Pt•••C short contacts.

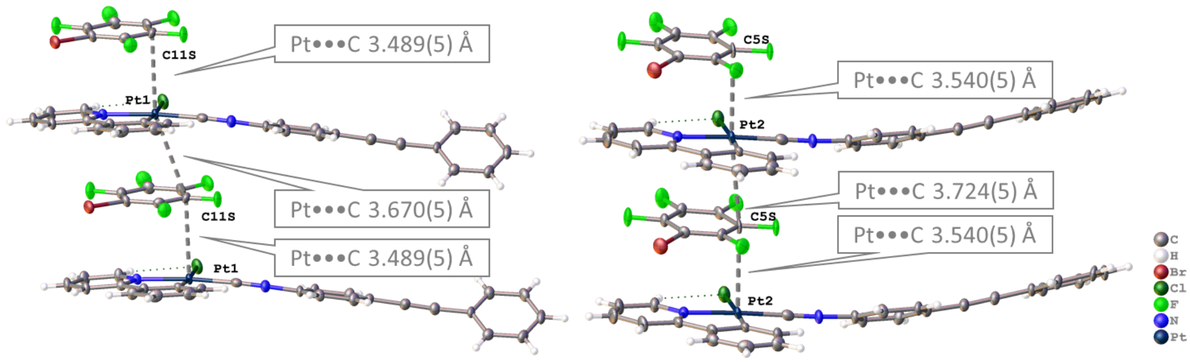


Figure S12. Two types of crystallography independent isocyanide complexes and two types of crystallography independent X-^{F}Arenes in **2**·(BrC_6F_5). The dashed lines denote the Pt•••C short contacts.

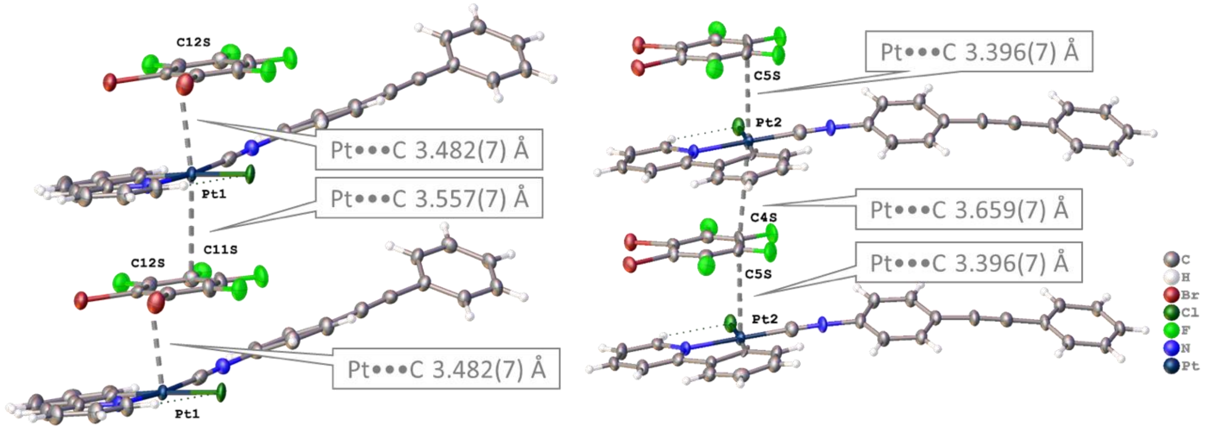


Figure S13. Two types of crystallography independent isocyanide complexes and two types of crystallography independent X-^{F}Arenes in **2**·(*o*-$Br_2C_6F_4$). The dashed lines denote the Pt•••C short contacts.

S4. Computational details

The full geometry optimization of BrC_6F_5, IC_6F_5, *o*-$Br_2C_6F_4$, and *p*-$Br_2C_6F_4$ model species and single point calculations based on the experimental X-ray geometries of **1**, **2**, **1**·(IC_6F_5), **1**·(*o*-$Br_2C_6F_4$), **2**·(BrC_6F_5), and **2**·(*o*-$Br_2C_6F_4$) have been carried out at the DFT level of theory using the dispersion-corrected hybrid functional ωB97XD [Phys. Chem. Chem. Phys. 2008, 10, 6615.] with the help of Gaussian-09 [M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, M. J. A.;, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, C. J.;, D. J. Fox, in Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2010.] program package. The Douglas–Kroll–Hess 2^{nd} order scalar relativistic calculations requested relativistic core Hamiltonian were carried out using the DZP-DKH basis sets [Mol. Phys. 2010, 108, 1965. || J. Chem. Phys. 2009, 130, 064108. || Chem. Phys. Lett. 2013, 582, 158. || J. Mol. Struct. - Theochem 2010, 961, 107.] for all atoms. The molecular surface electrostatic potential calculations and topological analysis of the electron density distribution with the help of the atoms in molecules (QTAIM) method developed by Bader [Chem. Rev. 1991, 91, 893.] has been performed by using the Multiwfn program (version 3.7) [J. Comput. Chem. 2012, 33, 580.]. The Cartesian atomic coordinates for all model species and supramolecular associates presented in **Table S4**, Supporting Information.

Table S1. Values of maximal electrostatic potential calculated on the 0.001 a.u. molecular surfaces ($V_S(\mathbf{r})_{max}$,) for the optimized equilibrium geometries of BrC_6F_5, IC_6F_5, *o*-$Br_2C_6F_4$, and *p*-$Br_2C_6F_4$ model species (ωB97XD/DZP-DKH level of theory).

Model species	$V_S(\mathbf{r})_{max}$ (σ-holes on Br or I atoms), kcal/mol
BrC_6F_5	22.7
IC_6F_5	31.0
o-$Br_2C_6F_4$	21.4
p-$Br_2C_6F_4$	22.4

Table S2. Values of the density of all electrons – ρ(**r**), Laplacian of electron density – ∇^2ρ(**r**) and appropriate λ_2 eigenvalues, energy density – H_b, potential energy density – V(**r**), and Lagrangian kinetic energy – G(**r**) (a.u.) at the bond critical points (3, –1), corresponding to intermolecular noncovalent interactions Pt···C and X···Cl (X = Br, I) in **1**·(IC_6F_5), **1**·(*o*-$Br_2C_6F_4$), **2**·(BrC_6F_5), and **2**·(*o*-$Br_2C_6F_4$), as well as energies for these contacts E_{int} (kcal/mol), defined by different approaches.

Contact	ρ(**r**)	∇^2ρ(**r**)	λ_2	H_b	V(**r**)	G(**r**)	E_{int}[a]	E_{int}[b]	E_{int}[c]	E_{int}[d]
2·(BrC_6F_5)										
Br···Cl, 3.414 Å	0.009	0.030	–0.009	0.001	–0.005	0.006	1.6	1.6	1.8	2.1
Br···Cl, 3.432 Å	0.008	0.028	–0.008	0.001	–0.004	0.006	1.3	1.6	1.5	2.1
Pt···C, 3.537 Å	0.008	0.021	–0.008	0.001	–0.003	0.004	0.9	1.1	---	---
Pt···C, 3.540 Å	0.008	0.025	–0.008	0.001	–0.003	0.005	0.9	1.3	---	---
Pt···C, 3.489 Å	0.009	0.025	–0.009	0.001	–0.004	0.005	1.3	1.3	---	---
Pt···C, 3.513 Å	0.009	0.024	–0.009	0.001	–0.004	0.005	1.3	1.3	---	---
2·(*o*-$Br_2C_6F_4$)										
Br···Cl, 3.343 Å	0.010	0.034	–0.010	0.001	–0.006	0.007	1.9	1.9	2.2	2.5
Br···Cl, 3.678 Å	0.006	0.017	–0.006	0.001	–0.003	0.004	0.9	1.1	1.1	1.4
Pt···C, 3.480 Å	0.009	0.024	–0.009	0.001	–0.004	0.005	1.3	1.3	---	---
Pt···C, 3.558Å	0.008	0.024	–0.008	0.001	–0.003	0.005	0.9	1.3	---	---
Pt···C, 3.394 Å	0.010	0.028	–0.010	0.001	–0.005	0.006	1.6	1.6	---	---
Pt···C, 3.659 Å	0.006	0.016	–0.006	0.001	–0.002	0.003	0.6	0.8	---	---
1·(IC_6F_5)										
I···Cl, 3.169 Å	0.018	0.057	–0.018	0.001	–0.013	0.014	4.1	3.8	5.5	5.9
Pt···C, 3.456 Å	0.009	0.026	–0.009	0.001	–0.004	0.005	1.3	1.3	---	---
Pt···C, 3.562 Å	0.007	0.020	–0.007	0.001	–0.003	0.004	0.9	1.1	---	---
1·(*o*-$Br_2C_6F_4$)										
Br···Cl, 3.482 Å	0.008	0.025	–0.008	0.001	–0.004	0.005	1.3	1.3	1.5	1.8
Pt···C, 3.482 Å	0.008	0.024	–0.008	0.001	–0.004	0.005	1.3	1.3	---	---
Pt···C, 3.555 Å	0.007	0.021	–0.007	0.001	–0.003	0.004	0.9	1.1	---	---

[a] E_{int} = –V(**r**)/2 for all types of noncovalent interactions [Chem. Phys. Lett. 1998, 285, 170.] (this correlation was initially developed for hydrogen bonding).

[b] E_{int} = 0.429G(**r**) for all types of noncovalent interactions [J. Comput. Chem. 2012, 33, 2303.] (this correlation was initially developed for hydrogen bonding).

[c] E_{int} = 0.58(−V(**r**)) or 0.68(−V(**r**)) for noncovalent interactions involving bromine and iodine atoms as halogen bond donor, respectively [Russ. Chem. Rev. 2014, 83, 1181.].

[d] E_{int} = 0.57G(**r**) or 0.67G(**r**) for noncovalent interactions involving bromine and iodine atoms as halogen bond donor, respectively [Russ. Chem. Rev. 2014, 83, 1181.].

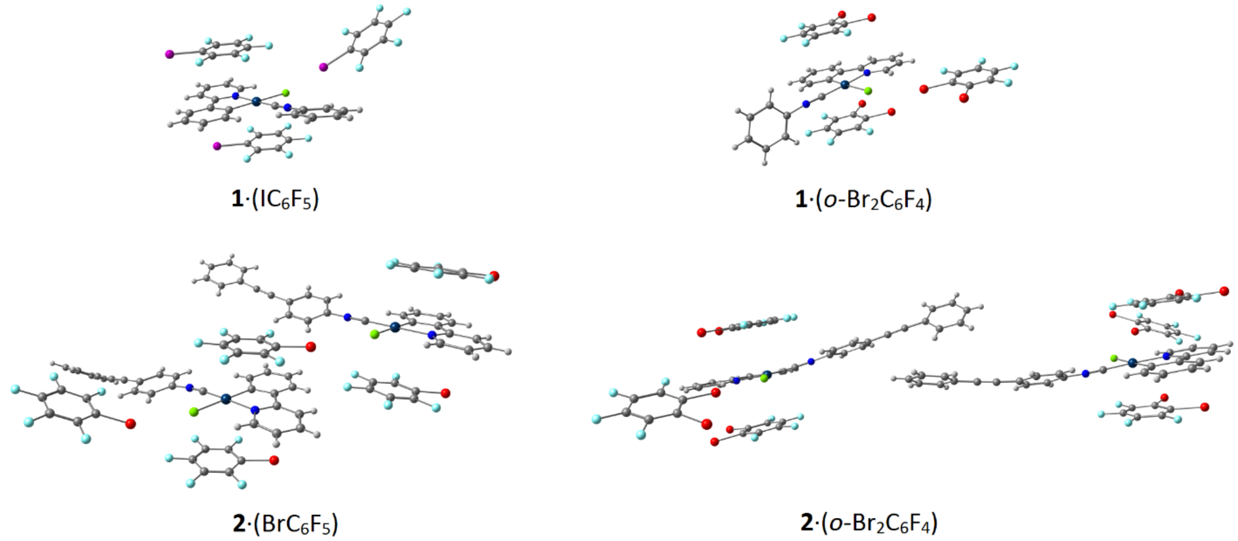


Figure S14. Structures of model supramolecular associates.

TD-DFT calculations (ωB97XD/DZP-DKH level of theory, 25 first exited states) were carried out for a correct assignment of the absorption bands and to elucidate the nature of the transitions in the absorbance profile. The simulated based on TD-DFT calculations and the experimental UV-vis spectra of complexes **1** and **2** [*Russ. J. Gen. Chem.*, 2020, 4, 648-654] have a good agreement. The lowest-energy spin-allowed transitions for all complexes to give S1 are HOMO → LUMO transitions (**Table S3**). This absorption is mainly assigned to a ^{1}IL/^{1}MLCT admixture located on the cyclometalated group.

Table S3. Theoretically calculated transition energies (in eV) for most important low-lying singlet excited states of **1** and **2** (in the area of absorption wavelengths <250 nm), absorption wavelengths (in nm), oscillator strengths *f* and main contributing transitions.

State[a]	Transition energy	Wavelength	*f*	Main contributing transitions[b]
1				
S1	2.7960	443.44	0.0152	HOMO → LUMO
S2	3.7270	332.67	0.0124	HOMO → LUMO+1
S3	3.7826	327.78	0.0680	HOMO → LUMO+4
S4	4.0189	308.50	0.0074	HOMO → LUMO+2
S5	4.2339	292.83	0.0442	HOMO-1 → LUMO
S6	4.6327	267.63	0.0879	HOMO-3 → LUMO
S7	4.6933	264.17	0.0029	HOMO-2 → LUMO
S8	4.6996	263.82	0.0047	HOMO → LUMO+5
S9	4.8347	256.45	0.0992	HOMO-1 → LUMO+1
S10	4.9342	251.28	0.0038	HOMO-1 → LUMO+4
2				
S1	2.7946	443.66	0.0159	HOMO → LUMO
S2	3.6823	336.70	0.0067	HOMO → LUMO+1
S3	3.8090	325.51	0.2103	HOMO → LUMO+6
S4	4.0178	308.59	0.0040	HOMO → LUMO+2
S5	4.1990	295.27	0.1312	HOMO-1 → LUMO
S6	4.3127	287.49	1.4202	HOMO-2 → LUMO
S7	4.6058	269.19	0.0496	HOMO → LUMO+7
S8	4.6455	266.89	0.0523	HOMO → LUMO+7
S9	4.6714	265.41	0.0021	HOMO-3 → LUMO
S10	4.8146	257.52	0.0579	HOMO-5 → LUMO

[a] The excited states are labeled according to their vertical transition energies.

[b] Plots of molecular orbitals involving in transitions are given in **Figures S15** and **S16**.

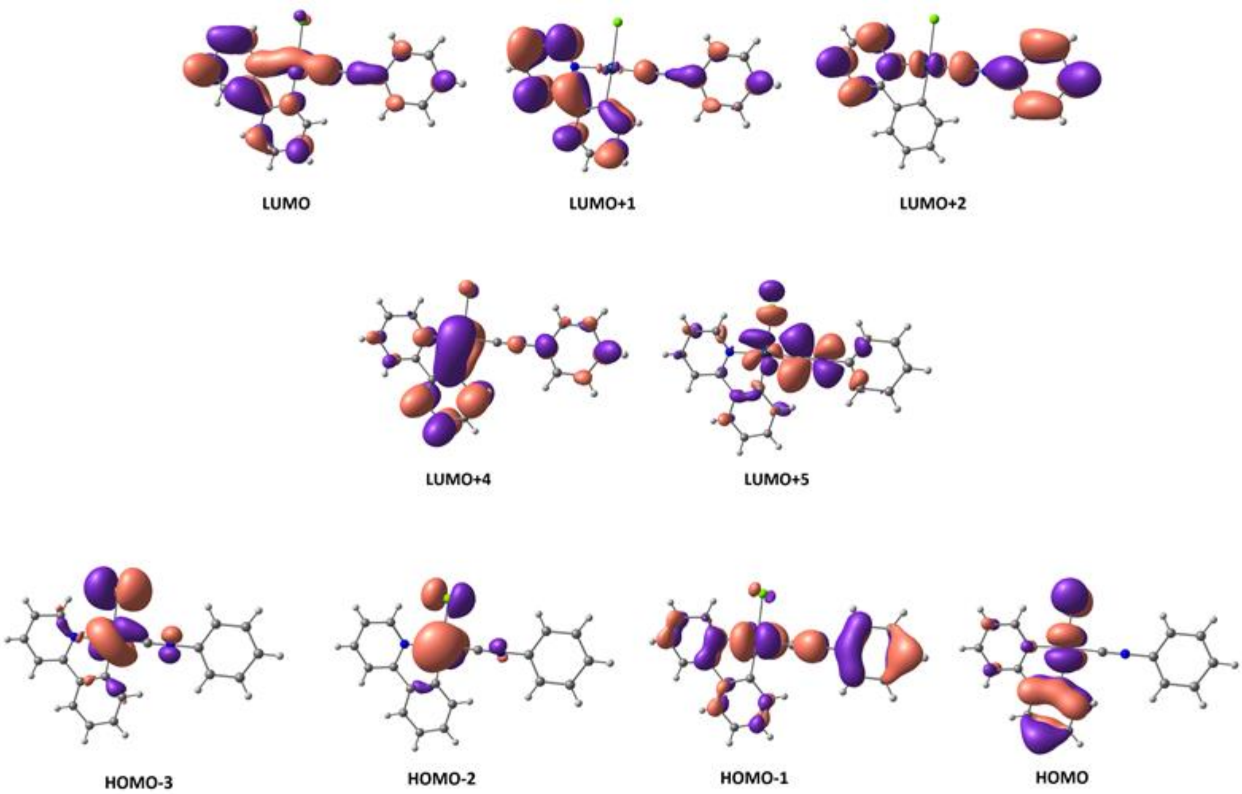


Figure S15. Surface plots of the HOMOs and LUMOs for complex **1**.

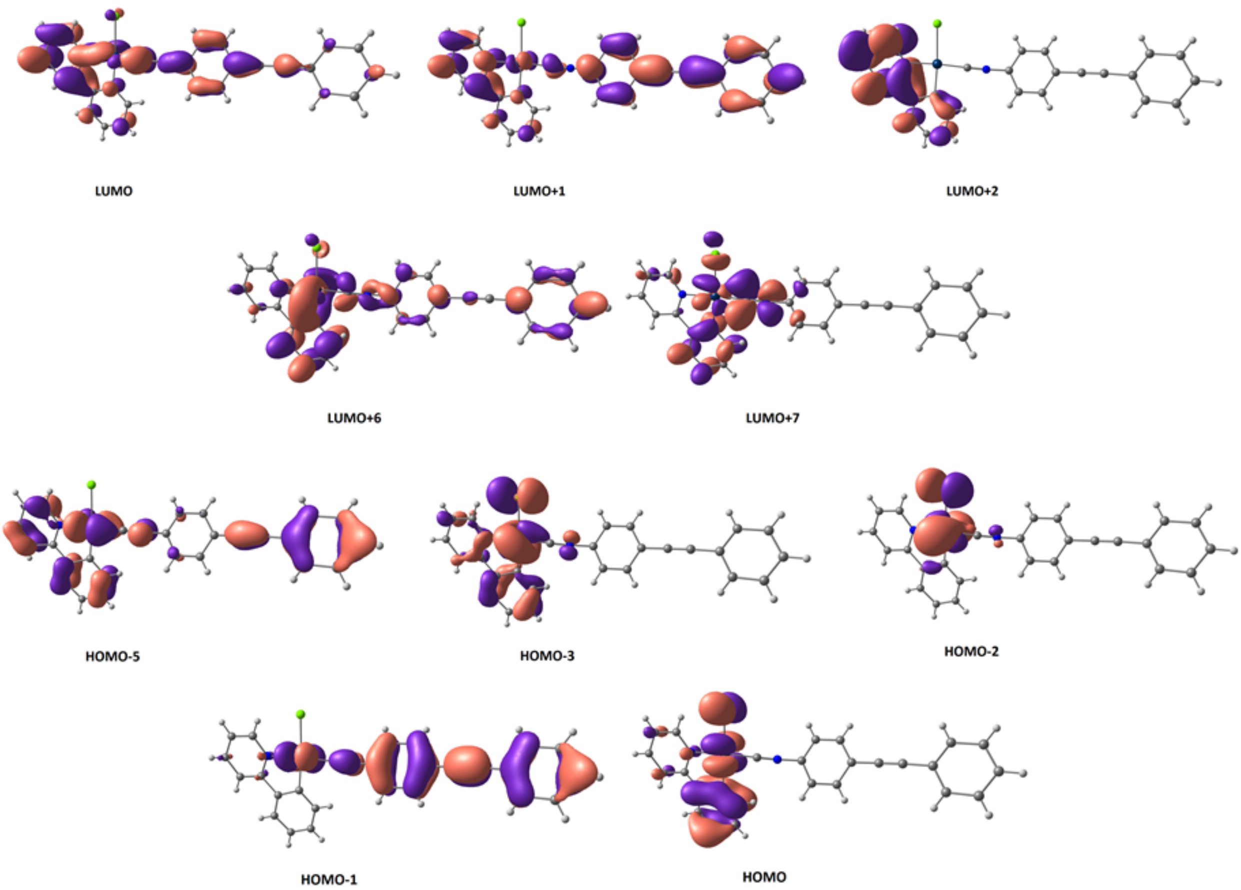
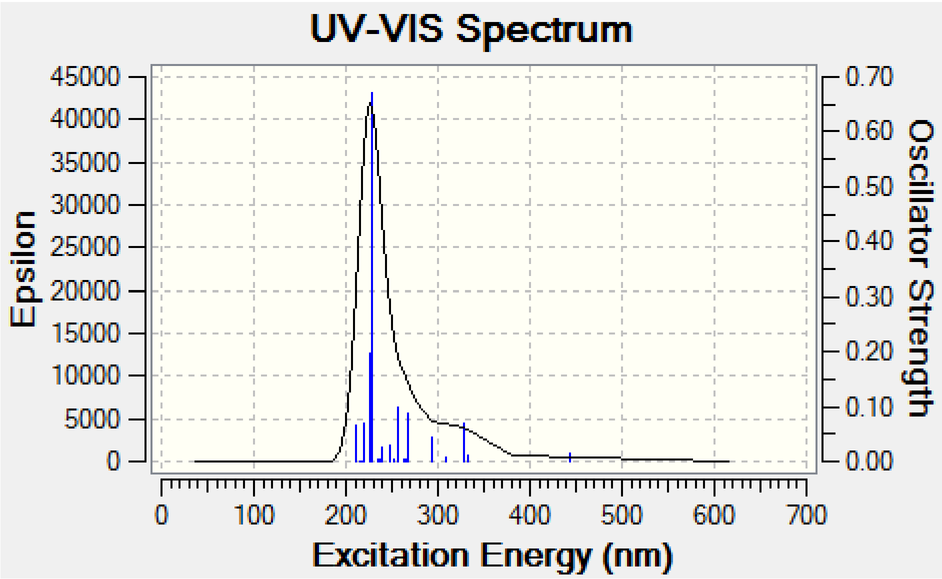


Figure S16. Surface plots of the HOMOs and LUMOs for complex **2**.



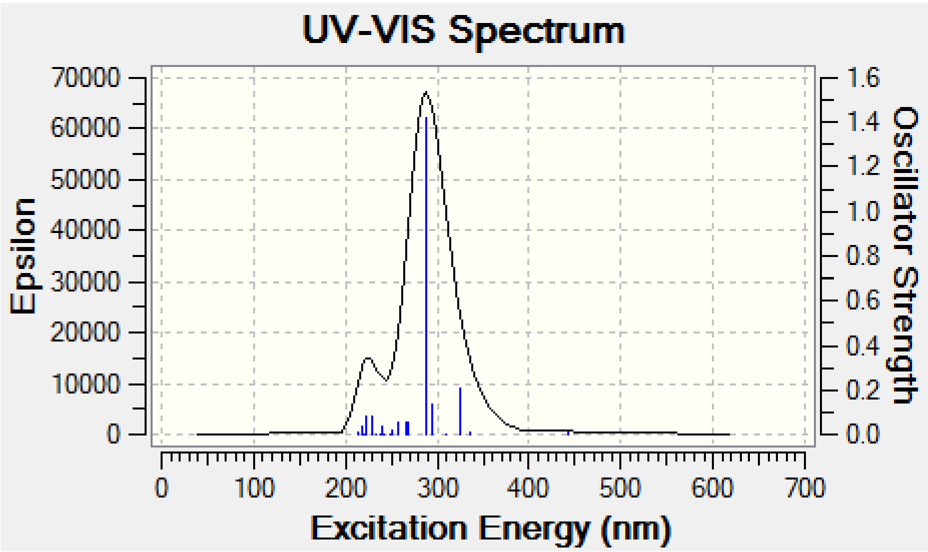


Figure S17. Calculated UV-Vis spectra for complexes **1** (top) and **2** (bottom).

Table S4. Cartesian atomic coordinates for all model species and supramolecular associates.

Atom	X	Y	Z
2·(BrC_6F_5)			
Pt	11.380854	1.031324	8.263357
Cl	9.107656	0.635857	7.625604
N	10.937295	1.377596	10.249477
N	12.211537	0.284142	5.435858
C	12.012962	1.675875	11.030184
C	13.208599	1.456760	8.914408
C	13.283621	1.764228	10.298514
C	11.846217	1.851874	12.401269

H	12.577174	2.061298	12.936627
C	12.704260	-1.095574	1.540081
C	13.648323	-0.098955	3.535067
H	14.370338	0.268684	3.991550
C	13.791822	-0.559803	2.240723
H	14.624117	-0.514050	1.828040
C	14.398807	1.564197	8.172764
H	14.389224	1.370033	7.263288
C	14.404411	-3.098001	-2.642989
H	15.054124	-3.281980	-2.003435
C	12.880045	-1.598125	0.201687
C	11.912685	0.605746	6.506351
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C	12.395040	-0.197203	4.142622
C	11.459133	-1.169084	2.162042
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C	12.233006	-2.204578	-3.235029
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C	7.060786	-0.404302	2.191409
Br	12.510532	-1.688456	11.698688
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Br	23.499597	4.152449	14.316817
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F	-6.797375	2.701845	29.895762
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H	19.333320	10.412052	-4.946616
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H	17.662879	12.175106	-0.977805
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F	10.465714	10.355658	-2.018433
C	13.739434	10.600377	-0.521541
C	13.443100	10.227507	0.767072
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C	12.157449	9.890113	1.112509
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F	13.726670	8.589773	-6.098478
F	11.758425	8.488410	-7.958924
F	16.257963	7.916435	-6.767507
F	12.315752	7.744842	-10.485013
C	15.589472	7.500123	-8.988122
C	15.293138	7.872993	-7.699508
C	13.309710	7.779595	-9.589249
C	14.007487	8.210387	-7.354072
C	14.611615	7.455234	-9.966858
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C	2.249522	-2.687608	9.489587
H	2.423587	-3.600916	9.494037
C	3.303357	-1.806172	9.354333
H	4.174046	-2.122886	9.277522
C	0.955716	-2.256168	9.616115
H	0.268462	-2.872865	9.724994
C	1.108944	4.329864	4.380481
H	1.076687	4.347833	3.452050
Br	1.953451	7.752158	13.319453
Br	2.061512	8.273752	16.679640
F	1.827697	10.394766	11.900378
F	1.792777	12.895263	12.888386
F	2.012835	11.218987	17.255777
F	1.913046	13.306600	15.549833
C	1.873120	10.571054	13.228702
C	1.987187	9.695803	15.460391

C	1.860408	11.849910	13.726087
C	1.940716	9.471578	14.068585
C	1.910214	12.054032	15.080808
C	1.966556	10.976205	15.938143
Br	4.559960	7.711642	8.495689
Br	4.451900	7.190048	5.135503
F	4.685714	5.069034	9.914764
F	4.720634	2.568537	8.926756
F	4.500576	4.244813	4.559365
F	4.600365	2.157200	6.265309
C	4.640291	4.892746	8.586440
C	4.526224	5.767997	6.354751
C	4.653003	3.613890	8.089055
C	4.572695	5.992223	7.746557
C	4.603197	3.409768	6.734334
C	4.546855	4.487595	5.876999
Br	-2.300340	7.711642	8.495689
Br	-2.408400	7.190048	5.135503
F	-2.174586	5.069034	9.914764
F	-2.139666	2.568537	8.926756
F	-2.359724	4.244813	4.559365
F	-2.259935	2.157200	6.265309
C	-2.220009	4.892746	8.586440
C	-2.334076	5.767997	6.354751
C	-2.207297	3.613890	8.089055
C	-2.287605	5.992223	7.746557
C	-2.257103	3.409768	6.734334
C	-2.313445	4.487595	5.876999
BrC_6F_5			
Br	2.506572	0.000052	-0.000088
F	0.556447	2.363735	0.000247
F	0.555592	-2.363984	0.000255
F	-3.494934	0.000867	0.000005
F	-2.135392	-2.355728	-0.000051
F	-2.136266	2.354914	-0.000118
C	-2.170000	-0.000267	-0.000068
C	-1.472940	1.205828	-0.000155
C	0.636057	-0.000244	0.000075
C	-1.473750	-1.205932	0.000044

C	-0.079578	-1.198935	-0.000154
C	-0.079629	1.199539	0.000265
IC_6F_5			
I	2.284072	0.000028	-0.000014
F	0.133945	2.367844	0.000015
F	-3.902848	-0.000413	-0.000056
F	-2.545058	-2.353937	-0.000018
F	-2.545438	2.353775	0.000055
F	0.134578	-2.367475	0.000058
C	-0.489594	1.195255	-0.000041
C	-1.882697	1.204349	0.000071
C	-0.489377	-1.195151	0.000129
C	-2.578049	-0.000098	-0.000094
C	0.233274	0.000254	-0.000009
C	-1.882299	-1.204551	-0.000011
o-$Br_2C_6F_4$			
Br	1.720538	1.715528	0.000066
Br	1.720585	-1.715484	-0.000094
F	-1.113408	-2.709574	0.000049
F	-1.113645	2.709531	-0.000252
F	-3.431995	-1.361454	0.000009
F	-3.431858	1.361423	-0.000093
C	-2.286637	0.694661	0.000069
C	0.143466	0.702334	0.000168
C	-1.075200	1.382462	-0.000015
C	-1.075224	-1.382502	0.000091
C	0.143444	-0.702287	0.000146
C	-2.286706	-0.694812	0.000130
p-$Br_2C_6F_4$			
Br	3.282135	-0.000316	0.000164
Br	-3.282101	-0.000183	-0.000027
F	1.331094	-2.362913	-0.000512
F	-1.331961	-2.362407	0.000028
F	1.331145	2.363024	-0.000745
F	-1.330537	2.363252	0.000290
C	0.696873	-1.196955	0.000059
C	-0.696498	-1.196774	0.000169
C	0.697152	1.197055	0.000111
C	1.412796	0.000242	-0.000050

C	-0.697124	1.197311	0.000029
C	-1.413007	0.000600	0.000289
1			
Pt	15.241121	11.412510	-7.767918
Cl	13.413570	12.238400	-6.446116
N	14.132784	11.235342	-9.489343
C	16.691545	10.777762	-8.999975
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C	16.247782	10.569244	-10.329228
C	14.821193	10.796586	-10.579839
C	12.805337	11.443860	-9.568929
H	12.351106	11.752604	-8.819687
C	17.731899	11.345393	-4.102905
C	12.098043	11.210726	-10.739010
H	11.180140	11.352822	-10.773791
C	16.332307	11.414175	-6.233096
C	18.024764	10.520011	-8.710418
H	18.340297	10.647185	-7.844151
C	17.135363	10.139900	-11.318124
H	16.837105	10.020567	-12.190758
C	18.892422	10.075462	-9.701008
H	19.779465	9.898563	-9.486583
C	14.153024	10.559832	-11.777013
H	14.624646	10.267132	-12.522597
C	17.214632	11.881168	-2.926050
H	16.365931	12.260388	-2.908761
C	18.455648	9.891561	-10.994701
H	19.048423	9.600976	-11.650319
C	19.265326	11.289644	-1.816928
H	19.788396	11.273911	-1.047164
C	19.005192	10.774866	-4.155398
H	19.333320	10.412052	-4.946616
C	17.996838	11.836279	-1.777982
H	17.662879	12.175106	-0.977805
C	19.763416	10.761833	-3.007329
H	20.618880	10.396131	-3.024923
C	12.787942	10.761109	-11.853212
H	12.334841	10.596351	-12.649139
2			

Pt	16.198362	7.250156	15.052846
Cl	13.917968	6.918727	14.424236
N	15.779526	7.584907	17.042845
N	17.021068	6.711982	12.166337
C	18.042863	7.572184	15.699187
C	16.863643	7.819572	17.820504
C	17.937041	6.205190	6.683936
C	19.647792	7.065393	2.224931
H	20.400910	7.509341	1.907385
C	18.746569	6.508417	1.328420
H	18.891754	6.581665	0.412738
C	17.293616	6.499935	10.825449
C	18.461203	7.046309	10.276904
H	19.076630	7.489274	10.815226
C	17.629598	5.842591	1.805765
H	17.032725	5.452955	1.208572
C	17.394325	5.754238	3.184885
H	16.636751	5.315796	3.499550
C	18.140882	7.833708	17.099084
C	19.239720	7.593389	14.975828
H	19.219260	7.433202	14.060146
C	18.678353	6.913426	8.922442
H	19.449936	7.267226	8.542727
C	16.380564	5.802302	10.046405
H	15.619544	5.430782	10.430663
C	20.452985	7.847845	15.589201
H	21.231200	7.856093	15.079941
C	19.432555	6.965731	3.587982
H	20.050517	7.329603	4.179884
C	18.077729	6.241238	5.494868
C	16.709211	8.032325	19.189096
H	17.452078	8.204917	19.721406
C	16.617737	5.669419	8.696098
H	16.021086	5.188787	8.168747
C	16.721304	6.924028	13.273677
C	20.525095	8.088871	16.945880
H	21.348283	8.248768	17.348035
C	17.746575	6.249720	8.111260
C	18.293612	6.321109	4.083889

C	14.345063	7.714255	18.935324
H	13.489557	7.660749	19.296478
C	15.442614	7.986382	19.753709
H	15.327992	8.135217	20.664404
C	19.361413	8.091698	17.711349
H	19.400953	8.265407	18.624095
C	14.545587	7.526947	17.592498
H	13.813770	7.354964	17.044923

S5. Photophysical data

Table S5. Photophysical properties of **1** and **2** and their co-crystals with X-^{F}Arenes in the solid state at RT.

Compound	λ_{em}, nm	Φ_{em}, %	τ_{obs}, µs
1[a]	481, 517, 549	4	0.9
1·IC_6F_5[b]	478, 504, 513, 544sh	7	1.0
1·(*o*-$Br_2C_6F_4$)[c]	484, 517, 549sh	9	1.3
2[a]	485, 519, 546sh	<1	0.4
2·(*o*-$I_2C_6F_4$)[a]	486, 520, 552sh	<1	0.5

[a] Excitation at 410 nm. [b] Excitation at 360 nm. [c] Excitation at 392 nm.
2·(BrC_6F_5) is not emissive at RT.

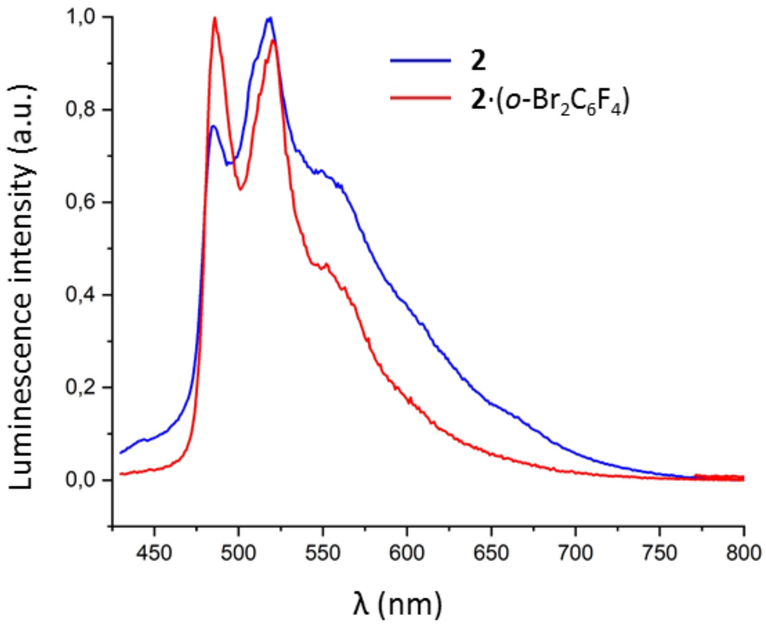

Figure S18. Normalized solid-state emission spectra of **2** and **2**·(*o*-$Br_2C_6F_4$) at 298 K.