Supporting Information

White light emission from planar remote phosphor based on NHC cycloplatinated complexes.

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EXPERIMENTAL SECTION.

General procedures and instrumentation. ^{1}H, $^{13}C\{^{1}H\}$, $^{195}Pt\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 400 and 300 MHz instrument using the standard references: TMS for ^{1}H and ^{13}C and Na_2PtCl_6 in D_2O for ^{195}Pt. Coupling constant, *J* is given in Hz and assignments are based on ^{1}H-^{1}H COSY and ^{1}H-^{13}C HSQC and HMBC experiments. Infrared spectra were recorded on Perkin-Elmer Spectrum 100 FT-IR spectrometer (ATR range 250-4000 cm^{-1}) as neat solids. Mass spectra were acquired using the Microflex matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) Bruker or an Autoflex III MALDI-TOF Bruker instruments. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS analyzer. Molar conductances were carried out on a Philips PW9509 conductimeter in acetone solution (5×10^{-4} M). UV-visible spectra were registered on a Unicam UV4 spectrophotometer. Diffuse reflectance UV-vis (DRUV) spectra were recorded on a Thermo electron corporation evolution 600 spectrophotometer equipped with a Praying Mantis integrating sphere. The solid samples were homogeneously diluted with silica. The mixtures were placed in a homemade cell equipped with quartz window. Steady-state photoluminescence spectra were recorded on a Jobin-Yvon Horiba Fluorolog FL-3-11 Tau 3 spectrofluorimeter. Phosphorescence lifetimes were recorded with a Fluoromax phosphorimeter accessory containing a UV xenon flash tube. Nanosecond lifetimes were recorded with a Datastation HUB-B with a nanoLED controller and software DAS6. The nanoLEDs employed for lifetime measurements were of 340, 370, 455 and 483 nm. The lifetime data were fitted using the Jobin-Yvon software package and the Origin Pro 8 program. Quantum yields in the solid state were measured using the Hamamatsu Absolute PL Quantum Yield Measurement System C11347-11.

X-ray Structure determinations. Single crystals of **6, 9** and **10**· were obtained by slow diffusion of *n*-hexane into a saturated CH_2Cl_2 (**6**) or acetone (**9** and **10**) solutions; Suitable crystals of **8** were obtained by slow diffusion of diethyl ether into a saturated CH_2Cl_2 solution. The crystal data, data collection parameters, and structure solution and refinement details for the crystal structures determined are summarized in Table S1. Crystals were mounted at the end of quartz fibres. Data collections were carried out on an Oxford Diffraction Xcalibur diffractometer using graphite monochromated $Mo_{K\alpha}$ radiation (0.71073 Å). The sample temperature was controlled using an Oxford Diffraction CryojetXL cooling device (100(2) K). The diffraction frames were integrated and corrected from absorption by using the CrysAlis RED program.[1] Structure solution, followed by full-matrix least-squares refinement (all data) was performed using SHELX[2] under the WinGX package.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters and refined without positional constraints, except as noted below. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *Ueq* value of the atoms they are linked to (1.5 times for methyl groups). For **8 · 0.5 Et_2O** and **9·Me_2CO** the solvent molecules are highly disordered and were modelled and refined with the use of geometry restrains and the use of a common set of anisotropic thermal parameters. In spite of the disorder described above, all molecular complexes are well defined. Full-matrix least-squares refinement of these models against *F*2 converged to final residual indices given in Table S1. CCDC Nos. 1439911-1439914 contain the supplementary crystallographic data for **6**, **8·0.5·Et_2O**, **9·Me_2CO** and **10·Me_2CO** respectively.

Computational Methods

Density functional calculations were performed using the B3LYP hybrid density functional[4, 5] under the Gaussian09 package.[6] The SDD pseudopotential and associated basis set[7] was used for platinum, and the 6-31G(d)[8, 9] basis set was used for all other atoms. Geometry optimisations were performed under no symmetry restrictions using the initial coordinates of models derived from X-ray data. Atomic coordinates (x, y, z) for the optimized structures are listed in the Tables S3−S6. The time-dependent density-functional (TD-DFT) calculations were also carried out in the presence of dichloromethane using the polarizable continuum model (PCM) implemented Gaussian 09 package. Mulliken population analysis was carried out using Gaussian 09 package for interpretation purposes. Molekel,[10] GaussView5 and ChemissianLab[11] program packages were used for analysis and graphic representation of molecular structures and orbitals.

Synthesis and characterization.

Ethyl 4-(1H-Imidazol-1-yl) benzoate (1). To a solution of ethyl 4-bromobenzoate (0.5 mL, 3.06 mmol) in degassed dimethylsulfoxide (10 mL), imidazole (312.7 mg, 4.59 mmol), K_2CO_3 (846.5 mg, 6.12 mmol) and Cu_2O (43.8 mg, 0.31 mmol) were added in the presence of 4 Å molecular sieves (400.0 mg). After 24 h at 110 ºC under an argon atmosphere the crude was cooled down to rt, washed with 100 mL of ethyl acetate and then filtered through Celite. The solution was treated with H_2O (2 x 20 mL) and brine (2 x 20 mL). The organic layer was dried using anhydrous $MgSO_4$. Evaporation under reduced pressure yielded a white solid which was washed with hexane to give a white-off powder (**1**, 520.9 mg, 80%). Elemental analysis Calcd (%) for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.24; H, 5.11; N, 12.99. IR (ATR): ν_{max} / cm^{-1}=

1697 (s, C=O). ^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.41 (s, H_1), 8.07 (d, $^{3}J_{H,H}$ = 8.7, 2H, H_7), 7.88 (t, $^{3}J_{H,H}$ = 1.3, H_{im}), 7.84 (d, $^{3}J_{H,H}$ = 8.7, 2H, H_6), 7.15 (s, H_{im}), 4.33 (q, $^{3}J_{H,H}$ = 7.1, 2H, OCH_2), 1.34 (t, $^{3}J_{H,H}$ = 7.1, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR plus HMBC and HSQC (101 MHz, DMSO-d_6): δ = 164.9 (s. *C*OOEt), 140.7 (s, C_5), 136.3 (s, C_1), 130.9 (s, 2C, C_7), 130.7 (s, C_{im}), 127.8 (s, C_8), 119.9 (s, 2C, C_6), 116.5 (s, C_{im}), 60.8 (s, OCH_2), 14.1 (s, OCH_2CH_3).

1-(4-(Ethoxycarbonyl)phenyl)-3-methyl-1*H*-imidazolium Iodide (2). Methyl iodide (0.22 mL, 3.44 mmol) was added to a solution of **1** (496.1 mg, 2.29 mmol) in dried THF (10 mL) under Ar atmosphere. The mixture was refluxed for 24 h and after cooling, the solvent was removed in vacuo and hexane (10 mL) was added to the residue to a white solid (**2**, 778.3 mg, 95%). Elemental analysis Calcd (%) for $C_{13}H_{15}IN_2O_2$: C, 43.59; H, 4.22; N, 7.82. Found: C, 43.37; H, 3.84; N, 7.88. IR (ATR): ν_{max} / cm^{-1} = 1701 (s, C=O). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.91 (s, br, H_1), 8.39 (t, $^{3}J_{H,H}$ = 1.8, H_2), 8.20 (d, $^{3}J_{H7,H6}$ = 8.7, 2H, H_7), 8.00 (t, $^{3}J_{H,H}$ = 1.8, H_3), 7.95 (d, $^{3}J_{H7,H6}$ = 8.7, 2H, H_6), 4.36 (q, $^{3}J_{H,H}$ = 7.1, 2H, OCH_2), 3.97 (s, 3H, H_4), 1.35 (t, $^{3}J_{H\text{-}H}$ = 7.1, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR plus HMBC and HSQC (101 MHz, DMSO-d_6): δ = 164.5 (s, *C*OOEt), 138.0 (s, C_5), 136.4 (s, C_1), 131.0 (s, 2C, C_7), 130.7 (s, C_8), 124.6 (s, C_3), 121.9 (s, 2C, C_6), 120.7 (s, C_2), 61.3 (s, OCH_2), 36.3 (s, C_4), 14.1 (s, OCH_2CH_3).

[PtCl(η^3-2-Me-C_3H_4)(HC^C*-κC*)] (3) (HC^C* = 1-(4-ethoxycarbonylphenyl)-3-methyl-1*H*-imidazol-2-ylidene). To a suspension of **2** (412.8 mg, 1.15 mmol) in anhydrous dichloromethane (30 mL), Ag_2O (133.5 mg, 0.58 mmol) was added in the absence of light under an argon atmosphere. After 3 h of stirring at rt, [{Pt(μ-Cl)(η^3-2-Me-C_3H_4)}$_2$] (312.6 mg, 0.55 mmol) was added and the mixture was allowed to react for 3 h to give a yellow precipitate (AgI), which was separated by filtration through Celite under Ar. The resulting solution was evaporated to dryness and treated with *n*-

hexane (3 x 15 mL) to afford pale-yellow solid, **3** (379.2 mg, 70%). Elemental analysis Calcd (%) for $C_{17}H_{21}ClN_2O_2Pt$: C, 39.58; H, 4.10; N, 5.43. Found: C, 39.71; H, 3.84; N, 5.05. IR (ATR): ν_{max} / cm^{-1} = 1711 (s, C=O), 281 (s, Pt-Cl). ^{1}H NMR (400 MHz, methylene chloride-d_2): δ = 8.08 (d, $^3J_{H7,H6}$ = 8.6, 2H, H_7), 7.85 (d, $^3J_{H7,H6}$ = 8.6, 2H, H_6), 7.27 (d, $^3J_{H2,H3}$ = 2.1, $^4J_{H,Pt}$ = 13.5, 1H, H_2), 7.14 (d, $^3J_{H2,H3}$ = 2.1, $^4J_{H,Pt}$ = 10.6, 1H, H_3), 4.36 (q, $^3J_{H,H}$ = 7.1, 2H, OCH_2), 3.90 (s, 3H, Me (NHC)), 3.60 (m, 1H$_{syn}$, η^3-2-Me-C_3H_4), 2.62 (m, $^2J_{H,Pt}$ = 28.2, 1H$_{syn}$, η^3-2-Me-C_3H_4), 2.34 (m, $^2J_{H,Pt}$ = 34.1, 1H$_{anti}$, η^3-2-Me-C_3H_4), 1.72 (s, $^3J_{H,Pt}$ = 64.7, 3H, Me, η^3-2-Me-C_3H_4), 1.41 (m, 1H$_{anti}$, η^3-2-Me-C_3H_4), 1.35 (t, $^3J_{H,H}$ = 7.1, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR plus HMBC and HSQC (101 MHz, methylene chloride-d_2): δ = 176.6 (s, C_1), 165.5 (s, *C*OOEt), 143.8 (s, C_5), 130.1 (s, 2C, C_7), 125.1 (s, 2C, C_6), 122.8 (s, $^3J_{C,Pt}$ = 41.2, C_3), 120.5 (s, $^3J_{C,Pt}$ = 43.1, C_2), 117.9 (s, $^1J_{C,Pt}$ = 69.8, $C^{2'}$, η^3-2-Me-C_3H_4), 61.2 (s, OCH_2), 57.3 (s, $^1J_{C,Pt}$ = 77.1, $C^{1'}$, η^3-2-Me-C_3H_4), 37.8 (s, C_4 (Me), NHC)), 36.5 (s, $^1J_{C,Pt}$ = 289.1, $C^{3'}$, η^3-2-Me-C_3H_4), 22.9 (s, $^2J_{C,Pt}$ = 40.1, $C^{4'}$ (Me), η^3-2-Me-C_3H_4), 14.1 (s, OCH_2CH_3). ^{195}Pt{^{1}H} NMR (85.6 MHz, methylene chloride-d_2): δ = –4457 ppm.

[{Pt(*μ*-Cl)(EtOOC–C^C*)}$_2$] (4). Compound **3** (476.6 mg, 0.92 mmol) was refluxed in 2-methoxyethanol (15 mL) for 3 h and then it was cooled down to rt. The resulting solid was filtered and washed with dichloromethane (10 mL) and diethylether (15 mL). Then, it was treated with activated carbon in hot acetonitrile (3 x 40 mL) and the suspension was filtered through Celite. The resulting solution was evaporated to dryness and the residue was washed with hexane to give a yellow solid, **4** (303.6 mg, 71%). Elemental analysis Calcd (%) for $C_{26}H_{26}Cl_2N_4O_4Pt_2 \cdot 2\ CH_3CN$: C, 35.97; H, 3.22; N, 8.39. Found: C, 35.70; H, 2.82; N, 8.35. IR (ATR): ν_{max} / cm^{-1} = 1711 (s, C=O), 294 (m, Pt-Cl). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.06 (s, $^3J_{H7,Pt}$ = 58.6, 1H, H_7), 8.12 (d, $^3J_{H2,H3}$ = 2.0, 1H, H_2), 7.73 (dd, $^3J_{H9,H10}$ = 8.1, $^3J_{H9,H7}$ = 1.8, 1H, H_9), 7.51 (d, $^3J_{H2,H3}$ = 2.0, 1H, H_3),

7.48 (d, $^{3}J_{H9,H10}$ = 8.1, 1H, H_{10}), 4.26 (q, $^{3}J_{H,H}$ = 7.1, 2H, OCH_2), 4.15 (s, 3H, H_4), 1.29 (t, $^{3}J_{H,H}$ = 7.1, 3H, OCH_2CH_3). $^{13}C\{^{1}H\}$ NMR plus HMBC and HSQC (101 MHz, DMSO-d_6): δ = 166.0 (s, *C*OOEt), 155.6 (s, C_1), 149.8 (s, C_5), 135.4 (s, C_7), 126.8 (s, C_6), 126.5 (s, C_9), 126.2 (s, C_8), 125.3 (s, C_3), 115.6 (s, C_2), 111.5 (s, C_{10}), 60.2 (s, OCH_2), 37.7 (s, C_4), 14.3 (s, OCH_2CH_3).

[Pt(EtOOC–C^C*)(CN^{t}Bu)$_2$]PF$_6$ (5). *Tert*-butyl isocyanide (51.4 μL, 0.44 mmol) and KPF_6 (40.8 mg, 0.22 mmol) were added to a suspension of **4** (100.0 mg, 0.11 mmol) in acetone (25 mL). The mixture was allowed to react for 4 h at rt. The solvent was evaporated under reduced pressure and the crude was extracted with dichloromethane (4 x 30 mL) and filtered through Celite. The solution was then evaporated to *c.a.* 2 mL and Et_2O (15 mL) was added to give a white solid, which was then filtered and dried (**5**, 122.5 mg, 77%). Elemental analysis Calcd (%) for $C_{23}H_{31}F_6N_4O_2PPt$: C, 37.56; H, 4.25; N, 7.62. Found: C, 37.27; H, 3.76; N, 7.54. IR (ATR): ν_{max} / cm^{-1} = 2239, 2218 (m, C≡N), 1707 (m C=O). ^{1}H NMR (400 MHz, methylene chloride-d_2): δ = 8.30 (d, $^{4}J_{H7,H9}$ = 1.6, $^{3}J_{H7,Pt}$ = 61.3, H_7), 7.93 (dd, $^{3}J_{H9,H10}$ = 8.2, $^{4}J_{H9,H7}$ = 1.6, H_9), 7.46 (d, $^{3}J_{H2,H3}$ = 2.1, H_2), 7.24 (d, $^{4}J_{H10,Pt}$ = 11.5, H_{10}), 7.15 (d, $^{4}J_{H3,Pt}$ = 9.8, 1H, H_3), 4.35 (q, $^{3}J_{H,H}$= 7.1, 2H, OCH_2), 3.96 (s, 3H, H_4), 1.76 (s, 9H, Me (^{t}Bu)), 1.66 (s, 9H, Me (^{t}Bu)), 1.38 (t, $^{3}J_{H,H}$= 7.1, 3H, OCH_2CH_3). $^{13}C\{^{1}H\}$ NMR plus HMBC and HSQC (101 MHz, methylene chloride-d_2): δ = 166.5 (s. *C*OOEt), 165.8 (s, C_1), 151.6 (s, C_5), 139.9 (s, C_7), 136.5 (s, C_6), 129.8 (s, C_9), 129.4 (C_8), 124.4 (s, C_3), 116.5 (s, C_2), 112.1 (s, C_{10}), 61.6 (s, OCH_2), 39.2 (s, C_4), 30.41 (s, 3C, Me (^{t}Bu)), 30.25 (s, 3C, Me (^{t}Bu)), 14.8 (s, OCH_2CH_3). $^{195}Pt\{^{1}H\}$ NMR (85.6 MHz, methylene chloride-d_2): δ = –4681.2 (s). MS (MALDI+): m/z 590.2 [Pt(C^C*)(CN^{t}Bu)$_2$]$^+$. Λ_M (5x10^{-4} M acetone solution) = 78.2 Ω^{-1} cm^2 mol^{-1}.

[Pt(EtOOC–C^C*)(CNXyl)$_2$]PF$_6$ (6). It was prepared following the method described for **5**. CNXyl (80.3 mg, 0.60 mmol), KPF_6 (56.4 mg, 0.30 mmol) and **4** (138.0 mg, 0.15 mmol). **6** (214.9 mg, 86%). Elemental analysis Calcd (%) for $C_{31}H_{31}F_6N_4O_2PPt$: C, 44.77; H, 3.76; N, 6.74. Found: C, 44.84; H, 3.45; N, 6.68. IR (ATR): ν_{max} / cm^{-1} = 2200, 2179 (m, C≡N), 1698 (m, C=O). ^{1}H NMR (400 MHz, methylene chloride-d_2): δ = 8.51 (d, $^4J_{H7,H9}$ = 1.7, $^3J_{H7,Pt}$ = 62.5, H_7), 7.98 (dd, $^3J_{H9,H10}$ = 8.2, $^4J_{H9,H7}$ = 1.7, H_9), 7.55 (d, $^3J_{H2,H3}$ = 2.1, H_2), 7.41 (m, 2H, H_p (Xyl)), 7.33 (d, $^4J_{H10,Pt}$ = 11.5, H_{10}), 7.27 (d, $^3J_{H,H}$ = 7.7, 4H, H_m (Xyl)), 7.24 (d, $^4J_{H3,Pt}$ = 9.6, H_3), 4.30 (q, $^3J_{H,H}$= 7.1, 2H, OCH_2), 4.02 (s, 3H, H_4), 2.57 (s, 6H, Me (Xyl)), 2.54 (s, 6H, Me (Xyl)), 1.28 (t, $^3J_{H-,}$= 7.1, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR plus HMBC and HSQC (101 MHz, methylene chloride-d_2): δ = 166.3 (s. *C*OOEt), 165.1 (s, C_1), 151.4 (s, C_5), 140.6 (s, $^2J_{C7,Pt}$ = 59.9, C_7), 136.6 (s, 3C, C_6 and C_o (Xyl)), 136.3 (s, 2C, C_o (Xyl)), 131.76 (s, C_p (Xyl)), 131.74 (s, C_p (Xyl)), 130.2 (s, C_9), 129.5 (C_8), 129.3 (s, 2C, C_m (Xyl)), 129.2 (s, 2C, C_m (Xyl)), 124.8 (s, C_3), 116.8 (s, C_2), 112.4 (s, $^3J_{C10,Pt}$ = 37.0, C_{10}), 61.5 (s, OCH_2), 39.6 (s, C_4), 19.27 (s, 2C, Me (Xyl)), 19.24 (s, 2C, Me (Xyl)), 14.6 (s, OCH_2CH_3). ^{195}Pt{^{1}H} NMR (85.6 MHz, methylene chloride-d_2): δ = –4595.7 (s). MS (MALDI+): m/z 686.2 $[Pt(C^C^*)(CNXyl)_2]^+$. Λ_M (5x10^{-4} M acetone solution) = 74.7 Ω^{-1} cm^2 mol^{-1}.

[Pt(NC–C^C*)(CN^{t}Bu)$_2$]PF$_6$ (7). It was prepared following the method described for **5**. CN^{t}Bu (69.4 μL, 0.59 mmol), KPF_6 (55.2 mg, 0.29 mmol) and **4a** (121.2 mg, 0.15 mmol). **7** (164.2 mg, 81%). Elemental analysis Calcd (%) for $C_{21}H_{26}F_6N_5PPt$: C, 36.63; H, 3.81; N, 10.17. Found: C, 36.85; H, 4.20; N, 10.09. IR (ATR): ν_{max} / cm^{-1} = 2239 (m, C≡N, CN^{t}Bu), 2221 (s, C≡N, CN^{t}Bu and C^C*). ^{1}H NMR (400 MHz, methylene chloride-d_2): δ = 7.79 (d, $^3J_{H7,H9}$ = 1.7, $^3J_{H7,Pt}$ = 60.2, 1H, H_7), 7.57 (dd, $^3J_{H9,H10}$ = 8.1, $^4J_{H9,H7}$ = 1.7, 1H, H_9), 7.46 (d, $^3J_{H2,H3}$ = 2.1, 1H, H_2), 7.27 (d, $^3J_{H10,H9}$ = 8.1, $^3J_{H10,Pt}$ = 11.3, 1H, H_{10}), 7.19 (d, $^3J_{H3,H2}$ = 2.1, $^4J_{H3,Pt}$ = 9.7, 1H, H_3), 3.97 (s, 3H, H_4), 1.74 (s, 9H,

Me (^{t}Bu)), 1.66 (s, 9H, Me (^{t}Bu)). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC (101 MHz, methylene chloride-d_2): δ = 164.9 (s, C_1), 150.5 (s, C_5), 146.0 (s, C_6), 142.1 (s, C_7), 132.4 (C_9), 124.9 (s, C_3), 118.6 (s, CN, C^C*), 116.7 (s, C_2), 112.8 (s, C_{10}), 110.5 (s, C_8), 39.3 (s, C_4), 30.5 (s, 3C, Me (^{t}Bu)), 30.2 (s, 3C, Me (^{t}Bu)). $^{195}Pt\{^1H\}$ NMR (85.6 MHz, methylene chloride-d_2): δ = –4678.5 (s). MS (MALDI+): m/z 543.2 [Pt(NC-C^C*)(CN^{t}Bu)$_2$]$^+$. Λ_M (5x10^{-4} M acetone solution) = 77.8 Ω^{-1} cm^2 mol^{-1}.

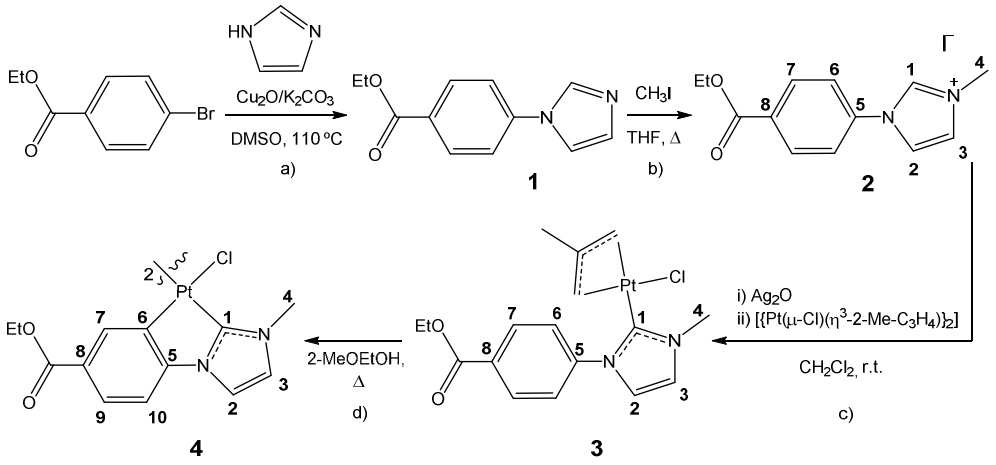
[Pt(NC–C^C*)(CNXyl)$_2$]PF$_6$ (8). It was prepared following the method described for **5**. CNXyl (96.7 mg, 0.72 mmol), KPF_6 (67.8 mg, 0.36 mmol) and **4a** (149.1mg, 0.18 mmol). **8** (248.4 mg, 88%). Elemental analysis Calcd (%) for $C_{29}H_{26}F_6N_5PPt$: C, 44.39; H, 3.34; N, 8.93. Found: C, 44.32; H, 3.37; N, 9.03. IR (ATR): ν_{max} / cm^{-1} = 2220 (w, CN, C^C*), 2201 and 2180 (m, C≡N, CNXyl). ^1H NMR (400 MHz, methylene chloride-d_2): δ = 8.06 (d, $^3J_{H7,H9}$ = 1.7, $^3J_{H7,Pt}$ = 61.3, 1H, H_7), 7.62 (dd, $^3J_{H9,H10}$ = 8.1, $^4J_{H9,H7}$ = 1.7, 1H, H_9), 7.57 (d, $^3J_{H3,H2}$ = 2.1, $^4J_{H2,Pt}$ = 5.2, 1H, H_2), 7.43 (t, $^3J_{Hp,Hm}$ = 7.2, 1H, H_p (Xyl)), 7.41 (t, $^3J_{Hp,Hm}$ = 7.0, 1H, H_p (Xyl)), 7.37 (d, $^3J_{H10,H9}$ = 8.1, $^3J_{H10,H9}$ = 11.6, 1H, H_{10}), 7.31 – 7.22 (m, 5H, H_3 and H_m (Xyl)), 4.04 (s, 3H, H_4), 2.55 (s, 6H, Me (Xyl)), 2.52 (s, 6H, Me (Xyl)). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC (101 MHz, methylene chloride-d_2): δ = 164.8 (s, C_1), 151.2 (s, C_5), 142.7 (s, C_7), 136.5 (s, 2C, C_o (Xyl)), 136.4 (s, 2C, C_o (Xyl)), 132.80 (s, C_9), 131.9 (s, 2C, C_p (Xyl)), 129.4 (s, 4C, C_m (Xyl)), 125.2 (s, C_3), 119.1 (s, CN, C^C*), 117.0 (s, C_2), 113.2 (s, C_{10}), 111.2 (s, C_8), 39.8 (s, C_4), 19.3 (s, 2C, Me (Xyl)) $^{195}Pt\{^1H\}$ NMR (85.6 MHz, methylene chloride-d_2): δ = –4598.9 (s). MS (MALDI+): m/z 639.2 [Pt(NC-C^C*)(CNXyl)$_2$]$^+$. Λ_M (5x10^{-4} M acetone solution) = 76.1 Ω^{-1} cm^2 mol^{-1}.

[Pt(Naph–C^C*)(CN^{t}Bu)$_2$]PF$_6$ (9). It was prepared following the method described for **5**. CN^{t}Bu (63.3 μL, 0.56 mmol), KPF_6 (52.6 mg, 0.28 mmol) and **4b** (122.5 mg, 0.14

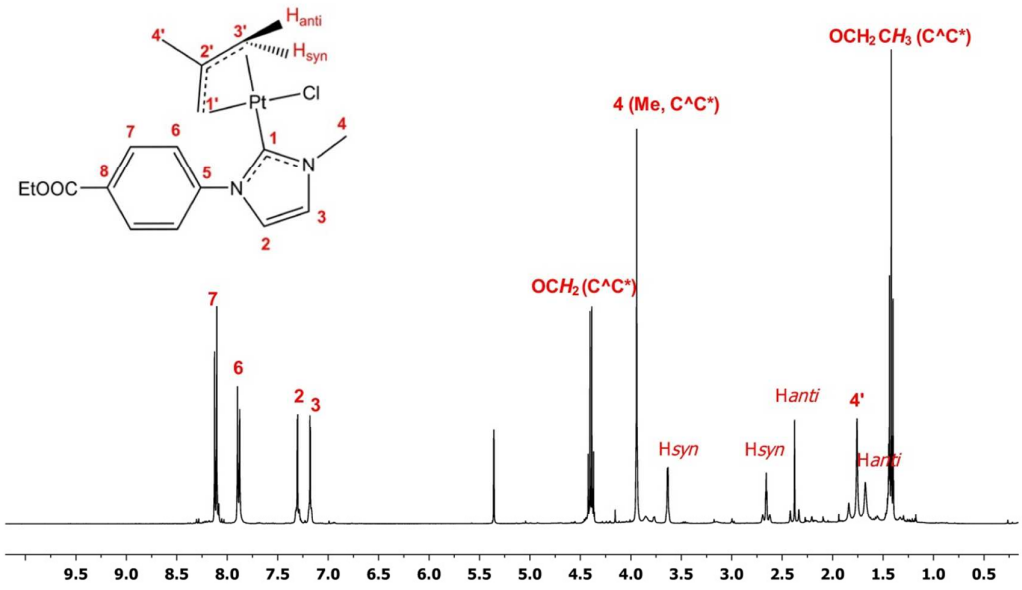
mmol). **9** (164.0 mg, 82%). Elemental analysis Calcd (%) for $C_{24}H_{29}F_6N_4PPt$: C, 40.40; H, 4.10; N, 7.85. Found: C, 40.01; H, 3.40; N, 7.84. IR (ATR): ν_{max} / cm^{-1} = 2237, 2216 (m, C≡N). ^1H NMR (400 MHz, methylene chloride-d_2): δ = 8.01 (s, $^3J_{H7,Pt}$ = 63.5, H_7), 7.79 (m, 1H, H_9), 7.73 (m, 1H, H_{12}), 7.59 (d, $^3J_{H2,H3}$ = 2.0, 2H, 1H, H_2), 7.57 (s, $^4J_{H14,Pt}$ = 11.1, 1H, H_{14}), 7.46 (m, 2H, H_{10}, H_{11}), 7.16 (d, $^3J_{H3,H2}$ = 2.0, $^4J_{H3,Pt}$ = 10.3, 1H, H_3), 3.92 (s, 3H, H_4), 1.78 (s, 3H, Me (^{t}Bu)), 1.67 (s, 3H, Me (^{t}Bu)). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC (101 MHz, methylene chloride-d_2): δ = 165.2 (s, C_1), 146.0 (s, C_6), 139.0 (s, $^2J_{C7,Pt}$ = 56.6, C_7), 133.5 (s, C_{13}), 132.8 (s, C_8), 128.3 (C_9), 128.1 (s, C_{12}), 127.2, 126.6 (s, 2C, C_{10}, C_{11}), 124.6 (s, C_3), 116.2 (s, C_2), 109.6 (s, $^3J_{C2,Pt}$ = 24.2, C_{14}), 39.2 (s, C_4), 30.5 (s, 3C, Me (^{t}Bu)), 30.3 (s, 3C, Me (^{t}Bu)). $^{195}Pt\{^1H\}$ NMR (85.6 MHz, methylene chloride-d_2): δ = –4639.1 (s). MS (MALDI+): m/z 568.2 [Pt(Naph-C^C*)($CN^tBu)_2]^+$ Λ_M (5x10^{-4} M acetone solution) = 81.9 Ω^{-1} cm^2 mol^{-1}.

[Pt(Naph–C^C*)(CNXyl)$_2$]PF_6 (10). It was prepared following the method described for **5**. CNXyl (73.4 mg, 0.55 mmol), KPF_6 (56.4 mg, 0.30 mmol) and **4b** (120.0 mg, 0.14 mmol). **10** (188.8 mg, 85%). Elemental analysis Calcd (%) for $C_{32}H_{29}F_6N_4PPt$: C, 47.47; H, 3.61; N, 6.92. Found: C, 47.20; H, 3.19; N, 6.91. IR (ATR): ν_{max} / cm^{-1} = 2201, 2168 (m, C≡N). ^1H NMR (400 MHz, methylene chloride-d_2): δ = 8.28 (s, $^3J_{H7,Pt}$ = 64.9, H_7), 7.83 (m, 1H, H_9), 7.72 (m, 1H, H_{12}), 7.69 (d, $^3J_{H2,H3}$ = 2.0, 2H, 1H, H_2), 7.67 (s, $^4J_{H14,Pt}$ = 11.1, 1H, H_{14}), [7.38-7.50] (m, 4H, H_{10}, H_{11}, 2 H_p (Xyl)), [7.33-7.26] (m, 4H, H_m (Xyl)), 7.25 (d, $^3J_{H3,H2}$ = 2.0, $^4J_{H3,Pt}$ = 11.0, 1H, H_3), 4.03 (s, 3H, H_4), 2.60 (s, 6H, Me (Xyl)), 2.54 (s, 6H, Me (Xyl)). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC (101 MHz, methylene chloride-d_2): δ = 164.8 (s, C_1), 151.2 (s, C_6), 139.4 (s, C_7), 135.9 (s, 2C, C_o (Xyl)), 135.7 (s, 2C, C_o (Xyl)), 133.1 (s, C_{13}), 132.4 (s, C_8), 131.1 (s, 2C, C_p (Xyl)), 128.7 (s, 4C, C_m (Xyl)), 127.8 (C_9), 127.6 (s, C_{12}), 126.9, 126.3 (s, 2C, C_{10}, C_{11}), 124.3 (s, C_3), 115.9 (s, C_2), 109.4 (s, C_{14}), 39.1 (s, C_4), 18.7 (s, 2C, Me (Xyl)). $^{195}Pt\{^1H\}$

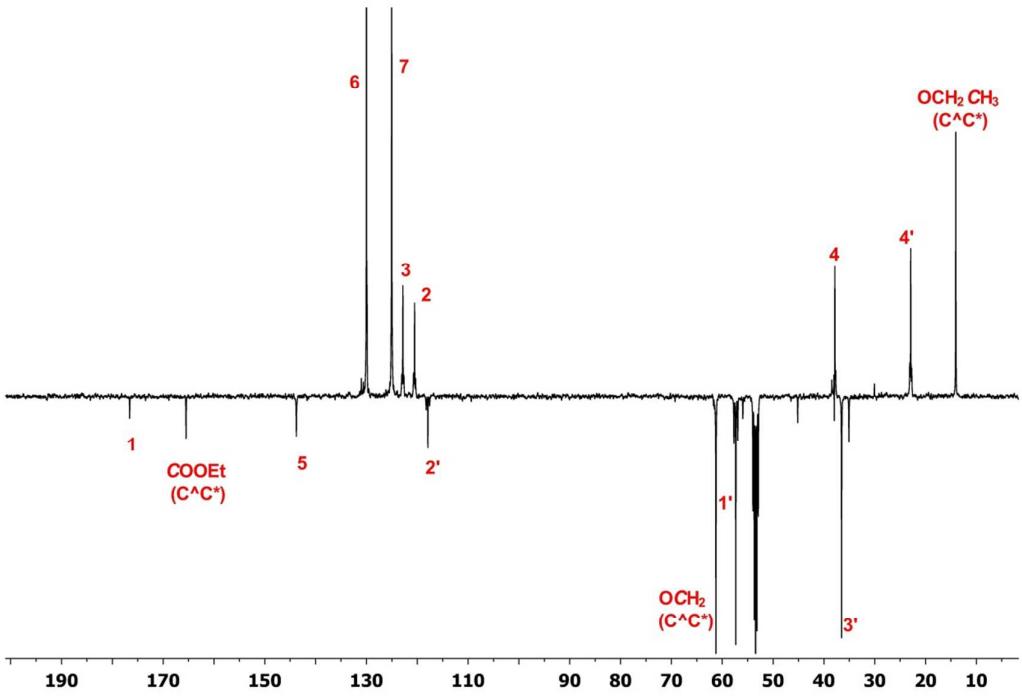
NMR (85.6 MHz, methylene chloride-d_2): δ = –4557.5 (s). MS (MALDI+): m/z 664.2 $[Pt(Naph\text{-}C\hat{}C^*)(CNXyl)_2]^+$ Λ_M ($5x10^{-4}$ M acetone solution) = 77.7 Ω^{-1} cm^2 mol^{-1}.



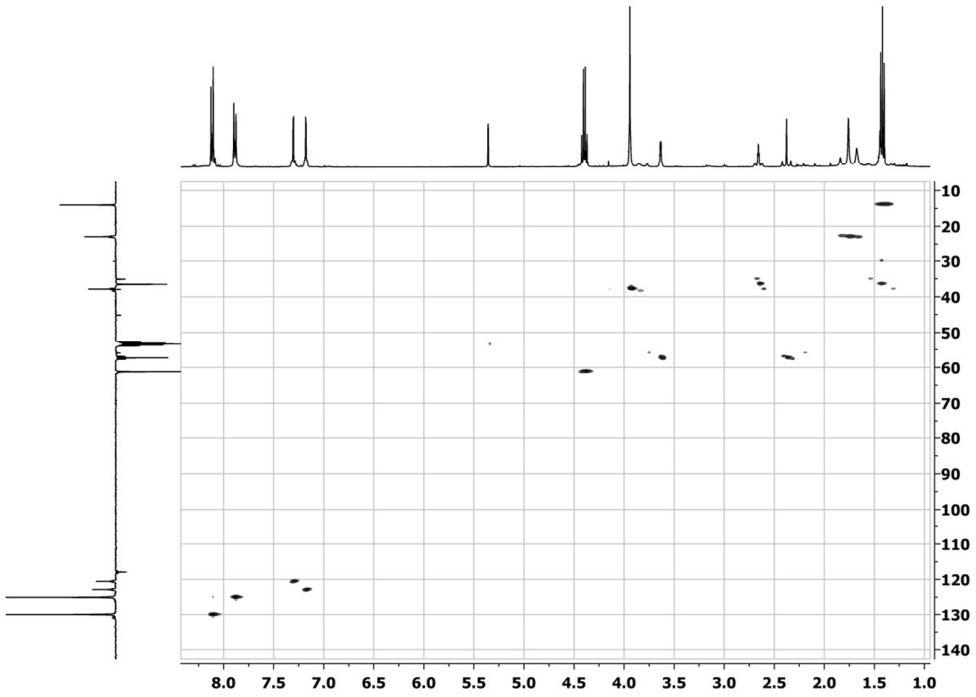
Scheme S1. Synthesis of **1**-**4**. Numerical scheme for NMR purposes.


Hanti
Hsyn
Pt
Cl
EtOOC
N
OCH2CH3 (C^C*)
4 (Me, C^C*)
OCH2 (C^C*)
Hsyn
Hsyn
Hanti
Hanti
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

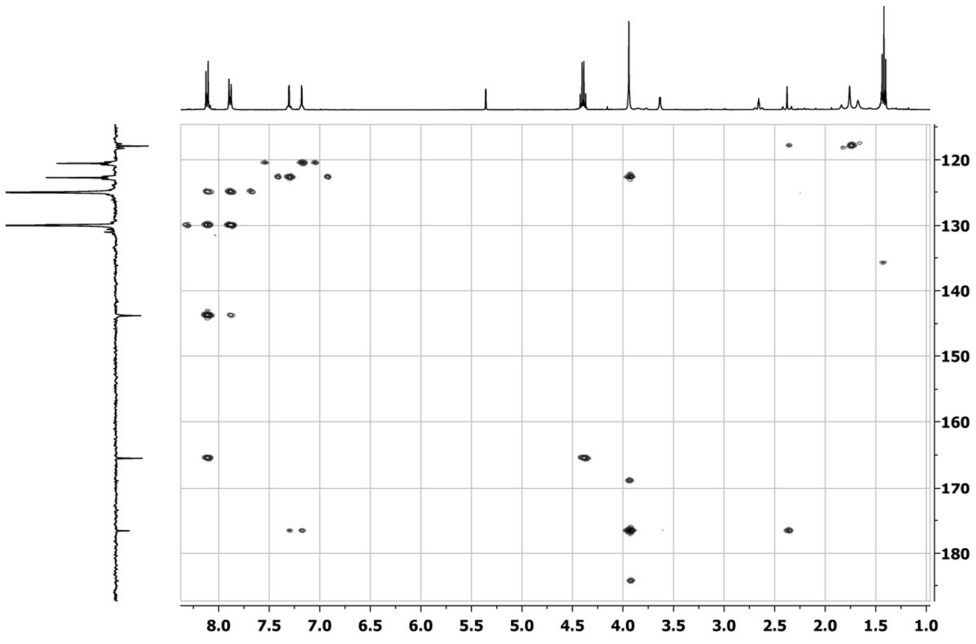
(a)


OCH2 CH3 (C^C*)
COOEt (C^C*)
OCH2 (C^C*)
190 170 150 130 110 90 80 70 60 50 40 30 20 10

(b)

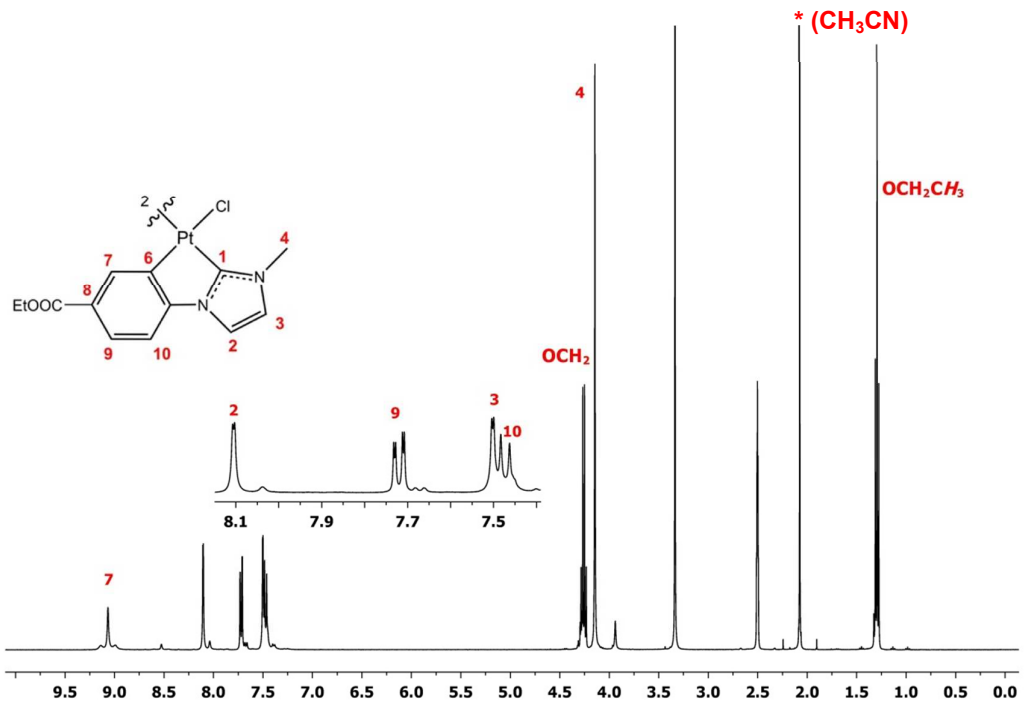


(c)

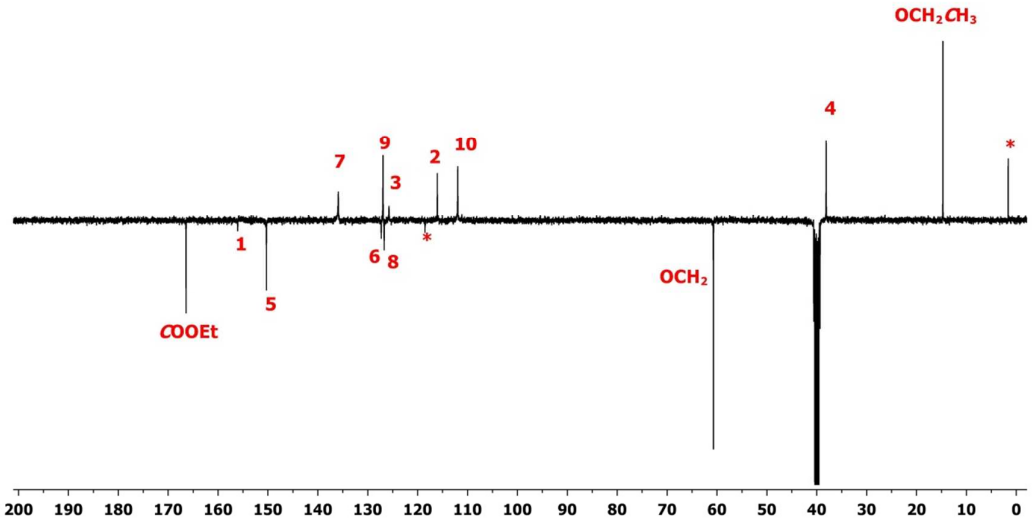


(d)

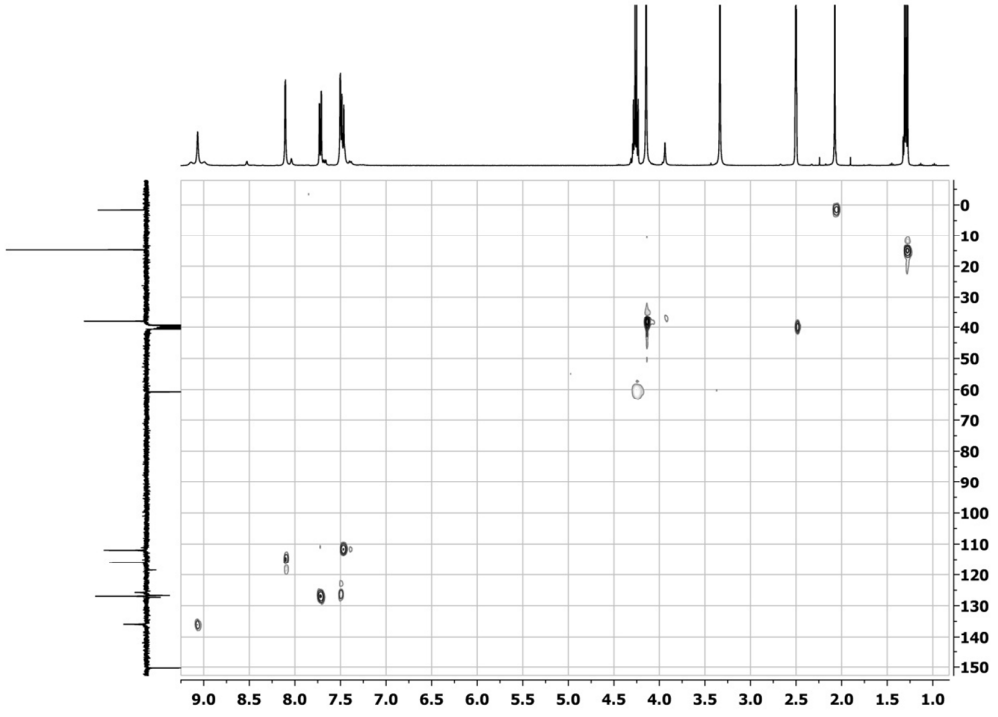
Fig. S1. NMR spectra of **3** in CD_2Cl_2. a) ^{1}H; b) $^{13}C\{^{1}H\}$ APT; c) HSQC ^{1}H-^{13}C; d) HMBC ^{1}H-^{13}C


* (CH3CN)
4
OCH2CH3
OCH2
EtOOC
Cl
Pt
N
2
9
3
10
7
8.1
7.9
7.7
7.5
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

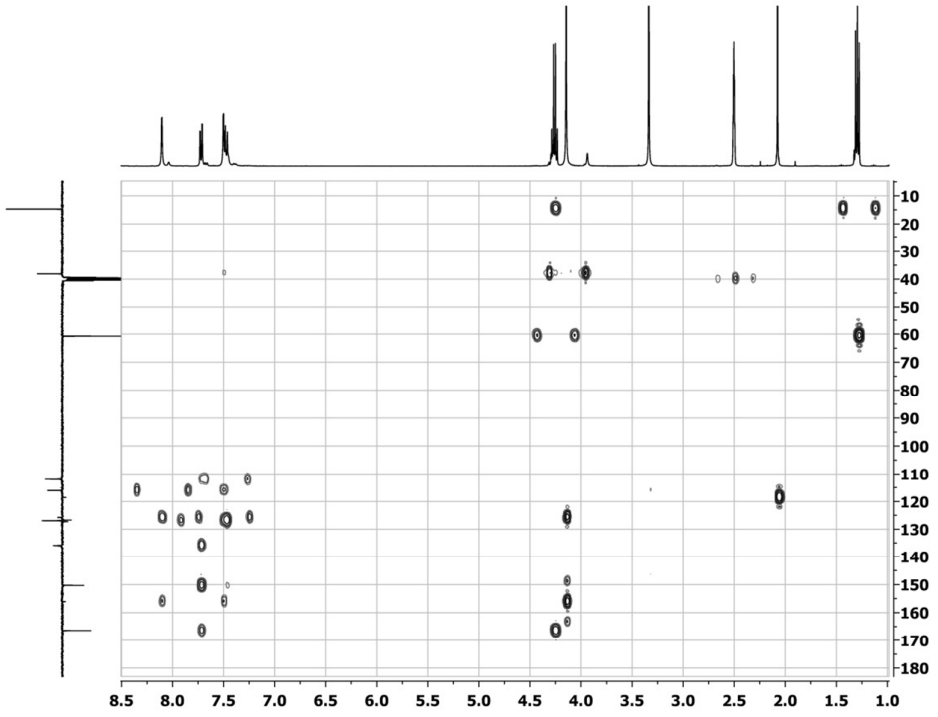
(a)


OCH2CH3
4
*
7
9
3
2
10
1
6
8
5
COOEt
OCH2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

(b)

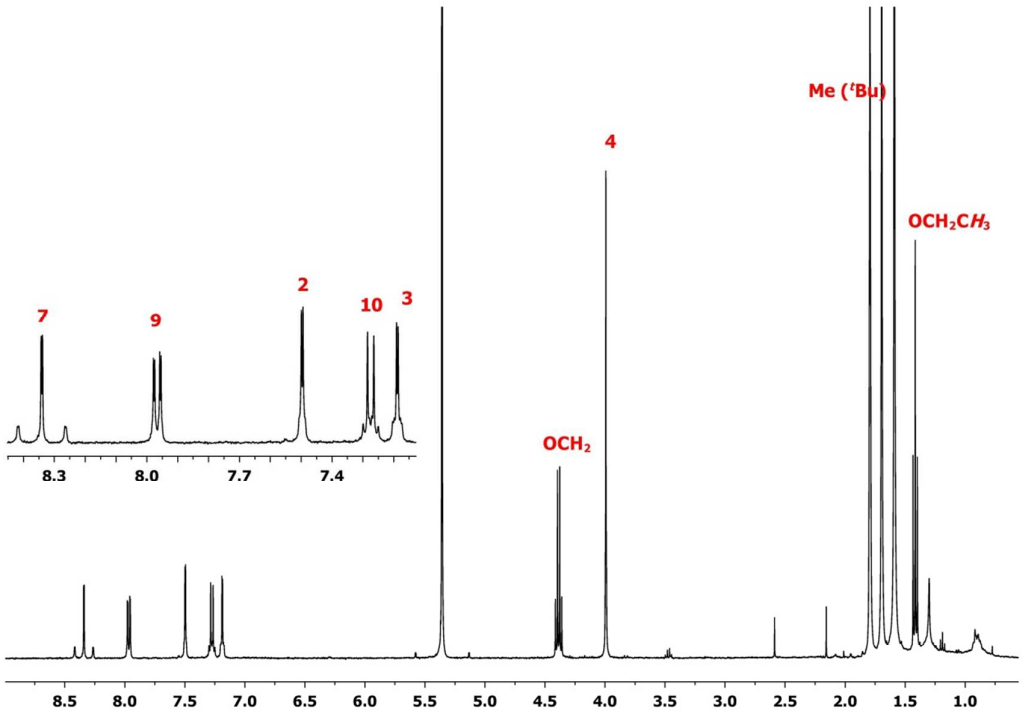


(c)

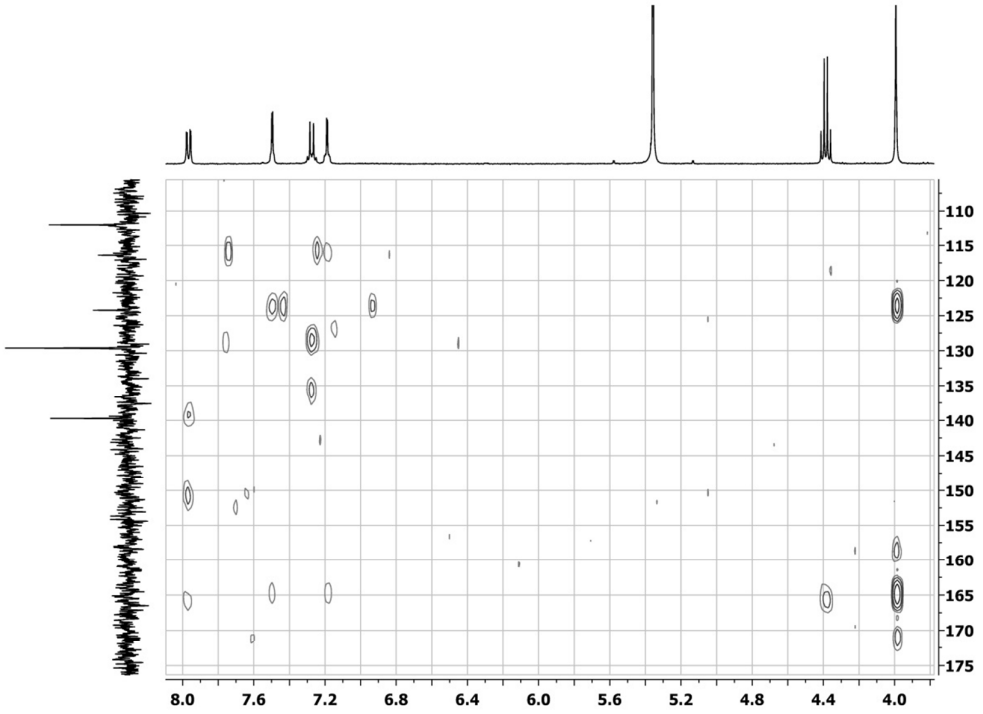


(d)

Fig. S2. NMR spectra of **4** in DMSO-d^6. a) ^{1}H; b) ^{13}C{^{1}H} APT; c) HSQC ^{1}H-^{13}C; d) HMBC ^{1}H-^{13}C

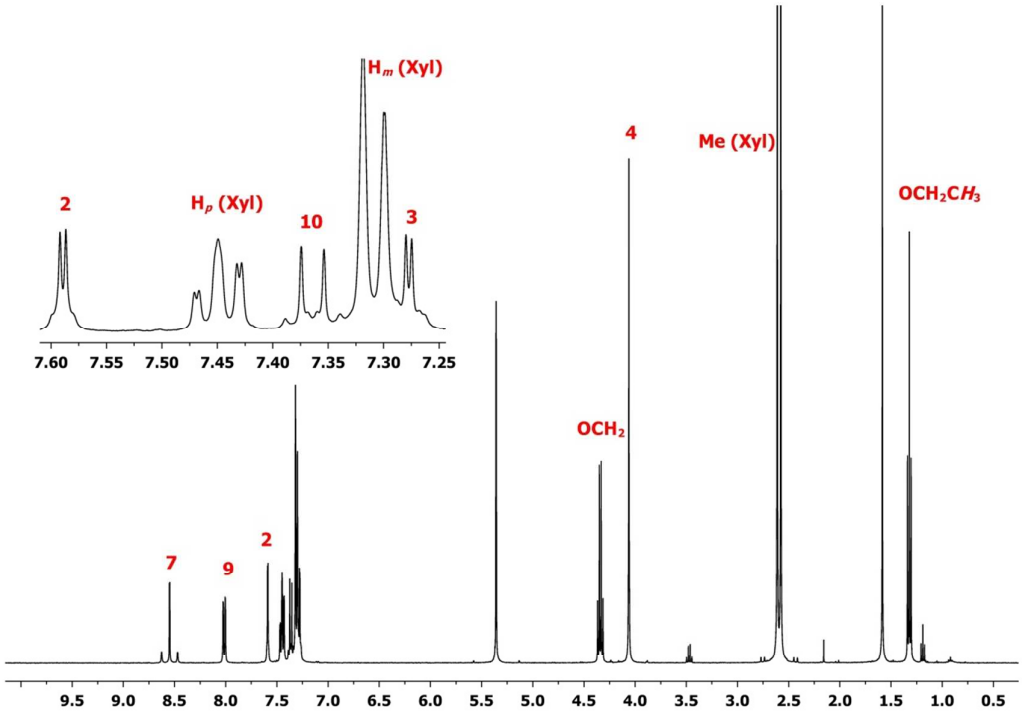


(a)

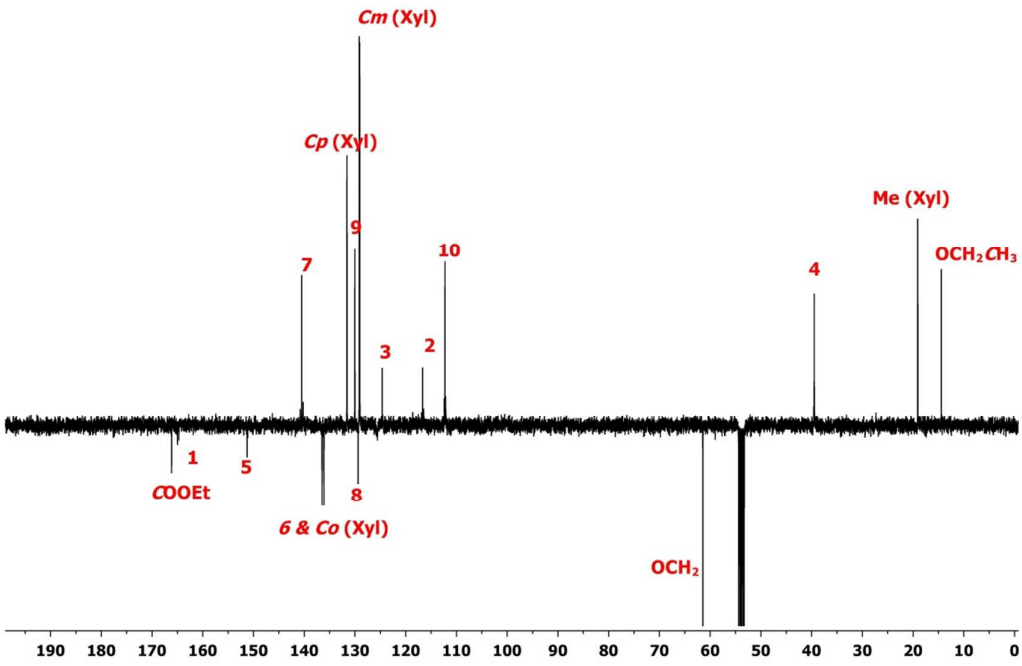


(b)

Fig. S3. NMR spectra of **5** in CD_2Cl_2. a) ^{1}H; b) HMBC ^{1}H-^{13}C



(a)



(b)

Fig. S4. NMR spectra of **6** in in CD_2Cl_2. a) ^{1}H; b) $^{13}C\{^{1}H\}$ APT

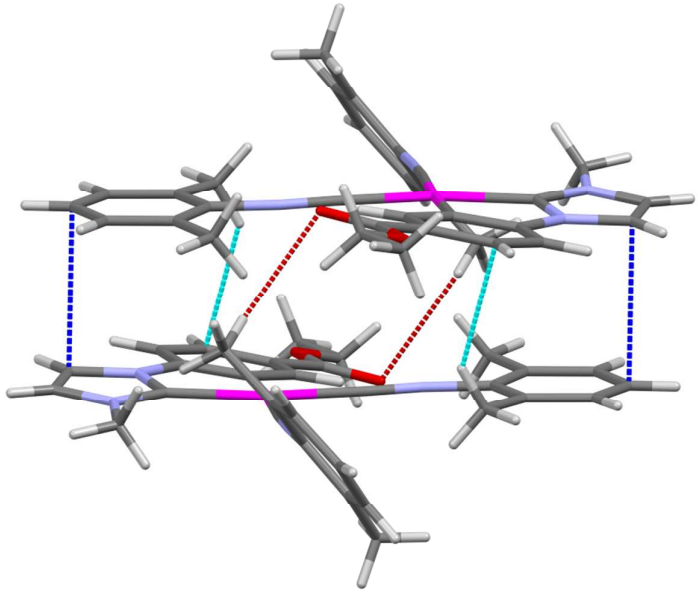
Table S1. Crystallographic data

	6	**8·0.5 Et_2O**	**9·Me_2CO**	**10·Me_2CO**
Empirical formula	$C_{31}H_{31}F_6N_4O_2PPt$	$C_{31}H_{31}F_6N_5O_{0.5}PPt$	$C_{27}H_{35}F_6N_4OPPt$	$C_{70}H_{70}F_{12}N_8O_2P_2Pt_2$
Formula weight	831.66	821.67	771.65	1735.46
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P*-1	*P* 21/n	*C* 2/m	*P*-1
a (Å)	8.653 (18)	17.600(5)	28.699(5)	9.785(5)
b (Å)	11.977(2)	10.418(5)	6.988(5)	11.870(5)
c (Å)	15.992(2)	18.459(5)	15.388(5)	31.557(5)
α (°)	68.573(15)	90	90	85.773(5)
β (°)	86.341(14)	111.062(5)	90.933(5)°	89.808(5)
γ (°)	86.764(16)	90	90	67.175(5)
Volume ($Å^3$) / Z	1539(5)/ 2	3158(2) / 4	3086(2) / 4	3368(2) / 2
ρ (Mg/m^3)	1.795	1.728	1.661	1.711
μ (Mo-Kα)/mm^{-1}	4.683	4.560	4.662	4.282
F(000)	816	1612	1520	1712
Crystal size (mm)	0.45 x 0.24 x 0.10	0.40 x 0.23 x 0.10	0.24 x 0.10 x 0.10	0.41 x 0.10 x 0.10
Theta range (°)	4.24 - 29.20	4.51 - 25.00	4.48 - 29.27	4.35 - 25.68
Reflections collected	23846	23430	20310	66871
Independent reflections [R(int)]	7362 [0.0373]	5497 [0.0426]	4149 [0.0515]	12698 [0.0672]
Final R_1, wR_2[a] [I>2σ(I)]	0.0273, 0.0553	0.0465, 0.1096	0.0331, 0.0712	0.0493, 0.0977
R_1, wR_2[a] (all data)	0.0324, 0.0574	0.0587, 0.1180	0.0411, 0.0743	0.0586, 0.1011
GOF (F^2)[b]	1.018	1.204	1.092	1.185
Largest diff. peak, hole/e.$Å^{-3}$	2.188 and - 1.002	2.260, -1.258	1.099, -1.342	3.160, -1.407

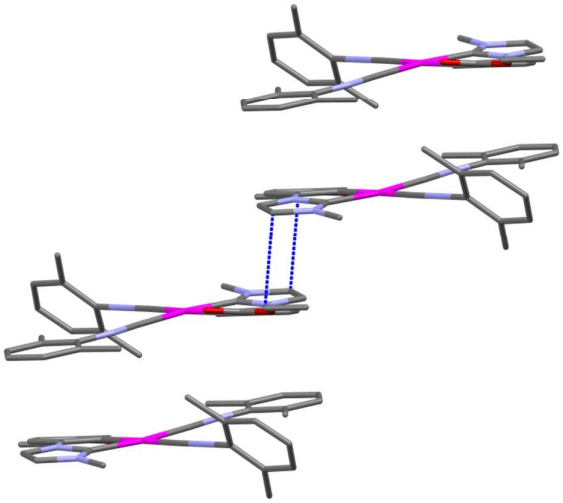
[a] $R_1 = \Sigma(|F_o|-|F_c|) / \Sigma |F_o|$. $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$. [b] Goodness-of-fit = $[\Sigma w (F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (º) for **6** and **8–10**

	6	**8·0.5 Et_2O**	**9·Me_2CO**	**10·Me_2CO**	
				Pt(1)	**Pt(1a)**
Pt(1)–C(1)	2.017(3)	2.021(8)	2.020(5)	2.023(6)	2.007(6)
Pt(1)–C(6)	2.048(3)	2.027(8)	2.042(5)	2.028(6)	2.041(7)
Pt(1)–C(20)	1.996(3)	1.991(9)	1.972(5)	1.977(7)	1.964(6)
Pt(1)–C(30)	2.003(3)	1.987(10)	2.011(5)	1.986(7)	1.987(7)
C(20)–N(3)	1.118(4)	1.125(10)	1.139(7)	1.140(3)	1.144(8)
C(30)–N(4)	1.152(4)	1.146(11)	1.129(7)	1.156(8)	1.160(8)
C(1)-Pt(1)-C(6)	78.8(12)	79.9(6)	79.3(2)	79.7(2)	79.4(3)
C(6)-Pt(1)-C(20)	95.3(13)	93.7(3)	89.4(2)	93.0(2)	93.1(3)
C(1)-Pt(1)-C(30)	97.9(12)	97.7(3)	100.7(2)	98.4(2)	98.9(3)
C(20)-Pt(1)-C(30)	87.8(13)	88.7(3)	90.6(2)	88.9(2)	88.7(3)
Pt(1)-C(20)-N(3)	174.9(3)	177.1(8)	172.9(5)	177.6(6)	176.2(6)
Pt(1)-C(30)-N(4)	176.7(3)	176.7(7)	174.1(5)	175.3(5)	174.0(6)

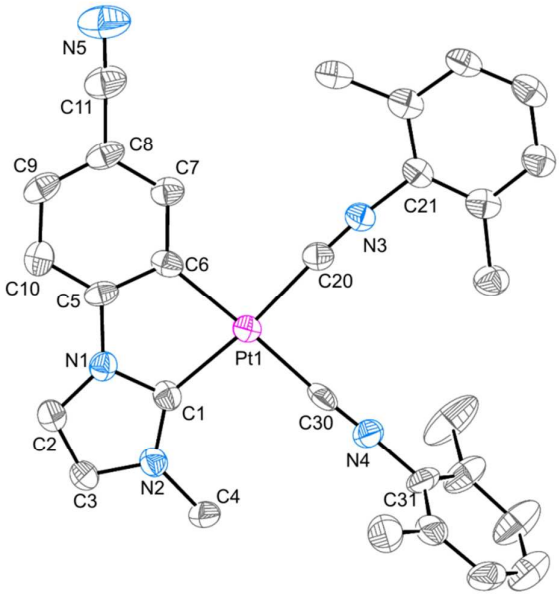


a)

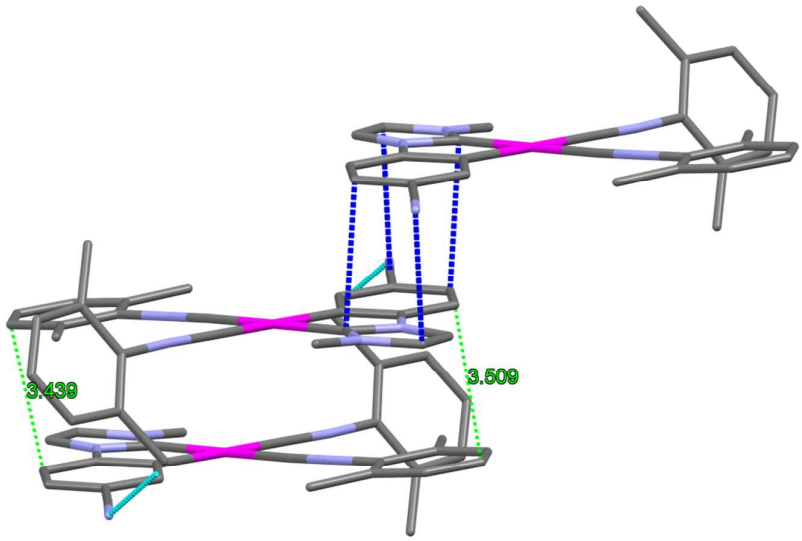


b)

Fig. S5 a) Supramolecular arrangement of the cations of complex **6** showing intermolecular interactions: π···π contacts between the NHC and C21-C26 Xyl rings (3.30 Å, dark blue line); C-H···π contacts between the Me (Xyl) and NHC groups (C28-C9 = 3.63 Å, cyan line); C-H···O contacts between the Me (Xyl) and EtOOC groups (C37-O2 = 3.43 Å, red line); b) Offset π···π interactions between the NHC fragments (3.29 Å; dark blue line). PF_6 has been omitted for clarity



a)



b)

Fig S6 a) Molecular structure of the cation of complex **8**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, solvent molecules and PF_6 have been omitted for clarity; b) Supramolecular arrangement of the cations showing intermolecular interactions: π···π contacts between the NHC and C21-C26 Xyl rings (3.43, 3.50 Å, green line); C-H···N contacts between the Me (Xyl) and NHC groups (C38-N5 = 3.45 Å, cyan line); Offset π···π interactions between the NHC fragments of adjacent pairs (3.29, 3.32 Å; dark blue lines).

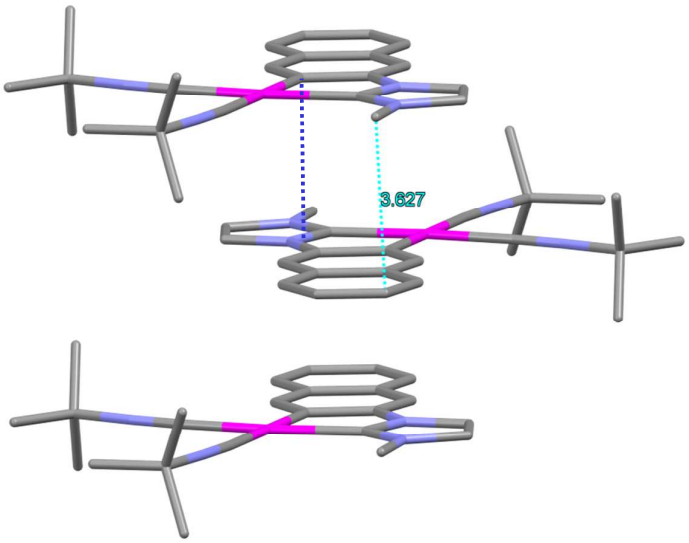


Fig. S7 Supramolecular arrangement of the cations of complex **9** showing intermolecular interactions: C-H···π contacts between the Me (NHC) and NHC groups (C4-C10 = 3.62 Å, cyan line and π···π interactions between the NHC fragments (~ 3.5 Å; dark blue line) and Hydrogen atoms, solvent molecules and PF_6 have been omitted for clarity.

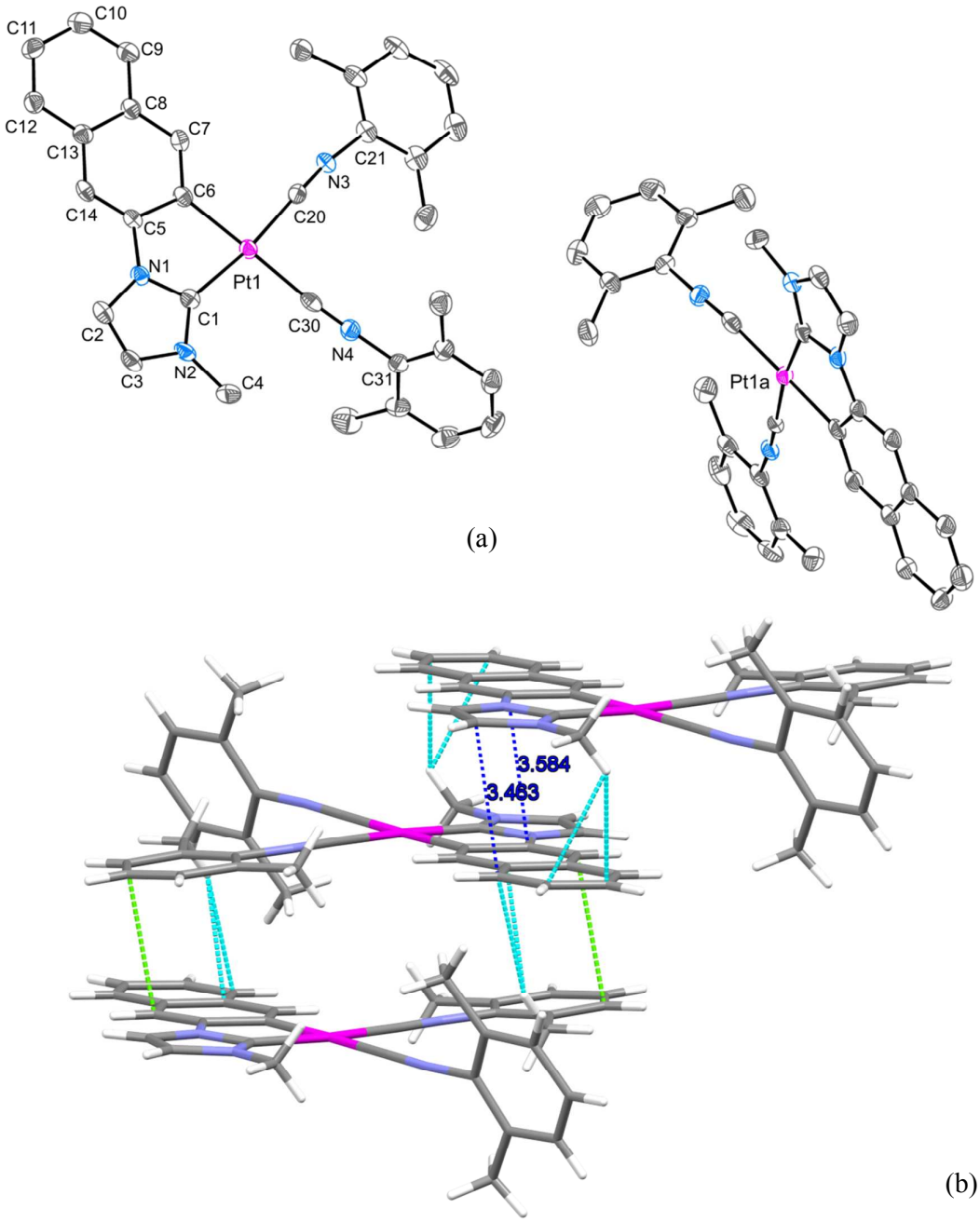


Fig. S8 a) Molecular structures of the cation of complex **10.** Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, solvent molecules and PF_6 have been omitted for clarity; b) Supramolecular arrangement of the cations showing intermolecular interactions: π···π contacts between the NHC and C21-C26 Xyl rings (3.35 Å, green line); C-H···π contacts between the Me (Xyl) and NHC groups (C28-C8/C9 = 3.62/3.72 Å, cyan line); π···π interactions between the NHC fragments of adjacent pairs (3.46 Å; dark blue lines) and C-H···π contacts between the Me (NHC) and NHC groups (C4-C10/C11 = 3.44 /3.56 Å, cyan line)

Table S3. Absorption Data in $5 \cdot 10^{-5}$ M solutions for compounds **5**–**10** at 298 K

Comp	λ abs / nm (10^3 ε $M^{-1}cm^{-1}$)
5	251 (26,9), 261 (40,7), 270 (27,6), 281 (18,4), 307 (6,6), 318 (9,3) ***CH_2Cl_2***
	253 (16,7), 262 (23,5), 269 (18,2), 282 (12,4), 306 (4,7), 318 (5,6) ***THF***
	252 (22,2), 261 (34,7), 267 (26,6), 281 (15,3), 306 (5,6), 317 (8,3) ***MeOH***
	251 (25,2), 260 (35,6), 267 (26,6), 281 (16,1), 305 (5,8), 315 (8,2) ***MeCN***
	261, 280, 304, 317 ***Solid***
6	242 (35,1), 266 (44,4), 288 (26,1), 324 (16,4) ***CH_2Cl_2***[a]
	238 (21,4), 266 (26,9), 290 (15,8), 324 (10,5) ***THF***
	240 (27,4), 264 (35,4), 288 (20,8), 322 (13,6) ***MeOH***
	240 (34,2), 264 (43,5), 288 (24,9), 322 (16,7) ***MeCN***
	266, 288, 300, 322 ***Solid***
7	250 (30,3), 260 (41,9), 282 (18,1), 316 (9,1) ***CH_2Cl_2***
	252 (14,0), 260 (19,2), 282 (11,6), 315 (3,9) ***THF***
	250 (26,1), 258 (36,6), 282 (15,2), 314 (8,0) ***MeOH***
	250 (43.3), 258 (58.2), 280 (25,7), 314 (13,3) ***MeCN***
	258, 280, 303, 315 ***Solid***
8	244 (39,8), 261 (48,9), 288 (26,8), 322 (16,7) ***CH_2Cl_2***
	242 (30,8), 262 (35,4), 290 (19,9), 322 (12,7) ***THF***
	242 (27,7), 260 (32,4), 288 (18,3), 320 (11,7) ***MeOH***
	242 (36,1), 260 (43,5), 288 (23,9), 320 (15,7) ***MeCN***
	263, 290, 322 ***Solid***
9	230 (45,5), 286 (39,2), 308 (11,6), 350 (5,5), 365 (5,4) ***CH_2Cl_2***
	226 (42,8), 282 (42,7), 306 (12,6), 342 (5,2), 360 (4,9) ***MeCN***
	230, 286, 304sh, 349, 362 ***Solid***
10	236 (54,1), 288 (40,8), 298 (36,9), 316 (17,3), 358 (8,0), 372 (7,6) ***CH_2Cl_2***
	236 (28,7), 286 (22,2), 296 (20,4), 316 (9,6), 354 (4,3), 370 (3,9) ***THF***
	234 (68,0), 284 (53,4), 292 (49,6), 314 (23,9), 350 (9,8), 364 (8,3) ***MeCN***
	234 (41,6), 284 (31,7), 294 (29,8), 316 (14,0), 354 (6,1), 368 (5,5) ***MeOH***
	250, 289, 314, 358, 370 ***Solid***

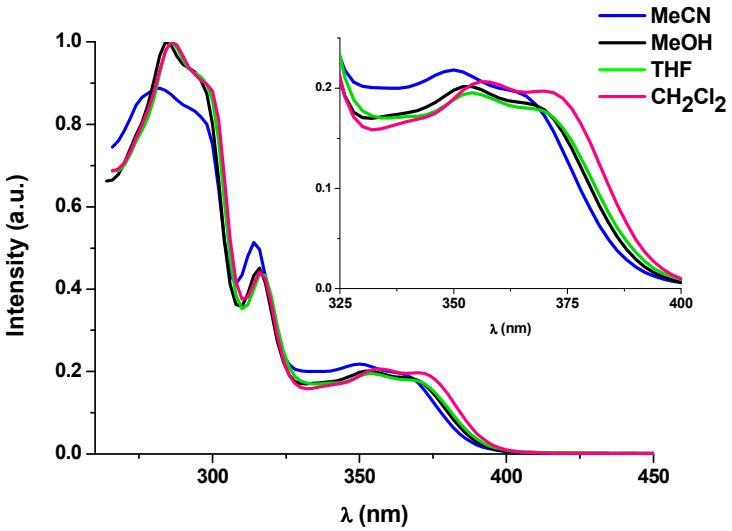


Fig S9 Normalized UV-Vis absorption spectra of **10** in different solvents ($5 \cdot 10^{-5}$ M) at room temperature.

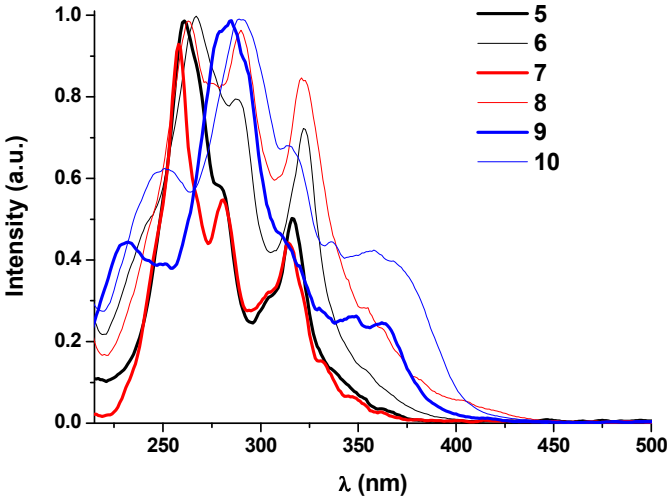


Fig. S10 Normalized Diffuse Reflectance spectra of solid samples of **5–10** at r.t.

Table S4 DFT-Optimized coordinates of **6**

Center	Coordinates (Angstroms)		
	X	Y	Z
Pt	-0.37000000	-0.81600000	-0.01200000
C	-2.35300000	-0.41600000	-0.04500000
C	-0.46900000	-2.86400000	-0.01300000
C	1.63700000	-1.31900000	0.02800000
N	0.33100000	2.26500000	-0.01300000
O	6.38300000	-0.57200000	0.15900000
N	-1.39900000	-3.84900000	-0.03700000
N	-3.48600000	-0.12400000	-0.06400000
O	5.01200000	1.21400000	-0.02000000
C	-0.78000000	-5.09400000	-0.02500000
N	0.73200000	-3.50800000	0.01300000
C	1.69300000	4.09200000	-0.80000000
C	2.49300000	3.17500000	-1.68800000
C	3.19000000	-3.23700000	0.06300000
C	1.24400000	6.30800000	0.10000000
C	0.56200000	-4.87800000	0.00700000
C	0.64400000	3.62000000	0.01700000
C	0.21200000	5.80600000	0.89500000
C	1.96900000	5.46100000	-0.73600000
C	1.90700000	-2.70200000	0.03600000
C	-2.84900000	-3.66700000	-0.07200000
C	2.74800000	-0.47700000	0.04800000
C	4.27800000	-2.36300000	0.07900000
C	4.05900000	-0.98200000	0.06800000
C	-4.83400000	0.21800000	-0.09800000
C	-1.22400000	3.89100000	1.72500000
C	5.17700000	0.00900000	0.06300000
C	7.52900000	0.31800000	0.15300000
C	-0.11400000	4.45000000	0.87200000
C	-5.56000000	0.19400000	1.11100000
C	-4.90300000	-0.18300000	2.41500000
C	-7.50500000	0.89300000	-0.16600000
C	-6.91200000	0.53900000	1.04600000
C	-4.57600000	0.59600000	-2.60200000
C	8.77500000	-0.54200000	0.23800000
C	-5.40000000	0.57500000	-1.33900000
C	-6.75600000	0.91100000	-1.34300000
C	0.05600000	1.13000000	-0.01300000
H	-1.34500000	-6.01300000	-0.04000000
H	3.02500000	3.75400000	-2.44900000
H	1.85800000	2.44600000	-2.20300000
H	3.24600000	2.61800000	-1.11500000
H	3.35700000	-4.31000000	0.07100000
H	1.48100000	7.36700000	0.13100000
H	1.38400000	-5.57500000	0.02400000
H	-0.34900000	6.47300000	1.54300000
H	2.76800000	5.86200000	-1.35300000
H	-3.18900000	-3.16400000	0.83600000

H	-3.31900000	-4.64900000	-0.13100000
H	-3.13400000	-3.08200000	-0.94800000
H	2.63600000	0.60000000	0.05200000
H	5.29000000	-2.75100000	0.09600000
H	-1.68700000	4.68200000	2.32000000
H	-0.85400000	3.12300000	2.41700000
H	-2.00900000	3.42700000	1.11400000
H	7.43900000	1.00200000	1.00200000
H	7.49900000	0.91600000	-0.76300000
H	-5.62500000	-0.14500000	3.23500000
H	-4.07700000	0.49500000	2.66300000
H	-4.48700000	-1.19700000	2.38400000
H	-8.55800000	1.15800000	-0.19400000
H	-7.50200000	0.53100000	1.95700000
H	-3.74300000	1.30500000	-2.52800000
H	-5.19000000	0.88800000	-3.45800000
H	-4.14200000	-0.38800000	-2.82100000
H	9.66400000	0.09700000	0.23900000
H	8.84300000	-1.22200000	-0.61700000
H	8.78000000	-1.13700000	1.15700000
H	-7.22600000	1.19000000	-2.28200000

Table S5 DFT-Optimized coordinates of **8**

Center		Coordinates (Angstroms)	
	X	Y	Z
Pt	0.150374	-0.831606	0.000096
N	-2.898817	0.106766	0.000267
N	1.091704	2.184763	-0.000336
N	-1.121242	-3.768974	0.000255
N	1.030839	-3.601088	-0.000018
N	6.684872	0.121467	0.000043
C	2.261205	5.433523	1.211280
C	2.115111	-1.492836	0.000007
C	0.722801	1.077224	-0.000136
C	-1.794491	-0.278168	0.000202
C	3.291630	-0.744528	0.000027
C	1.783721	4.121580	-1.243923
C	-0.604460	-5.059284	0.000094
C	-0.114219	-2.863304	0.000205
C	1.784815	4.121258	1.243192
C	4.659451	-2.765060	-0.000113
C	-2.553012	-3.469623	0.000149
C	2.496982	6.083499	-0.000437
C	5.738854	-0.555115	-0.000020
C	1.530563	3.401962	2.543297
C	-4.211218	0.568508	0.000224
C	1.557067	3.495977	-0.000361
C	3.499574	-3.539091	-0.000125
C	-4.118614	0.546950	2.544258
C	4.557921	-1.368053	-0.000041
C	0.750804	-4.953936	-0.000022
C	-6.155037	1.260731	1.211657
C	2.267449	-2.895320	-0.000074
C	2.260147	5.433856	-1.212106
C	-4.839745	0.791950	-1.242713
C	1.528201	3.402671	-2.543998
C	-4.839096	0.793898	1.243148
C	-6.155685	1.258834	-1.211267
C	-6.807570	1.490741	0.000180
C	-4.119977	0.542992	-2.543845
H	2.451262	5.947277	2.148928
H	3.261852	0.338984	0.000086
H	-1.241832	-5.929562	0.000151
H	5.634587	-3.239376	-0.000140
H	-2.820438	-2.901779	-0.892943
H	-2.820560	-2.902031	0.893349
H	-3.101723	-4.412146	-0.000006
H	2.869830	7.103338	-0.000450
H	1.755570	4.051318	3.392807
H	2.151886	2.502525	2.635587
H	0.484244	3.083628	2.631325
H	3.575234	-4.621874	-0.000162
H	-3.801223	-0.498907	2.641512

H	-4.765999	0.778485	3.393516
H	-3.216977	1.165893	2.630372
H	1.512958	-5.715893	-0.000121
H	-6.670260	1.446554	2.149406
H	2.449363	5.947840	-2.149798
H	1.753458	4.051902	-3.393540
H	0.481502	3.085428	-2.631576
H	2.148555	2.502618	-2.636679
H	-6.671385	1.443158	-2.149049
H	-7.830730	1.854361	0.000181
H	-3.218422	1.161848	-2.631435
H	-4.767851	0.773151	-3.393104
H	-3.802581	-0.502984	-2.639631

Table S6 DFT-Optimized coordinates of **9**

Center	Coordinates (Angstroms)		
	X	Y	Z
Pt	0.43900000	-0.27800000	0.001000000
N	0.81400000	-3.45500000	0.006000000
C	-0.04900000	-4.54400000	0.007000000
C	-3.53500000	-1.91800000	0.000000000
C	-3.94700000	0.49900000	-0.004000000
N	-1.20100000	-2.67900000	0.003000000
C	-4.45800000	-0.83700000	-0.003000000
C	-2.19000000	-1.65500000	0.001000000
C	-6.72700000	0.03100000	-0.006000000
C	-2.53400000	0.70600000	-0.002000000
N	3.63100000	-0.23600000	-0.004000000
C	0.10600000	-2.29800000	0.003000000
C	-1.31700000	-4.05500000	0.005000000
N	0.43800000	2.87800000	0.003000000
C	2.26900000	-3.57500000	0.008000000
C	-4.86400000	1.58100000	-0.006000000
C	0.44600000	1.71300000	0.001000000
C	-5.86100000	-1.04200000	-0.004000000
C	-6.22400000	1.35400000	-0.007000000
C	2.46600000	-0.29900000	-0.002000000
C	-1.63100000	-0.33700000	0.000000000
C	5.08300000	-0.12400000	-0.007000000
C	5.60000000	-0.68100000	1.333000000
C	5.61700000	-0.94300000	-1.196000000
C	5.43400000	1.36700000	-0.159000000
C	0.39000000	4.33400000	0.005000000
C	-0.31800000	4.77800000	-1.288000000
C	-0.39800000	4.77000000	1.254000000
C	1.83900000	4.85000000	0.053000000
H	0.31400000	-5.56000000	0.009000000
H	-3.91700000	-2.93600000	0.000000000
H	-7.80000000	-0.13600000	-0.007000000
H	-2.18800000	1.73500000	-0.003000000
H	-2.26600000	-4.56600000	0.006000000
H	2.68800000	-3.10700000	-0.885000000
H	2.52800000	-4.63500000	0.009000000
H	2.68500000	-3.10600000	0.902000000
H	-4.47800000	2.59800000	-0.007000000
H	-6.24600000	-2.05900000	-0.003000000
H	-6.91600000	2.19100000	-0.009000000
H	5.19300000	-0.11600000	2.177000000
H	5.33200000	-1.73500000	1.452000000
H	6.69100000	-0.60000000	1.357000000
H	5.22000000	-0.56600000	-2.144000000
H	6.70800000	-0.86600000	-1.223000000
H	5.35200000	-2.00100000	-1.098000000
H	6.52200000	1.48000000	-0.162000000
H	5.04400000	1.76700000	-1.100000000

H	5.02800000	1.95200000	0.672000000
H	0.23000000	4.44100000	-2.172000000
H	-1.33700000	4.38300000	-1.334000000
H	-0.37000000	5.87100000	-1.308000000
H	0.09300000	4.42700000	2.170000000
H	-0.45200000	5.86300000	1.278000000
H	-1.41800000	4.37600000	1.233000000
H	1.82900000	5.94400000	0.055000000
H	2.34800000	4.50800000	0.960000000
H	2.40500000	4.51200000	-0.821000000

Table S7 DFT-Optimized coordinates of **10**

Center	Coordinates (Angstroms)		
	X	Y	Z
Pt	0.050020	-0.690421	-0.000144
N	-0.473819	-3.846524	-0.000261
C	0.332870	4.516346	1.242371
C	0.286174	3.851345	-0.000303
C	0.337514	-4.973548	-0.000221
C	0.281805	3.754845	-2.543209
C	3.942911	-2.510891	0.000089
C	4.464379	-0.113654	0.000363
N	1.576092	-3.164871	-0.000138
C	4.914527	-1.472172	0.000278
C	2.611605	-2.186571	0.000009
C	0.281029	3.755287	2.542611
C	-4.525916	-0.428399	0.000197
C	7.219936	-0.707145	0.000599
C	3.062888	0.157579	0.000248
N	-3.139347	-0.537565	-0.000088
C	-5.191370	-0.373783	1.242630
C	-5.192026	-0.374794	-1.241931
C	0.288575	-2.724015	-0.000193
C	1.627821	-4.544726	-0.000143
C	-6.584325	-0.266640	-1.210489
N	0.191773	2.463746	-0.000199
C	-1.934162	-3.899346	-0.000333
C	0.430682	5.909367	1.210846
C	-7.274218	-0.213686	0.000839
C	5.429524	0.925804	0.000568
C	0.130273	1.297116	-0.000157
C	6.306865	-1.740469	0.000401
C	6.777946	0.636725	0.000683
C	0.431027	5.909156	-1.211764
C	-4.432562	-0.426853	-2.543262
C	-4.431217	-0.425016	2.543596
C	0.478817	6.599570	-0.000513
C	-1.972815	-0.633713	-0.000205
C	2.113864	-0.844507	0.000063
C	0.333245	4.516126	-1.243081
C	-6.583684	-0.265632	1.211841
H	-0.071597	-5.971665	-0.000317
H	0.342213	4.439296	-3.392973
H	-0.649203	3.182140	-2.638698
H	1.109534	3.040004	-2.627171
H	4.279603	-3.544197	0.000036
H	-0.649995	3.182573	2.637883
H	0.341126	4.439884	3.392277
H	1.108749	3.040481	2.626980
H	8.284349	-0.922738	0.000700
H	2.762991	1.201668	0.000335
H	2.551232	-5.100161	-0.000155

H	-7.130155	-0.222168	-2.148342
H	-2.331130	-3.412041	0.892246
H	-2.241095	-4.946019	0.000070
H	-2.331041	-3.412739	-0.893347
H	0.470230	6.455367	2.148822
H	-8.356826	-0.129366	0.001084
H	5.089014	1.958544	0.000638
H	6.645481	-2.773575	0.000339
H	7.507089	1.441684	0.000843
H	0.470826	6.455000	-2.149819
H	-3.715297	0.399040	-2.625393
H	-5.117367	-0.362287	-3.392370
H	-3.861619	-1.358404	-2.644232
H	-3.862475	-1.357769	2.646043
H	-5.115344	-0.357181	3.392997
H	-3.711903	0.399276	2.623641
H	0.555278	7.682803	-0.000603
H	-7.129007	-0.220351	2.149950

Table S8. Population Analysis (%) of Frontier MOs in the Ground State for **6** and **8**–**10** in solution of CH_2Cl_2

MO	eV				Pt				Imidazole (C*)				Ar (R-C)				CNR'			
	6	**8**	**9**	**10**	**6**	**8**	**9**	**10**	**6**	**8**	**9**	**10**	**6**	**8**	**9**	**10**	**6**	**8**	**9**	**10**
L+1	-1.78	-1.83	-1.47	-1.77	4	5	1	5	1	1	10	1	0	0	87	0	95	94	2	94
L	-2.51	-2.60	-2.20	-2.33	23	25	30	30	21	23	24	22	21	26	16	15	35	26	30	33
H	-6.70	-6.85	-6.14	-6.17	12	10	4	3	31	33	3	3	53	55	92	93	4	2	1	1
H-1	-7.10	-7.20	-6.49	-6.53	13	8	9	8	7	1	20	20	20	1	70	71	60	90	1	1

Egap: 4.19 (**6**); 4.25 (**8**); 3.94 (**9**); 3.84 (**10**)

Table S9. Selected singlet excited states calculated by TD-DFT for complexes **6** and **8**–**10** in solution of CH_2Cl_2

	λ_{exc} (calc.)/nm	o.s.	Transition (Percentage contribution)	Assignment[a]
		[(EtOOC-C^C*)Pt(CNXyl)$_2$] (6)		
S1	363.1	0.0079	H → L (97%)	LL'CT / LMCT
S2	316.6	0.3257	H-1→ L (91%)	L'LCT / L'MCT
		[(NC-C^C*)Pt(CNXyl)$_2$] (8)		
S1	352.7	0.0006	H → L (97%)	LL'CT / LMCT
S2	314.8	0.0004	H-1→ L (96%)	L'LCT / L'MCT
		[(Naph-C^C*)Pt(CN^{t}Bu)$_2$] (9)		
S1	365.8	0.2138	H → L (94%); H-1→ L+1 (4%)	ILCT / LL'CT / LMCT
S2	347.0	0.0038	H-1→ L (96%)	LL'CT / LMCT
		[(Naph-C^C*)Pt(CNXyl)$_2$] (10)		
S1	375.5	0.2410	H → L (95%); H-1 → L+3 (3%)	ILCT / LL'CT / LMCT
S2	355.2	0.0085	H-1→ L (97%)	LL'CT / LMCT

a: L = NHC; L' = CNR'

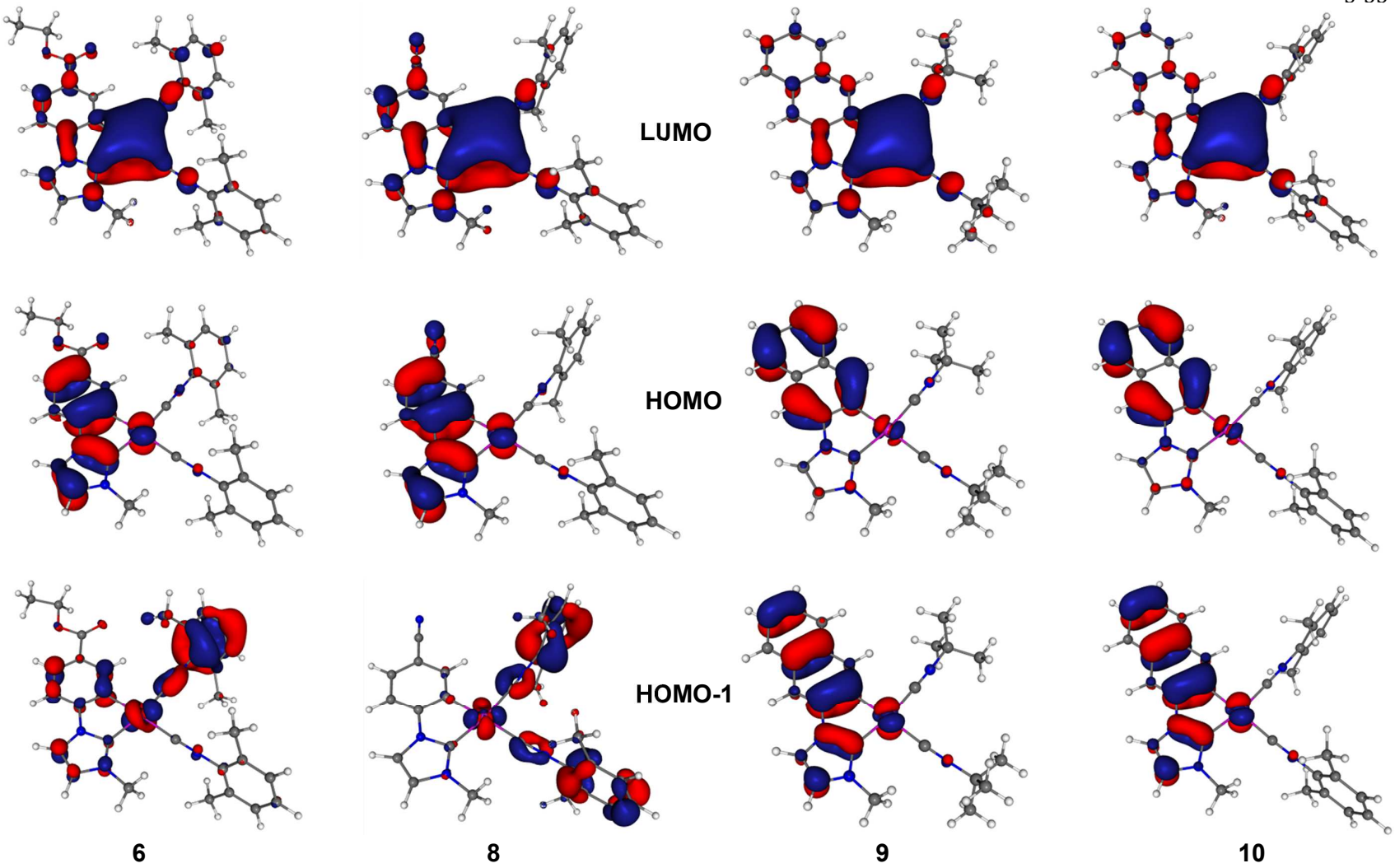
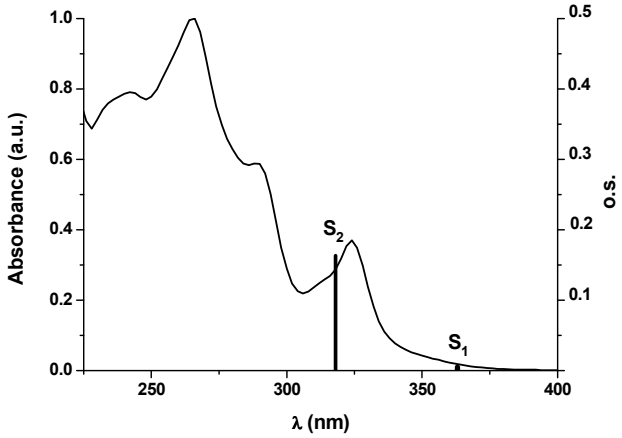
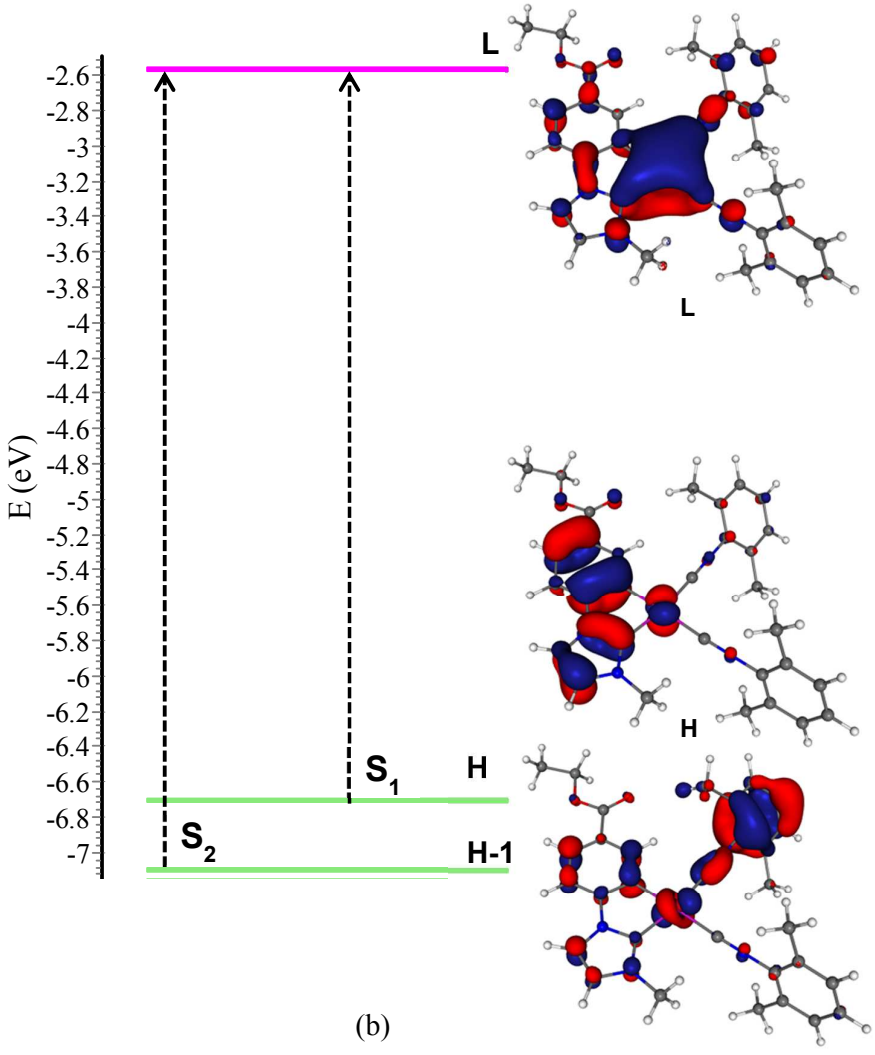


Fig. S11 Frontier molecular orbitals of **6** and **8–10**



(a)



(b)

Fig. S12 (a) Normalized UV-vis absorption spectrum of **6** in CH_2Cl_2, calculated transitions in CH_2Cl_2 (bars); (b) Calculated molecular orbitals for **6**

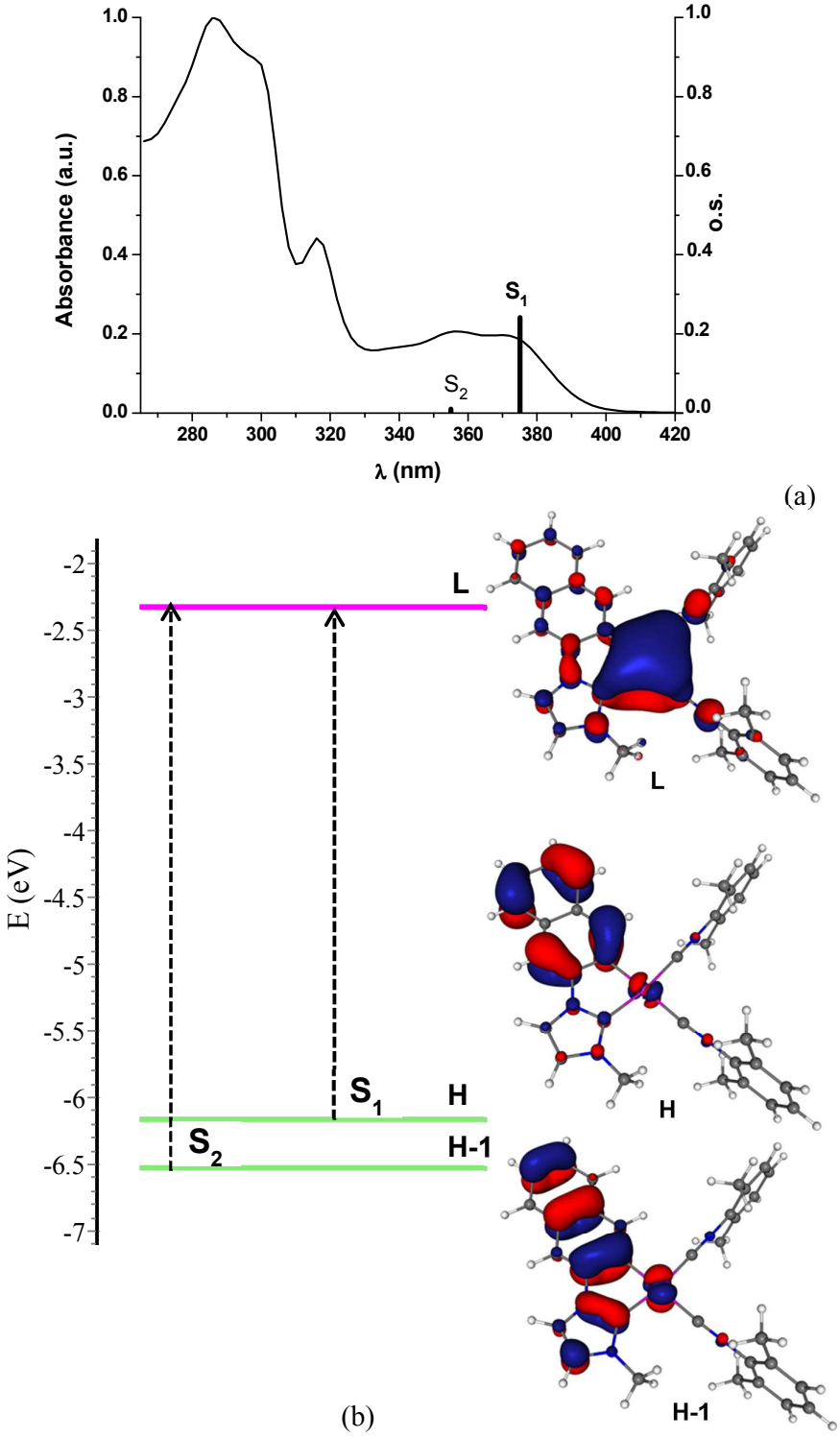


Fig. S13 (a) Normalized UV-vis absorption spectrum of **10** in CH_2Cl_2, calculated transitions in CH_2Cl_2 (bars); (b) Calculated molecular orbitals for **10**

Table S10 Photophysical Data for complexes **5–10**.

Comp	Media (T/K)	λ_{ex} (nm)	λ_{em} (nm)	τ (μs)[c]	ϕ
5	Solid (298)	365	455, 483$_{max}$, 513, 550$_{sh}$	19.5	0.41
		465	643	2.6	
	Solid (77)	365	454, 472, 487$_{max}$, 502, 520$_{sh}$	21.5	
	CH_2Cl_2[a] (77)	326	455$_{max}$, 486, 520	26.5	
	CH_2Cl_2[b] (77)	340, 365	454$_{max}$, 486, 520, 538$_{sh}$	26.6	
		485	665	4.0	
6	Solid (298)	370	464, 492$_{max}$, 528, 567	5.1	0.15
		475	620	2.1	
	Solid (77)	370	462, 492$_{max}$, 528, 567	16.8	
	CH_2Cl_2[a] (77)	325	464$_{max}$, 495, 531, 600$_{sh}$	14.5	
	CH_2Cl_2[b] (77)	370	464$_{max}$, 495, 531, 625	16.4	
		450	464, 495, 531, 625$_{max}$	2.5	
7	Solid (298)	360	449, 477$_{max}$, 510, 550$_{sh}$, 590	4.5	0.17
		450	477, 510, 550, 590$_{max}$	3.8	
	Solid (77)	360	454, 487$_{max}$, 510, 538$_{sh}$	30.0	
	CH_2Cl_2[a,b](77)	320	451, 482, 517	25.0	
8	Solid (298)	375	458, 488$_{max}$, 520, 570$_{sh}$	2.3	0.21
	Solid (77)	375	463, 495$_{max}$, 530, 570$_{sh}$	14.8	
	CH_2Cl_2[a] (77)	323	461$_{max}$, 494, 528, 569$_{sh}$	20.0	
	CH_2Cl_2[b] (77)	365	461$_{max}$, 494, 529, 569$_{sh}$, 609$_{sh}$	18.0	
		450	494, 529, 569$_{sh}$, 609$_{max}$	2.0	
9	Solid (298)	360	540$_{max}$, 586, 635	75.0	0.40
	Solid (77)	360	540$_{max}$, 586, 635	86.0	
	CH_2Cl_2[a,b](77)	365	481$_{max}$, 518, 553, 597, 652$_{sh}$	296 (481, 518)	
				52 (553, 597)	
10	Solid (298)	383	481$_{max}$, 513, 561,609, 661$_{sh}$	88.0	0.17
		440	481, 514, 565$_{max}$, 609, 661$_{sh}$	79.0	
	Solid (77)	402	476$_{max}$, 511, 559, 607, 664$_{sh}$	173.0	
	CH_2Cl_2[a] (77)	360	479$_{max}$, 517, 557, 601	178.0	
	CH_2Cl_2[b] (77)	360	478$_{max}$, 515, 564, 609		
		450	564$_{max}$, 612	30.0	

a = 10^{-5}M; *b* = 10^{-3}M; c = Lifetime measured at the λ_{max} if not specified

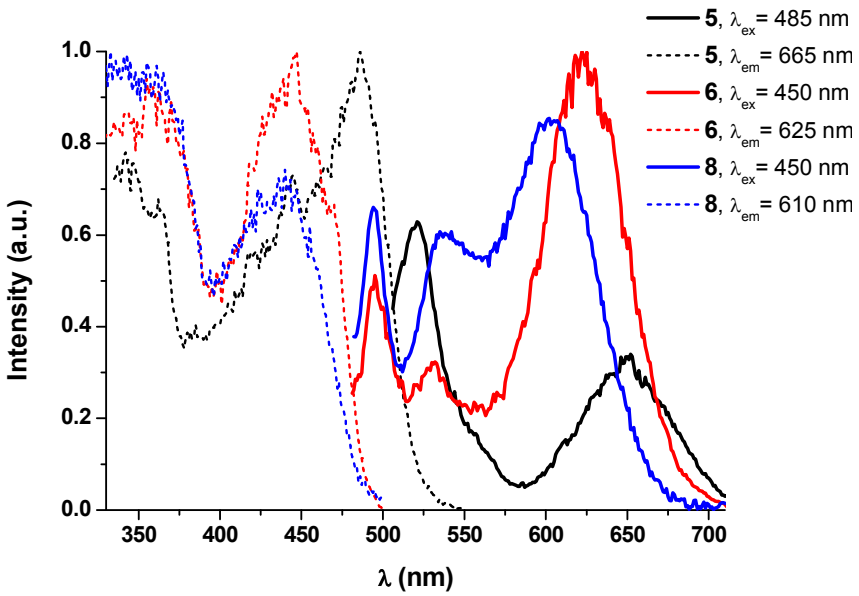


Fig. S14 Normalized excitation and emission spectra of **5**, **6** and **8** at 77 K in rigid matrix of CH_2Cl_2 (10^{-3} M).

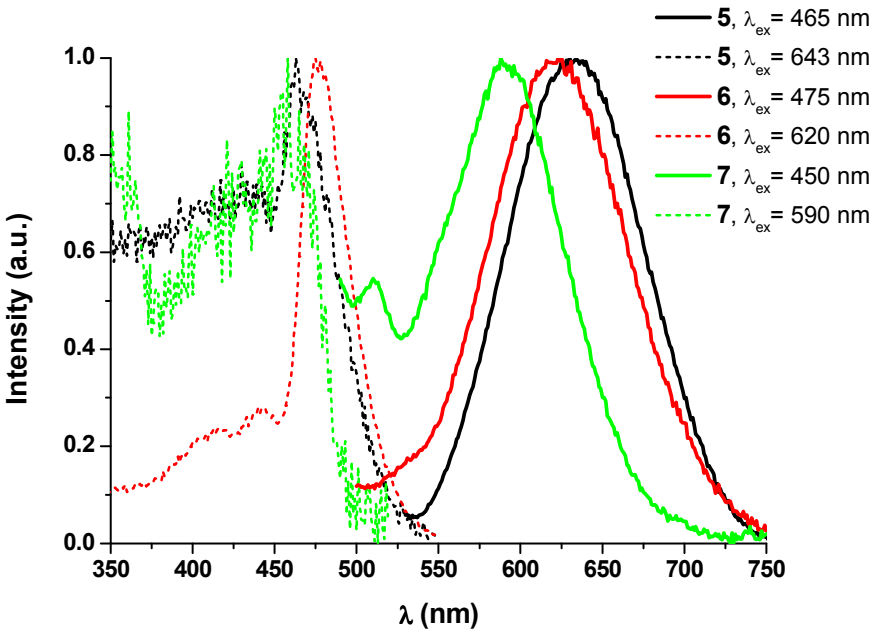


Fig S15 Normalized excitation and emission spectra of **5–7** in solid state at 298 K.

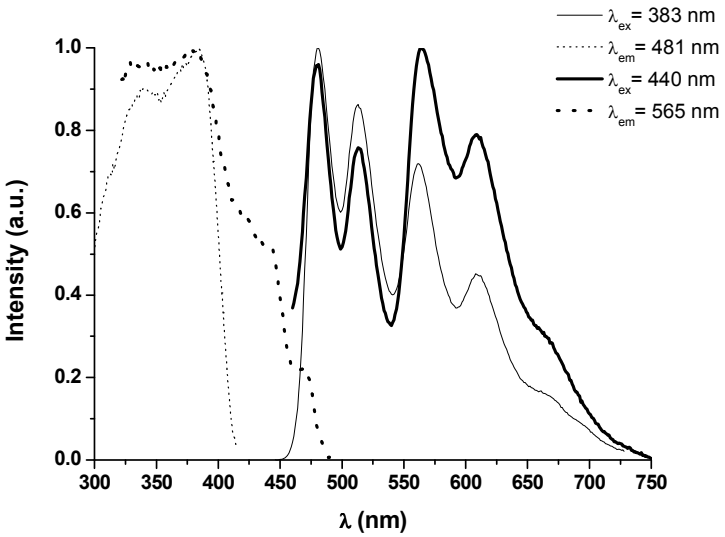


Fig. S16 Normalized excitation and emission spectra of **10** in solid state at 298 K.

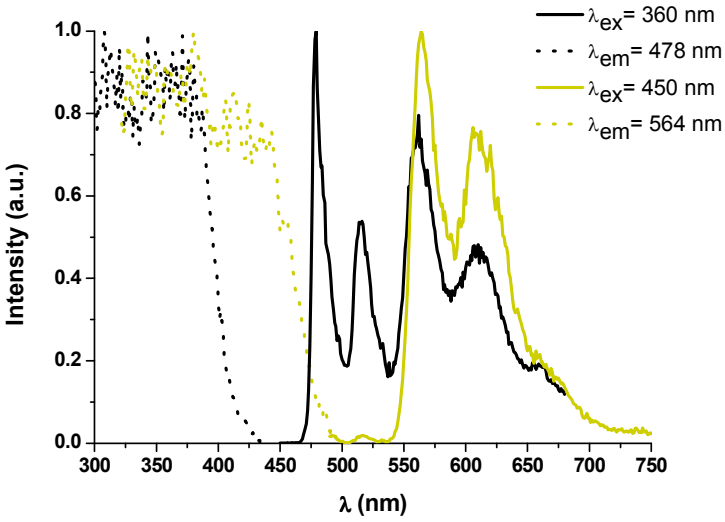


Fig. S17 Normalized excitation and emission spectra of **10** at 77 K in rigid matrix of CH_2Cl_2 (10^{-3} M).

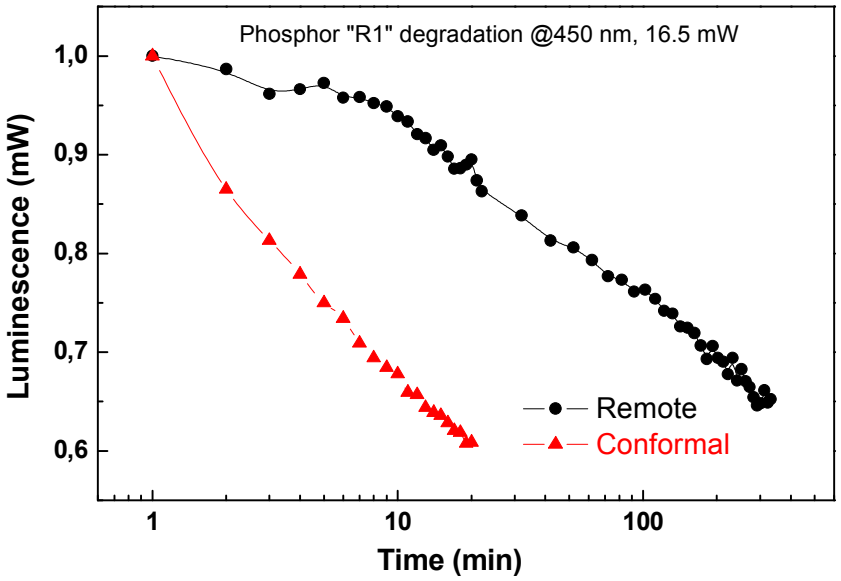


Fig. S18 Degradation study of two devices fabricated with "**R1**" in a conformal and a remote configuration. Both devices were subjected to the same pumping flux: 16.0 mW in order to establish a reliable comparison. It becomes clear that apart from the degradation induced by the UV irradiation, in the conformal architecture the heat from the junction accelerates the degradation of the emission, underlining the clear advantage of the remote phosphor approach in terms of durability.

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