Supporting Information

NEW C^N^C BIS-CYCLOMETALATED Pt(II) COMPLEXES: SYNTHESIS, STRUCTURES AND PHOTOPHYSICAL PROPERTIES

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Experimental Section: general procedures and materials, computational and crystallographic details, scheme S1 and full NMR data.
Xray structure analysis of **3**-**10**: Table S1 and Fig. S1-S8.
^{1}H NMR of complex **8** and aminopyridine at 203 K (Fig. S9).
Normalized UV-Vis spectra of complexes **6**-**10** (Fig. S10-S12)
Computational details: tables of atomic coordinates of compounds **5** and **8** (S2, S3) and pictures of the representative frontier orbitals for them (Fig. S13 and S14).
Solid state emission spectra (Fig. S15) and normalized spectra of 2-MeTHF glassy solutions of **5** at different concentrations (Fig. S16).
Crystallographic data in CIF format.

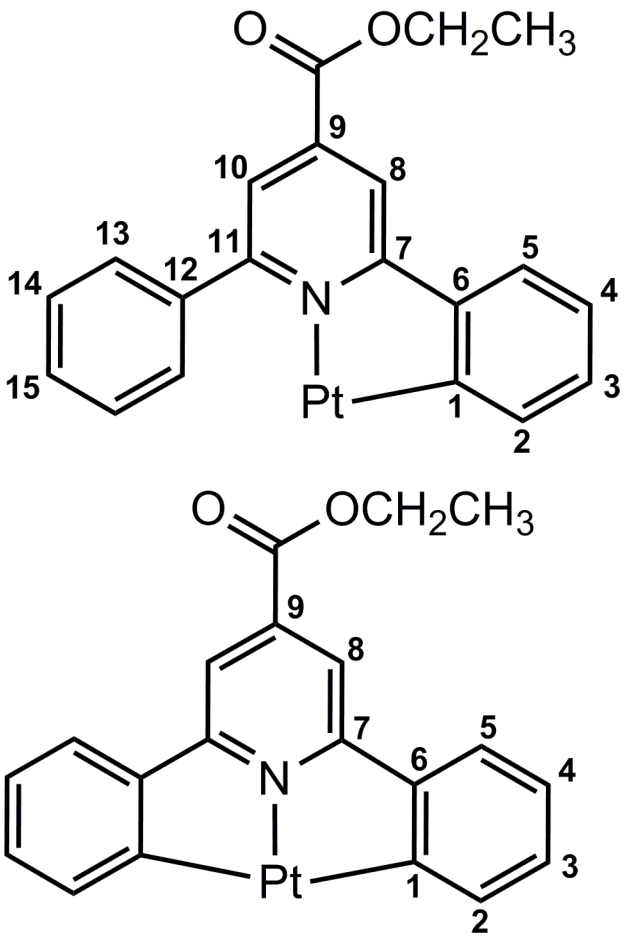
Experimental Section

General procedures and materials. The reactions were carried out without precautions to exclude atmospheric oxygen or moisture. All chemicals were used as supplied unless stated otherwise. ^{1}H, $^{31}P\{^{1}H\}$, and $^{13}C\{^{1}H\}$ NMR spectra were recorded on either a Bruker Avance 400 MHz or a Bruker Avance 500 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, $^{13}C\{^{1}H\}$) or external H_3PO_4 ($^{31}P\{^{1}H\}$). Coupling constant, *J* is given in hertz. Infrared spectra were recorded on a Spectrum One spectrometer as neat solids. Mass spectra were acquired using a micro TOF electrospray Time-of-Flight (ESI-TOF) mass spectrometer (Bruker Daltonik GmbH). C, H, and N analyses were carried out in a CE-440-Elemental Analyzer (Exeter Analytical). UV-visible spectra were obtained a Perkin Elmer, Lambda 650 UV/VIS Spectrometer. Steady-state photoluminescence spectra were recorded on a Jobin-Yvon Horiba Fluorolog FL-3-11 Tau 3 spectrofluorimeter using band pathways of 3 for both excitation and emission. Phosphorescence lifetimes were recorded with a Fluoromax phosphorimeter accessory containing a UV xenon flash tube. Nanosecond lifetimes were recorded with a IBH 5000F coaxial nanosecond flash lamp. The lifetime data were fitted using the Jobin-Yvon software and the Origin pro 7 program.

Computational Methods

Density functional calculations were performed using the B3LYP[1] hybrid density functional under the Gaussian09 package.[2] The SDD pseudopotential and associated basis set[3] was used for platinum, and the 6-31G(d)[4] basis set was used for all other atoms. Geometry optimisations were performed and frequency calculations were used to confirm the stationary points were true minima. TD-DFT calculations were performed at the optimised geometries.

X-ray Structure determinations. Single crystals of compounds **3** and **4** were obtained by slow diffusion of methanol into a saturated CH_2Cl_2 solution; Suitable crystals of complexes **2** and **5-10** were obtained by slow diffusion of *n*-hexane into a saturated CH_2Cl_2. The crystal data, data collection parameters, and structure solution and refinement details for the crystal structures determined are summarized in Table S1. Data collections were carried out on an Oxford Diffraction Gemini A Ultra diffractometer, using graphite monochromated Mo Ka radiation, equipped with a CryojetXL cooling device. The structures were solved using Sir92[10], SHELX-86[11] and refined by full-matrix least-squares F^2 using SHELXL-97[6]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms except those of the amide and amine groups were fixed at idealized positions and were allowed to ride on the relevant carbon atoms.



Scheme S1. Numerical scheme for NMR purposes

Full NMR data of A and 1-10

(EtO_2C-C^N^C-H_2) (A). ^{1}H NMR plus HMBC and HSQC (500 MHz, $CDCl_3$, 298 K) δ_H: 8.26 (s, 2H, H_m (py)), 8.22 (d, $^3J_{H-H}$= 7.0 Hz, 4H, H_o (Ph)), 7.53 (t, $^3J_{H-H}$= 7.5 Hz, 4H, H_m (Ph)), 7.47 (t, $^3J_{H-H}$= 7.3 Hz, 2H, H_p (Ph)), 4.49 (q, $^3J_{H-H}$= 7.0 Hz, 2H, CH_2), 1.48 (t, $^3J_{H-H}$= 7.3 Hz, 3H, CH_3).^{13}C{^{1}H} NMR plus HMBC and HSQC (125.8 MHz, $CDCl_3$, 298 K) δ_C: 165.96 (s, 1C, CO_2Et), 157.95 (s, 2C, C_o(py)), 139.61 (s, 1C, C_p(py)), 138.86 (s, 2C, C_i(Ph)), 129.58 (s, 2C, C_p(Ph)), 128.92 (s, 4C, C_o(Ph)), 127.23 (s, 4C, C_m (Ph)), 117.94 (s, 2C, C_m (py)), 62.02 (s, 1C, CH_2), 14.46 (s, 1C, CH_3),

[{(EtO_2C-C^N^C-H)Pt(μ-Cl)}$_2$] (1). ^{1}H NMR plus HMBC and HSQC (400 MHz, CD_2Cl_2, 298 K) δ_H: 8.13 (d, $^4J_{H-H}$= 1.6 Hz, 2H, H_8), 7.83 (m, 4H, H_{13}), 7.73 (d, $^4J_{H-H}$= 1.6 Hz, 2H, H_{10}), 7.55 (m, 6H, $H_{14,}$ H_{15}), 7.49 (dd, $^3J_{H-H}$= 7.8 Hz, $^5J_{H-H}$= 1.0 Hz, 2H, H_5), 7.11 (td, $^3J_{H-H}$= 7.4 Hz, $^4J_{H-H}$= 0.8 Hz, 2H, H_3), 7.03 (td, $^3J_{H-H}$= 7.4 Hz, $^4J_{H-H}$= 1.2 Hz, 2H, H_4), 6.82 (d, $^3J_{H-H}$= 7.6 Hz, 2H, H_2), 4.41 (q, $^3J_{H-H}$= 7.1 Hz, 4H, CH_2), 1.40 (t, $^3J_{H-H}$= 7.2 Hz, 6H, CH_3). ^{13}C{^{1}H} NMR plus HMBC and HSQC (100.6 MHz, CD_2Cl_2, 298 K) δ_C: 167.54 (s, 2C, C_7), 163.96 (s,

2C, CO_2Et), 162.35 (s, 2C, C_{11}), 143.77 (s, 2C, C_1), 139.12 (s, 2C, C_9), 139.00 (s, 2C, C_{12}), 133.38 (s, 2C, C_6), 131.58 (s, 2C, C_2), 130.19 (s, 2C, C_{15}), 129.51 (s, 4C, C_{13}), 128.97 (s, 2C, C_4), 128.30 (s, 4C, C_{14}), 124.23 (s, 2C, C_3), 124.06 (s, 2C, C_5), 123.34 (s, 2C, C_{10}), 116.12 (s, 2C, C_8), 62.40 (s, 2C, CH_2), 13.91 (s, 2C, CH_3).

[(EtO_2C-C^N^C)Pt(DMSO)] (2). ^{1}H NMR plus HMBC and HSQC (500MHz, CD_2Cl_2, 293 K): δ 7.84 (s, $^4J_{H\text{-}Pt}$ = 7.0, 2H, H^8), 7.78 (dd, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1, $^3J_{H\text{-}Pt}$ = 22.0, 2H, H^2), 7.58 (dd, $^3J_{H\text{-}H}$ = 8.0; $^4J_{H\text{-}H}$ = 1, 2H, H^5), 7.29 (td, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1.5, 2H, H^3), 7.15 (td, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1.5, 2H, H^4), 4.45 (q, $^3J_{H\text{-}H}$ = 7.0, 2H, OCH_2), 3.65 (s, $^3J_{H\text{-}Pt}$ = 27.0, 6H, DMSO), 1.45 (t, $^3J_{H\text{-}H}$ = 7.0, 3H, CH_3). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC (100.6 MHz, CD_2Cl_2, 293 K): δ 168.2 (s, $^2J_{C\text{-}Pt}$ = 76.1, 2C, C^7), 167.0 (s, $^1J_{C\text{-}Pt}$ = 713.7, 2C, C^1), 164.6 (s, 1C, CO_2Et), 149.6 (s, $^2J_{C\text{-}Pt}$ = 42.5, 2C, C^6), 143.1 (s, 1C, C^9), 136.8 (s, $^2J_{C\text{-}Pt}$ = 44.9, 2C, C^2), 131.5 (s, $^3J_{C\text{-}Pt}$ = 26.7, 2C, C^3), 125.4 (s, 2C, C^4), 125.4 (s, $^3J_{C\text{-}Pt}$ = 26.7, 2C, C^5), 115.1 (s, $^3J_{C\text{-}Pt}$ = 33.5, 2C, C^8), 62.9 (s, 1C, OCH_2), 48.8 (s, $^2J_{C\text{-}Pt}$ = 73.9, 2C, DMSO), 14.5 (s, 1C, CH_3).

[(EtO_2C-C^N^C)Pt(tht)] (3). ^{1}H NMR plus HMBC and HSQC (500MHz, CD_2Cl_2, 293 K): δ 7.80 (s, $^4J_{H\text{-}Pt}$ = 9.5, 2H, H^8), 7.55 (dd, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1, 2H, H^5), 7.50 (dd, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1; $^3J_{H\text{-}Pt}$ = 22.3, 2H, H^2), 7.26 (td, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1, 2H, H^4), 7.11 (td, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1, 2H, H^3), 4.43 (q, $^3J_{H\text{-}H}$ = 7.0, 2H, OCH_2), 3.56 (m, $^3J_{H\text{-}Pt}$ = 26.5, 4H, SCH_2), 2.16 (m, 4H, SCH_2CH_2), 1.45 (t, $^3J_{H\text{-}H}$ = 7.0, 3H, CH_3). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC (125.7 MHz, CD_2Cl_2, 293 K): δ 168.6 (s, $^1J_{C\text{-}Pt}$ = 713.7, 2C, C^1), 167.5 (s, $^2J_{C\text{-}Pt}$ = 76.1, 2C, C^7), 164.5 (s, 1C, CO_2Et), 149.2 (s, $^2J_{C\text{-}Pt}$ = 46.0, 2C, C^6), 141.1 (s, 1C, C^9), 136.2 (s, $^2J_{C\text{-}Pt}$ = 44.1, 2C, C^2), 130.8 (s, $^3J_{C\text{-}Pt}$ = 28.1, 2C, C^3), 124.5 (s, $^3J_{C\text{-}Pt}$ = 26.7, 2C, C^5), 123.9 (s, 2C, C^4), 114.3 (s, $^3J_{C\text{-}Pt}$ = 37.9, 2C, C^8), 62.1 (s, 1C, OCH_2), 40.2 (s, $^2J_{C\text{-}Pt}$ = 16.7, 2C, SCH_2), 29.8 (s, $^3J_{C\text{-}Pt}$ = 17.0, 2C, SCH_2CH_2), 14.0 (s, 1C, CH_3).

[(EtO_2C-C^N^C)Pt(PPh_3)] (4). ^{1}H NMR plus HMBC and HSQC (400MHz, CD_2Cl_2, 293 K): δ 7.89 (s, 2H, H^8), 7.83 (m, 6H, *o*-PhP), 7.53 (d, $^3J_{H\text{-}H}$ = 7.6, 2H, H^5), [7.46-7.38] (m, 9H, *p*-PhP and *m*-PhP), 6.94 (t, $^3J_{H\text{-}H}$ = 7.6, 2H, H^4), 6.68 (t, $^3J_{H\text{-}H}$ = 7.6, 2H, H^3), 6.26 (d, $^3J_{H\text{-}H}$ = 7.6, 2H, H^2), 4.46 (q, $^3J_{H\text{-}H}$ = 7.0, 2H, OCH_2), 1.46 (t, $^3J_{H\text{-}H}$ = 7.0, 3H, CH_3). $^{31}P\{^1H\}$ NMR (161.9MHz, CD_2Cl_2, 293 K): δ 27.9 (s, $^1J_{P\text{-}Pt}$ = 4096.4). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC (100.6 MHz, CD_2Cl_2, 293 K): δ 167.9 (s, $^2J_{C\text{-}Pt}$ = 70.5, 2C, C^7), 166.5 (d, $^2J_{C\text{-}P}$ = 6.9, $^1J_{C\text{-}Pt}$ = 691.6, 2C, C^1), 165.1 (s, 1C, CO_2Et), 150.7 (d, $^3J_{C\text{-}P}$ = 1.4; $^2J_{C\text{-}Pt}$ = 34.0, 2C, C^6), 142.4 (s, 1C, C^9), 139.2 (d, $^3J_{C\text{-}P}$ = 1.5; $^2J_{C\text{-}Pt}$ = 55.4, 2C, C^2), 135.8 (d, $^2J_{C\text{-}P}$ = 11.5; $^3J_{C\text{-}Pt}$ = 41.7, 6C, *o*-PhP), 132.4 (d, $^1J_{C\text{-}P}$ = 344.6, 3C, *i*-PhP), 131.1 (d, $^4J_{C\text{-}P}$ = 1.6, 3C, *p*-PhP), 130.4 (s, $^3J_{C\text{-}Pt}$ =

32.9, 2C, C^3), 128.7 (d, $^3J_{C\text{-}P}$ = 10.7, 6C, *m*-PhP), 124.8 (s, $^3J_{C\text{-}Pt}$ = 25.2, 2C, C^5), 124.2 (s, 2C, C^4), 115.0 (d, $^4J_{C\text{-}P}$ = 3.2; $^3J_{C\text{-}Pt}$ = 27.0, 2C, C^8), 62.7 (s, 1C, OCH_2), 14.6 (s, 1C, CH_3).

[(EtO_2C-C^N^C)Pt(CN-^{t}Bu)] (5). ^{1}H NMR plus HMBC and HSQC (500MHz, CD_2Cl_2, 293 K): δ 7.80 (s, $^4J_{H\text{-}Pt}$ = 6.5, 2H, H^8), 7.63 (d, $^3J_{H\text{-}H}$ = 6.5; $^3J_{H\text{-}Pt}$ = 32.7, 2H, H^2), 7.54 (d, $^3J_{H\text{-}H}$ = 7.5, 2H, H^5), 7.22 (td, $^3J_{H\text{-}H}$ = 7.0; $^4J_{H\text{-}H}$ = 1.0, 2H, H^3), 7.11 (td, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1.0, 2H, H^4), 4.44 (q, $^3J_{H\text{-}H}$ = 7.0, 2H, OCH_2), 1.69 (s, 9H, CN-*t*-Bu), 1.44 (t, $^3J_{H\text{-}H}$ = 7.0, 3H, CH_3). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC (125.7 MHz, CD_2Cl_2, 293 K): δ 168.8 (s, $^2J_{C\text{-}Pt}$ = 67.1, 2C, C^7), 168.3 (s, $^1J_{C\text{-}Pt}$ = 665.3, 2C, C^1), 164.3 (s, 1C, CO_2Et), 149.1 (s, $^2J_{C\text{-}Pt}$ = 34.3, 2C, C^6), 142.1 (s, 1C, C^9), 138.2 (s, $^2J_{C\text{-}Pt}$ = 69.5, 2C, C^2), 131.6 (s, $^3J_{C\text{-}Pt}$ = 36.2, 2C, C^3), 129.4 (s, $^1J_{C\text{-}Pt}$ = 1698.3, 1C, *C*N-*t*-Bu), 124.5 (s, $^3J_{C\text{-}Pt}$ = 24.6, 2C, C^5), 124.2 (s, 2C, C^4), 114.6 (s, $^3J_{C\text{-}Pt}$ = 30.6, 2C, C^8), 62.2 (s, 1C, OCH_2), 30.5 (s, 3C, CH_3, CN-*t*-Bu), 14.0 (s, 1C, CH_3).

[(EtO_2C-C^N^C)Pt(py)] (6). ^{1}H NMR plus HMBC and HSQC (500MHz, CD_2Cl_2, 293 K): δ 8.89 (dd, $J_{H\text{-}H}$ = 6.5, $J_{H\text{-}H}$ = 1.5, $^3J_{H\text{-}Pt}$ = 45.0, 2H, H_o (py)), 7.90 (tt, $J_{H\text{-}H}$ = 7.5, $J_{H\text{-}H}$ = 1.5, 1H, H_p (py)), 7.74 (s, 2H, H^8), 7.54 (d, $^3J_{H\text{-}H}$ = 8.0, 2H, H^5), 7.45 (td, $J_{H\text{-}H}$ = 6.5, $J_{H\text{-}H}$ = 1.0, 2H, H_m (py)), 7.21 (td, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1.0, 2H, H^3), 7.08 (td, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1.0, 2H, H^4), 6.90 (d, $^3J_{H\text{-}H}$ = 4.5; $^3J_{H\text{-}Pt}$ = 23.0, 2H, H^2), 4.44 (q, $^3J_{H\text{-}H}$ = 7.0, 2H, OCH_2), 1.49 (t, $^3J_{H\text{-}H}$ = 7.0, 3H, CH_3). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC (125.7 MHz, CD_2Cl_2, 293 K): δ 173.0 (s, $^1J_{C\text{-}Pt}$ = 734.1, 2C, C^1), 169.3 (s, $^2J_{C\text{-}Pt}$ = 76.4, 2C, C^7), 165.3 (s, 1C, CO_2Et), 154.1 (s, $^2J_{C\text{-}Pt}$ = 12.9, 2C, C_o(py)), 149.1 (s, $^2J_{C\text{-}Pt}$ = 55.0, 2C, C^6), 141.4 (s, 1C, C^9), 136.9 (s, $^4J_{C\text{-}Pt}$ = 14.3, 1C, C_p(py)), 133.7 (s, $^2J_{C\text{-}Pt}$ = 44.4, 2C, C^2), 131.3 (s, $^3J_{C\text{-}Pt}$ = 28.9, 2C, C^3), 126.9 (s, $^3J_{C\text{-}Pt}$ = 49.5, 2C, C_m(py)), 124.8 (s, $^3J_{C\text{-}Pt}$ = 29.1, 2C, C^5), 124.1 (s, 2C, C^4), 113.9 (s, $^3J_{C\text{-}Pt}$ = 38.7, 2C, C^8), 62.0 (s, 1C, OCH_2), 14.0 (s, 1C, CH_3).

[(EtO_2C-C^N^C)Pt(py-^{t}Bu)] (7). ^{1}H NMR plus HMBC and HSQC (500MHz, CD_2Cl_2, 293 K): δ 8.87 (d, $J_{H\text{-}H}$ = 6.0, $^3J_{H\text{-}Pt}$ = 43.5, 2H, H_o (py-^{t}Bu)), 7.77 (s, 2H, H^8), 7.55 (d, $^3J_{H\text{-}H}$ = 7.5, 2H, H^5), 7.47 (d, $J_{H\text{-}H}$ = 6.0, 2H, H_m (py-^{t}Bu)), 7.22 (td, $^3J_{H\text{-}H}$ = 7.0, 2H, H^3), 7.08 (td, $^3J_{H\text{-}H}$ = 7.5, 2H, H^4), 6.96 (d, $^3J_{H\text{-}H}$ = 7.0; $^3J_{H\text{-}Pt}$ = 24.0, 2H, H^2), 4.44 (q, $^3J_{H\text{-}H}$ = 7.0, 2H, OCH_2), 1.45 (t, $^3J_{H\text{-}H}$ = 7.0, 3H, CH_3), 1.42 (s, 9H, py-^{t}Bu). $^{13}C\{^1H\}$ NMR plus HMBC and HSQC (125.7 MHz, CD_2Cl_2, 293 K): δ 172.6 (s, $^1J_{C\text{-}Pt}$ = 736.6, 2C, C^1), 168.9 (s, $^2J_{C\text{-}Pt}$ = 76.3, 2C, C^7), 164.8 (s, 1C, CO_2Et), 161.4 (s, 1C, C_i(py-^{t}Bu)), 152.9 (s, $^2J_{C\text{-}Pt}$ = 14.7, 2C, C_o(py-^{t}Bu)), 148.6 (s, $^2J_{C\text{-}Pt}$ = 52.6, 2C, C^6), 140.9 (s, 1C, C^9), 133.3 (s, $^2J_{C\text{-}Pt}$ = 44.2, 2C, C^2), 130.8 (s, $^3J_{C\text{-}Pt}$ = 29.2, 2C, C^3), 124.3 (s, $^3J_{C\text{-}Pt}$ = 29.3, 2C, C^5), 123.6 (s, 2C, C^4), 123.6 (s, $^3J_{C\text{-}Pt}$ = 49.2, 2C, C_m(py-^{t}Bu)), 113.9 (s, $^3J_{C\text{-}Pt}$ = 38.9, 2C, C^8), 62.1 (s, 1C, OCH_2), 35.2 (s, 1C, (py-^{t}Bu)), 30.1 (s, 3C, CH_3(py-^{t}Bu)), 14.1 (s, 1C, CH_3).

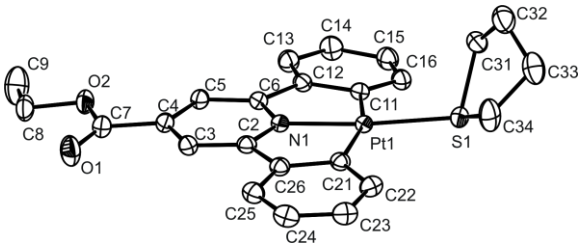
[(EtO$_2$C-C^N^C)Pt(py-NH$_2$)] (8). ^{1}H NMR plus HMBC and HSQC (500MHz, Acetone-d^6, 293 K): δ 8.39 (dd, $J_{H\text{-}H}$ = 6.0, $J_{H\text{-}H}$ = 1.0, $^3J_{H\text{-}Pt}$ = 43.0, 2H, H$_o$ (py-NH$_2$)), 7.79 (s, $^4J_{H\text{-}Pt}$ = 7.5, 2H, H^8), 7.59 (d, $^3J_{H\text{-}H}$ = 7.5, 2H, H^5), 7.19 (td, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1.0, 2H, H^3), 7.06 (d, $^3J_{H\text{-}H}$ = 7.5; $^3J_{H\text{-}Pt}$ = 23.0, 2H, H^2), 7.03 (td, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1.0, 2H, H^4), 6.83 (dd, $J_{H\text{-}H}$ = 5.5, $J_{H\text{-}H}$ = 1.5, 2H, H$_m$ (py-NH$_2$)), 6.35 (s, 2H, NH$_2$ (py-NH$_2$)), 4.44 (q, $^3J_{H\text{-}H}$ = 7.0, 2H, OCH$_2$), 1.44 (t, $^3J_{H\text{-}H}$ = 7.0, 3H, CH$_3$). ^{13}C{^{1}H} NMR plus HMBC and HSQC (125.7 MHz, Acetone-d^6, 293 K): δ 173.9 (s, 2C, C^1), 169.3 (s, 2C, C^7), 164.5 (s, 1C, CO$_2$Et), 152.8 (s, 2C, C$_o$(py-NH$_2$)), 148.4 (s, 2C, C^6), 140.8 (s, 1C, C^9), 133.7 (s, 2C, C^2), 130.6 (s, 2C, C^3), 124.1 (s, 2C, C^5), 123.0 (s, 2C, C^4), 113.3 (s, 2C, C^8), 110.7 (s, 2C, C$_m$(py-NH$_2$)), 61.7 (s, 1C, OCH$_2$), 13.6 (s, 1C, CH$_3$).

[(EtO$_2$C-C^N^C)Pt(py-CN)] (9). ^{1}H NMR plus HMBC and HSQC (500MHz, CD$_2$Cl$_2$, 293 K): δ 9.16 (dd, $J_{H\text{-}H}$ = 5.5; $J_{H\text{-}H}$ = 1.5 $^3J_{H\text{-}Pt}$ = 45.5, 2H, H$_o$ (py-CN)), 7.73 (s, $^4J_{H\text{-}Pt}$ = 7.5, 2H, H^8), 7.63 (dd, $J_{H\text{-}H}$ = 5.5; $J_{H\text{-}H}$ = 1.5, 2H, H$_m$ (py-CN)), 7.52 (d, $^3J_{H\text{-}H}$ = 7.5, 2H, H^5), 7.21 (td, $^3J_{H\text{-}H}$ = 7.0; $^4J_{H\text{-}H}$ = 1.0, 2H, H^3), 7.08 (td, $^3J_{H\text{-}H}$ = 7.5; $^3J_{H\text{-}H}$ = 1.0, 2H, H^4), 6.81 (dd, $^3J_{H\text{-}H}$ = 7.0; $^4J_{H\text{-}H}$ = 1.0, $^3J_{H\text{-}Pt}$ = 22.5, 2H, H^2), 4.44 (q, $^3J_{H\text{-}H}$ = 7.0, 2H, OCH$_2$), 1.45 (t, $^3J_{H\text{-}H}$ = 7.0, 3H, CH$_3$). ^{13}C{^{1}H} NMR plus HMBC and HSQC (125.7 MHz, CD$_2$Cl$_2$, 293 K): δ 172.3 (s, $^1J_{C\text{-}Pt}$ = 731.8, 2C, C^1), 168.9 (s, $^2J_{C\text{-}Pt}$ = 75.8, 2C, C^7), 165.1 (s, 1C, CO$_2$Et), 154.9 (s, 2C, C$_o$(py-CN)), 149.0 (s, $^2J_{C\text{-}Pt}$ = 55.1, 2C, C^6), 141.6 (s, 1C, C^9), 133.1 (s, $^2J_{C\text{-}Pt}$ = 44.2, 2C, C^2), 131.3 (s, $^3J_{C\text{-}Pt}$ = 29.4, 2C, C^3), 128.7 (s, $^3J_{C\text{-}Pt}$ = 52.9, 2C, C$_m$(py-CN)), 125.0 (s, $^3J_{C\text{-}Pt}$ = 28.6, 2C, C^5), 124.4 (s, 2C, C^4), 119.8 (s, 1C, C$_i$(py-CN)), 116.4 (s, 1C, CN (py-CN)), 114.7 (s, $^3J_{C\text{-}Pt}$ = 39.1, 2C, C^8), 62.6 (s, 1C, OCH$_2$), 14.6 (s, 1C, CH$_3$).

[(EtO$_2$C-C^N^C)Pt(py-CONH$_2$)] (10). ^{1}H NMR plus HMBC and HSQC (500MHz, Acetone-d^6, 293 K): δ 9.18 (dd, $J_{H\text{-}H}$ = 5.2, $J_{H\text{-}H}$ = 1.7, $^3J_{H\text{-}Pt}$ = 45.5, 2H, H$_o$ (py-CONH$_2$)), 8.09 (dd, $J_{H\text{-}H}$ = 5.2, $J_{H\text{-}H}$ = 1.7, 2H, H$_m$ (py-CONH$_2$)), 7.99 (s, 1H, NH$_2$ (py-CONH$_2$)), 7.74 (s, $^4J_{H\text{-}Pt}$ = 8.0, 2H, H^8), 7.64 (d, $^3J_{H\text{-}H}$ = 7.5, 2H, H^5), 7.23 (s, 1H, NH$_2$ (py-CONH$_2$)), 7.18 (td, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1.0, 2H, H^3), 7.06 (td, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1.0, 2H, H^4), 6.88 (dd, $^3J_{H\text{-}H}$ = 7.5; $^4J_{H\text{-}H}$ = 1.0; $^3J_{H\text{-}Pt}$ = 24.2, 2H, H^2), 4.47 (q, $^3J_{H\text{-}H}$ = 7.0, 2H, OCH$_2$), 1.46 (t, $^3J_{H\text{-}H}$ = 7.0, 3H, CH$_3$). ^{13}C{^{1}H} NMR plus HMBC and HSQC (125.7 MHz, Acetone-d^6, 293 K): δ 172.8 (s, $^1J_{C\text{-}Pt}$ = 734.1, 2C, C^1), 169.1 (s, $^2J_{C\text{-}Pt}$ = 76.4, 2C, C^7), 164.3 (s, 1C, CO$_2$Et), 153.9 (s, $^2J_{C\text{-}Pt}$ = 14.5, 2C, C$_o$(py-CONH$_2$)), 148.2 (s, 2C, C^6), 141.4 (s, 1C, C^9), 133.1 (s, $^2J_{C\text{-}Pt}$ = 47.4, 2C, C^2), 130.8 (s, $^3J_{C\text{-}Pt}$ = 28.8, 2C, C^3), 124.4 (s, $^3J_{C\text{-}Pt}$ = 51.5, 2C, C$_m$(py-CONH$_2$)), 124.3 (s, $^3J_{C\text{-}Pt}$ = 29.4, 2C, C^5), 123.4 (s, 2C, C^4), 113.5 (s, $^3J_{C\text{-}Pt}$ = 37.7, 2C, C^8), 61.8 (s, 1C, OCH$_2$), 13.5 (s, 1C, CH$_3$).

Table S1: Selected bond lengths (Å) and angles (º) for **3**-**10**

	3 (X= S(1))	**4** (X= P(1))	**5** CH_2Cl_2 (X= C(30))	**6** (X= N(2))	**7** (X= N(2))	**8** CH_2Cl_2 (X= N(2))	**9** (X= N(2))	**10** $2(CH_2Cl_2)$ (X= N(2))
Distances (Å)								
Pt(1)-C(11)	2.065(2)	2.075(15)	2.063(2)	2.063(2)	2.050(17)	2.044(3)	2.071(3)	2.054(2)
Pt(1)-C(21)	2.070(2)	2.087(15)	2.056(2)	2.051(2)	2.050(16)	2.053(3)	2.055(3)	2.051(2)
Pt(1)-N(1)	1.988(18)	2.023(12)	1.998(17)	1.963(19)	1.964(12)	1.964(2)	1.961(2)	1.966(16)
Pt(1)-X	2.257(6)	2.230(4)	1.899(2)	2.029(19)	2.033(13)	2.031(2)	2.022(2)	2.019(16)
C(7)-O(1)	1.202(3)	1.199(2)	1.210(3)	1.207(3)	1.204(19)	1.208(3)	1.202(4)	1.218(3)
C(7)-O(2)	1.335(3)	1.337(2)	1.342(3)	1.334(3)	1.340(2)	1.332(3)	1.330(4)	1.322(3)
C(4)-C(7)	1.499(3)	1.497(2)	1.490(3)	1.490(3)	1.498(2)	1.501(4)	1.484(4)	1.495(3)
C(3)-C(4)	1.394(3)	1.382(2)	1.384(3)	1.401(3)	1.391(2)	1.384(4)	1.403(4)	1.386(3)
C(8)-C(9)	1.495(4)	1.459(3)	1.509(4)	1.492(4)	1.499(3)	1.497(4)	1.503(5)	1.497(4)
Angles (º)								
C(11)-Pt(1)-C(21)	161.28(9)	158.62(6)	161.09(8)	162.44(9)	162.54(6)	162.96(11)	162.31(10)	162.40(8)
N(1)-Pt(1)-C(11)	81.01(8)	79.95(5)	80.55(7)	81.18(8)	81.51(6)	81.59(10)	81.10(10)	81.08(8)
N(1)-Pt(1)-C(21)	80.62(8)	79.69(6)	80.57(7)	81.56(9)	81.28(6)	81.37(10)	81.29(10)	81.55(8)
C(11)-Pt(1)-X	93.75(6)	97.58(4)	100.40(8)	98.98(8)	96.76(6)	96.00(9)	99.57(10)	100.64(8)
C(21)-Pt(1)-X	104.77(6)	103.45(4)	98.51(8)	98.52(9)	100.62(6)	101.04(10)	98.10(10)	96.86(8)



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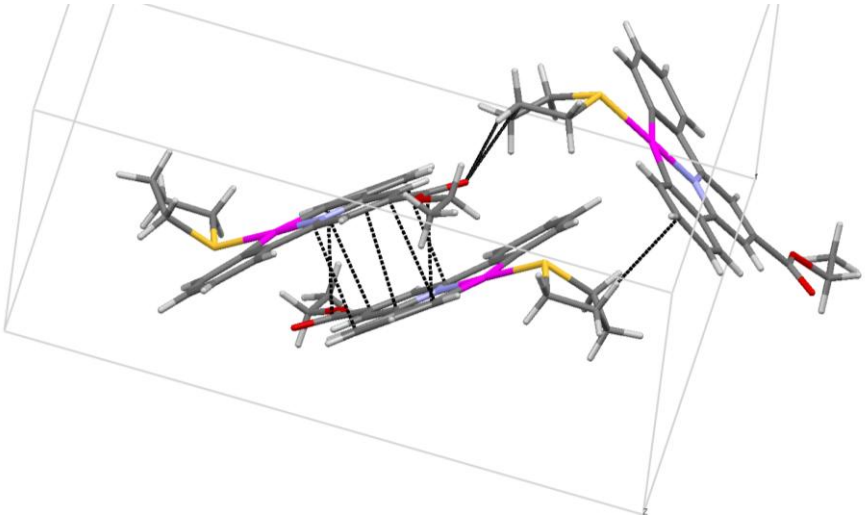
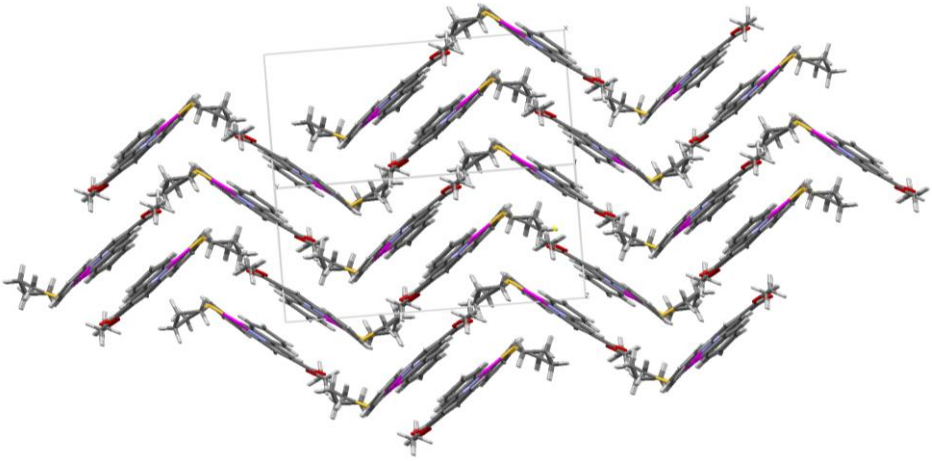
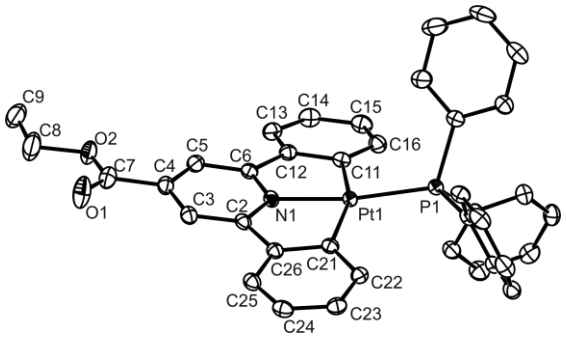


(b)

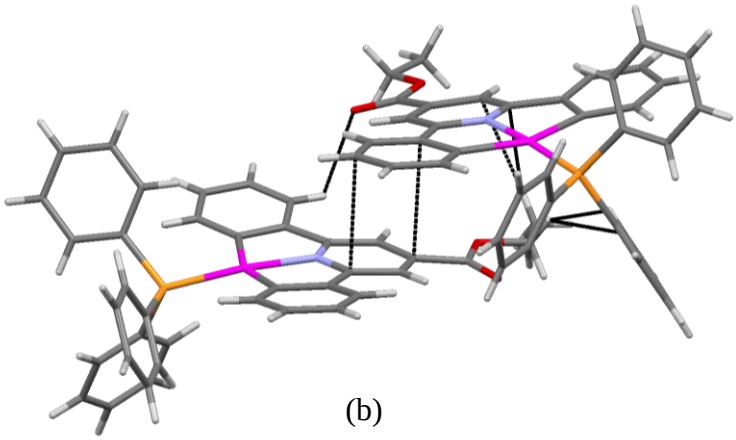


(c)

Figure S1. a) ORTEP view of **3**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity; b) head to tail molecular orientation. These molecular pairs show rather short π···π contacts (3.30-3.36 Å) between the aromatic rings of the CNC ligand. The zig-zag array of the molecules is supported by the weak interactions C-H (tht)···O (ester) (C···O 3.20 Å, H···O 2.27 Å) and C-H (tht)···aromatic (CNC) (C···C 3.69 Å, H···C 2.78 Å); c) Perspective view of the zig zag network.



(a)



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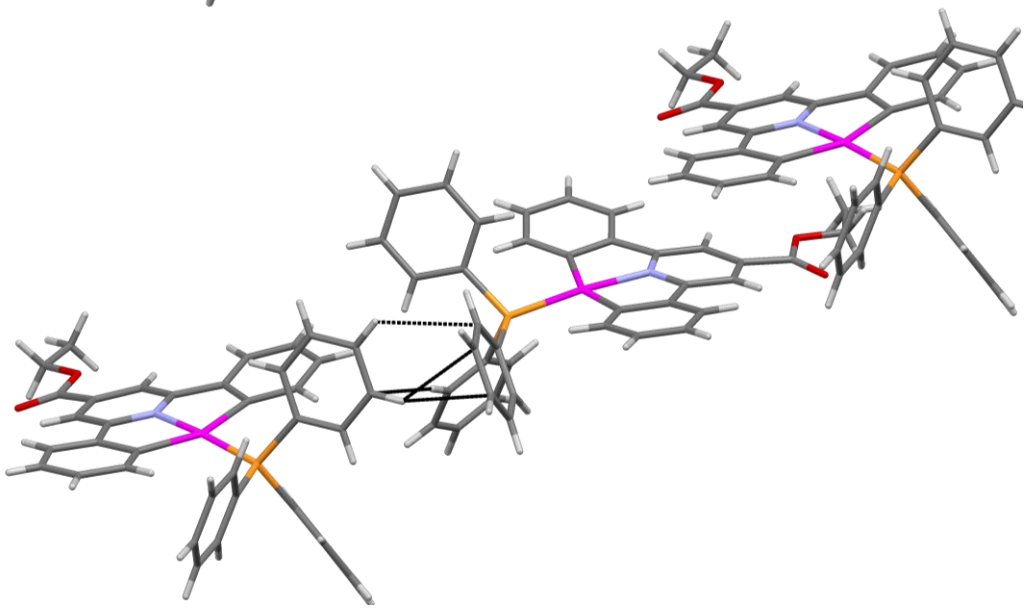
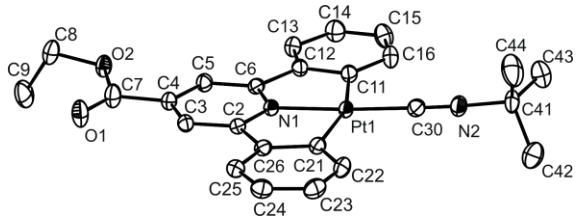


(c)

Figure S2. a) ORTEP view of **4**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity; b) side overlapping in molecular pairs. These molecular pairs show π···π contacts (3.23-3.30 Å) between the CNC aromatic rings and also C-H (CNC)···O (ester) contacts (C···O 3.30 Å, H···O 2.67 Å). c) These molecular pairs got connected with other pairs through C-H (PPh_3)···(aromatic) (PPh_3) contacts (C···C = 3.50-3.82 Å, H···C = 2.85 - 2.88 Å) .



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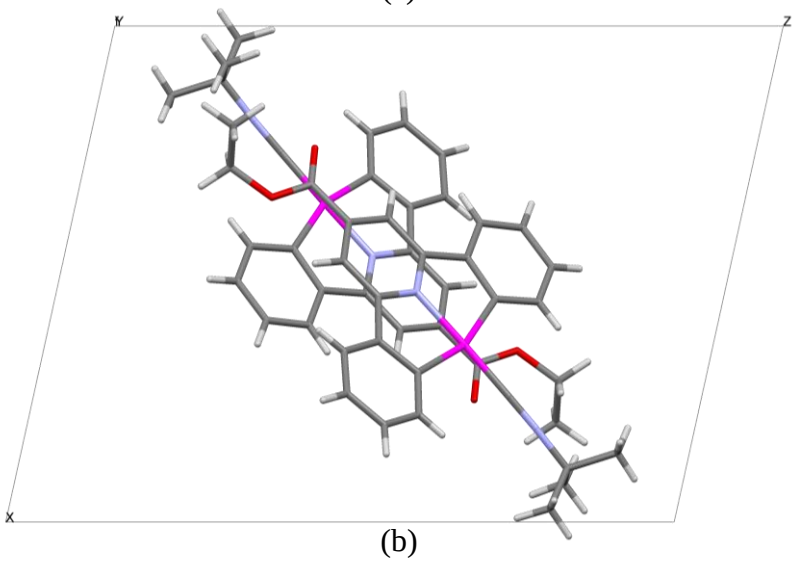

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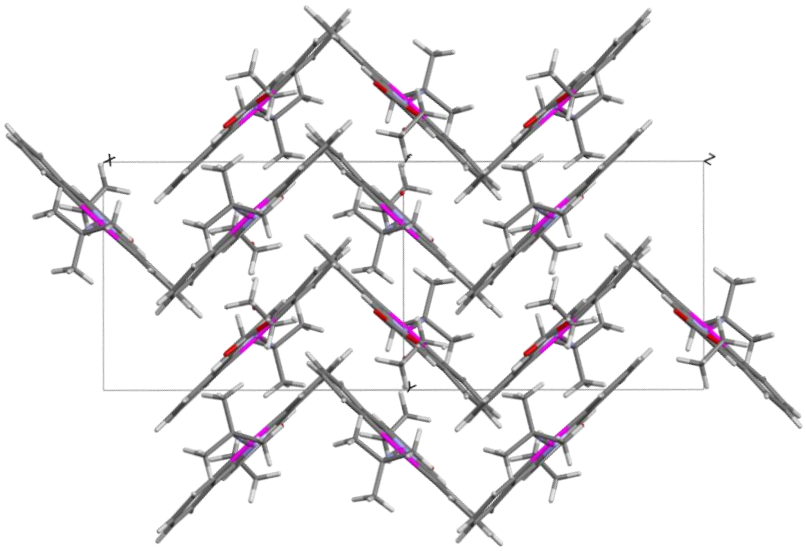
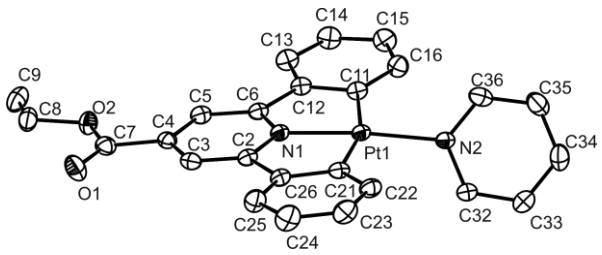


(c)

Figure S3. a) ORTEP view of **5**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity; b) View along b axis of the head to tail molecular pairs. These molecular pairs show π···π contacts (3.38-3.63 Å) between the aromatic rings of the CNC ligand. c) Crystal-packing showing molecular piles in a zig-zag network.



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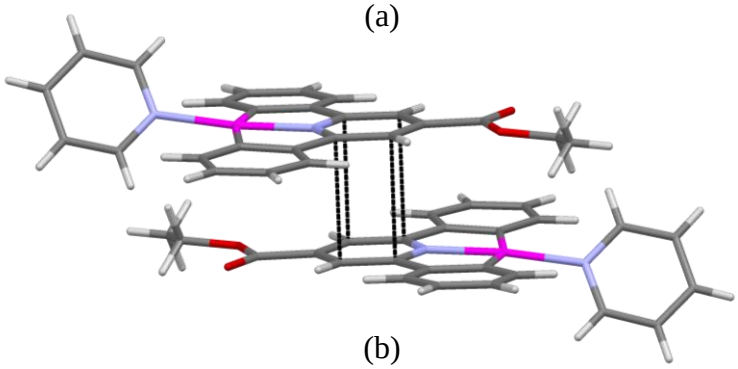

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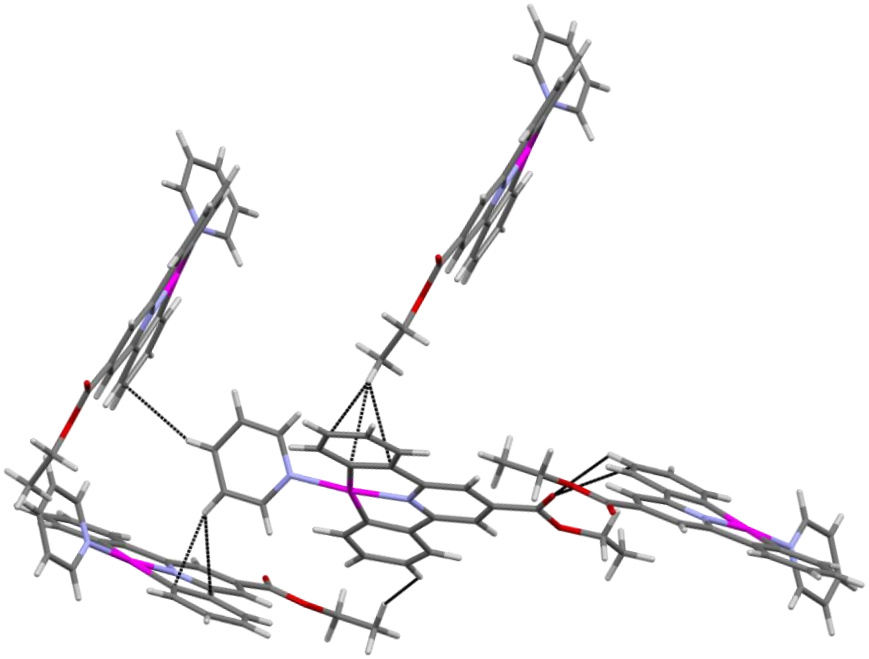
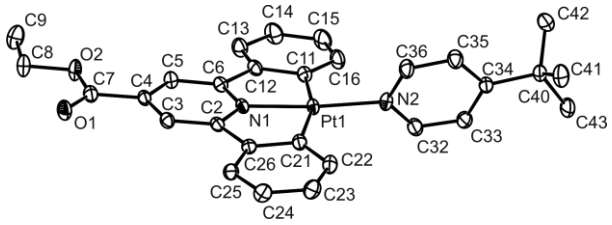


(c)

Figure S4. a) ORTEP view of **6**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity; b) Head to tail molecular orientation diagram shows the CNC pyridine ring overlapping with close π···π contacts (3.35 and 3.37 Å). c) Non covalent interactions of the upper monomer: C-H (CNC)···O (ester) contacts (C···O 3.21 Å, H···O 2.55 Å), C-H (ester)···(aromatic) (CNC) contacts (C···C = 3.57-3.77 Å, H···C = 2.73 - 2.89 Å), C-H (py)···(aromatic) (CNC) contacts (C···C = 3.49-3.63 Å, H···C = 2.61 - 2.88 Å).



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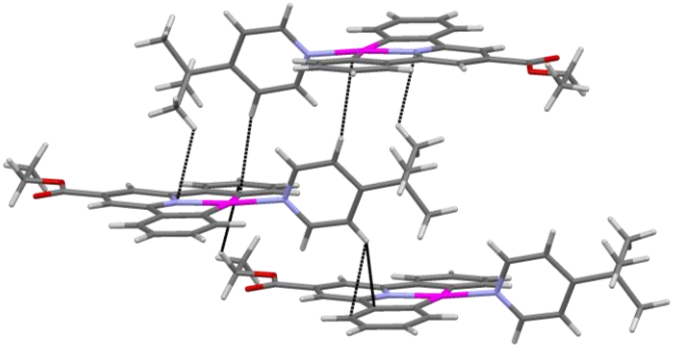


(b)

Figure S5. a) ORTEP view of **7**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity; b) Further non covalent contacts between the monomers: C-H (ester)···N (CNC) contacts (C···N = 3.40 Å, H···N = 2.72 Å), C-H (py)···(aromatic) (CNC) contacts (C···C = 3.49-3.77 Å, H···C = 2.83 - 2.86 Å).

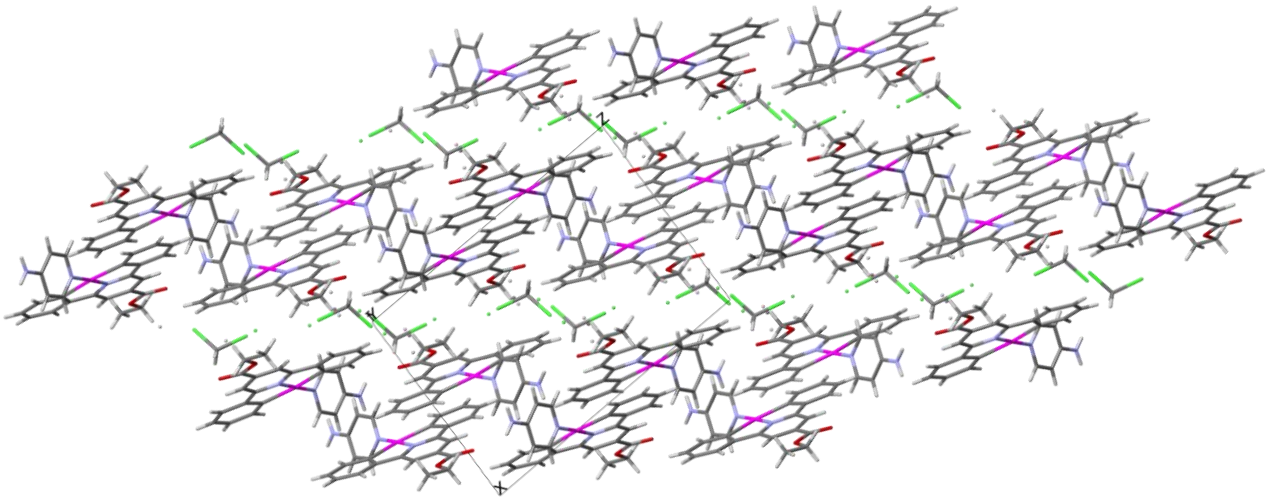
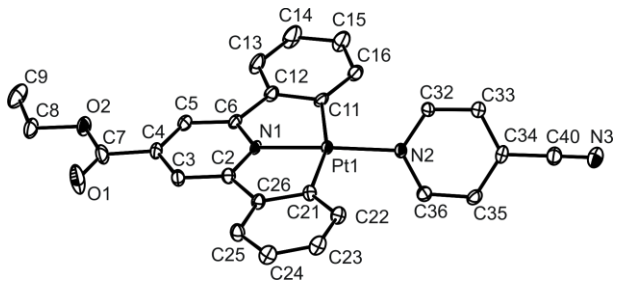


Figure S6. Crystal packing diagram of complex **8**. View along b axis showing the solvent molecules allocated in channels.



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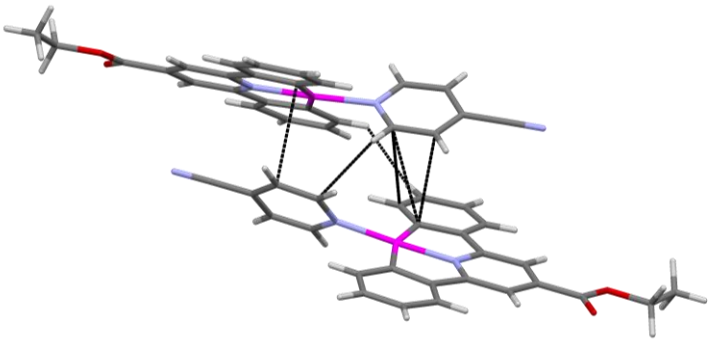

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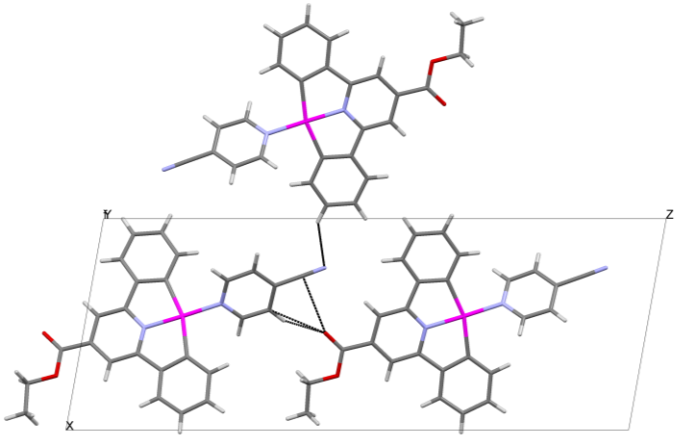
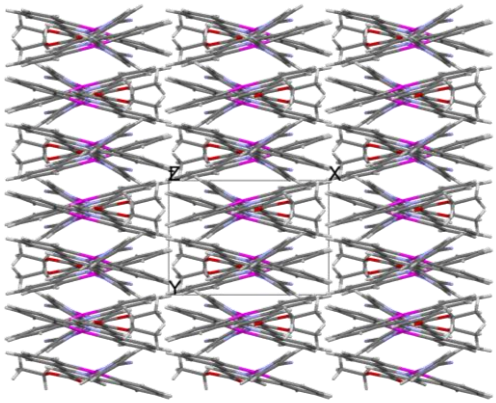
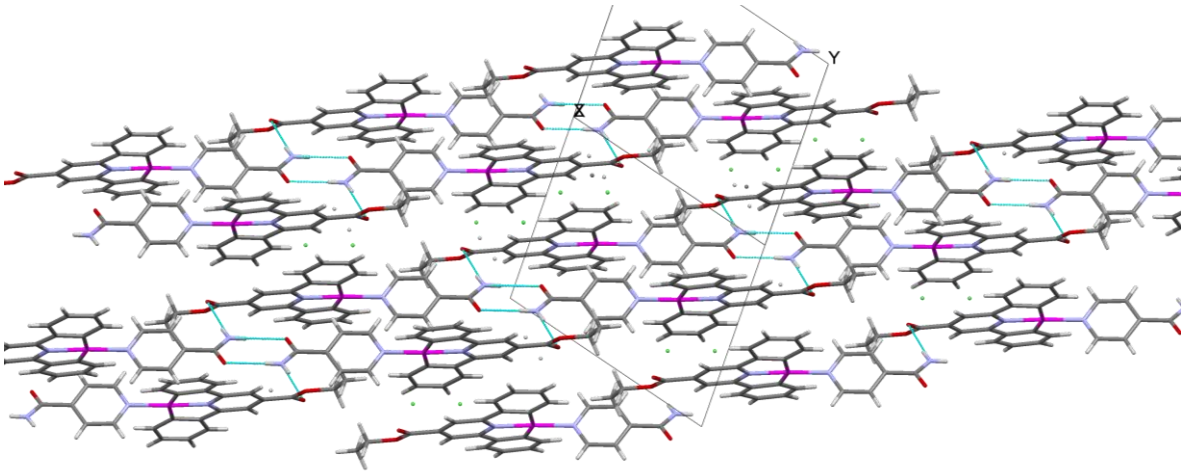


(c)

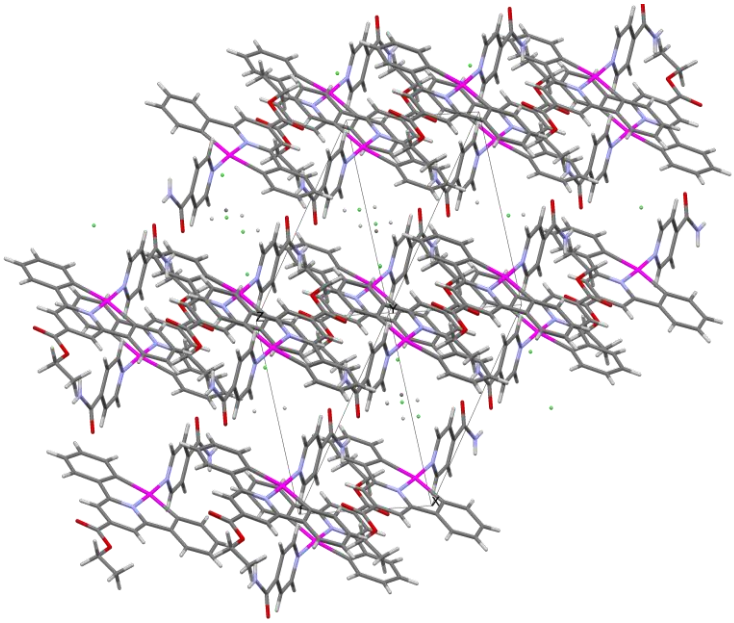


(d)

Figure S7. a) ORTEP view of **9**. Ellipsoids are drawn at 50% probability level. Hydrogen atoms have been omitted for clarity; b) Crystal packing diagram shows the close π···π contacts between the cyanopyridine and the CNC ligand (3.1 -3.4 Å); c) Crystal packing view along b axis shows rather short C-H (py)···O (ester) contacts (C···O 3.00 Å, H···O 2.15 Å), C-H···N (CN-py) (C···N 3.54 Å, H···N 2.74 Å) and also C-N (CN-py)···O (ester) contacts (C···O 3.20 Å) between monomers belonging to the same layer. d) Crystal packing view along c axis.



(a)



(b)

Figure S8. a) Crystal diagram of complex **10** showing the hydrogen bonds highlighted (light blue dashed line); b) Crystal packing view showing channels.

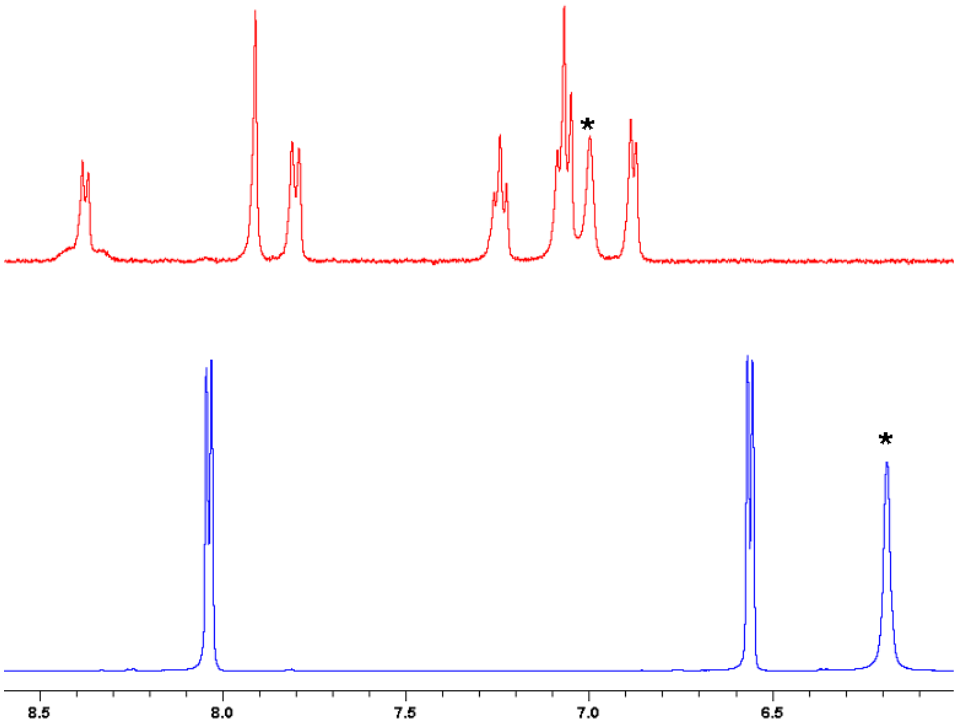


Figure S9. ^{1}H NMR of **8** (top) and free NH_2-py (bottom) in acetone-d^6 at 203 K, 400 MHz, δ ppm.

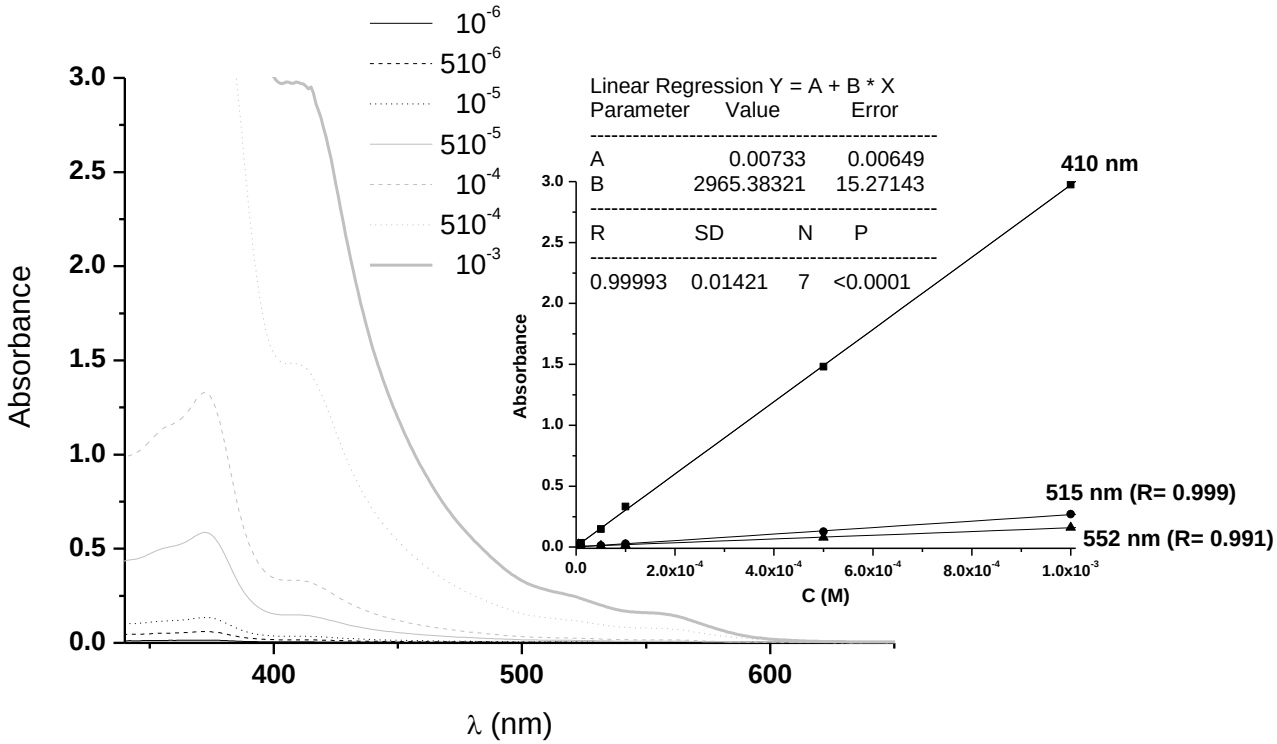


Figure S10. UV-Vis absorption spectra of **8** in dichloromethane at several concentrations (M) at 298 K. Inset: Linear fit representation of the absorbances at 410 nm, 515 nm and 552 nm *vs* concentration.

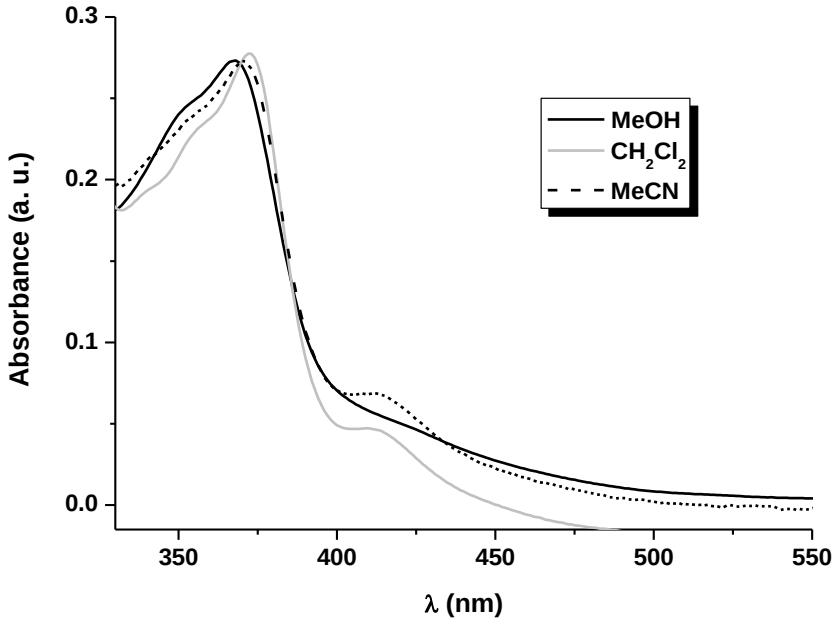


Figure S11. UV-Vis absorption spectra of **8** in different solvents (10^{-5} M) at 298 K.

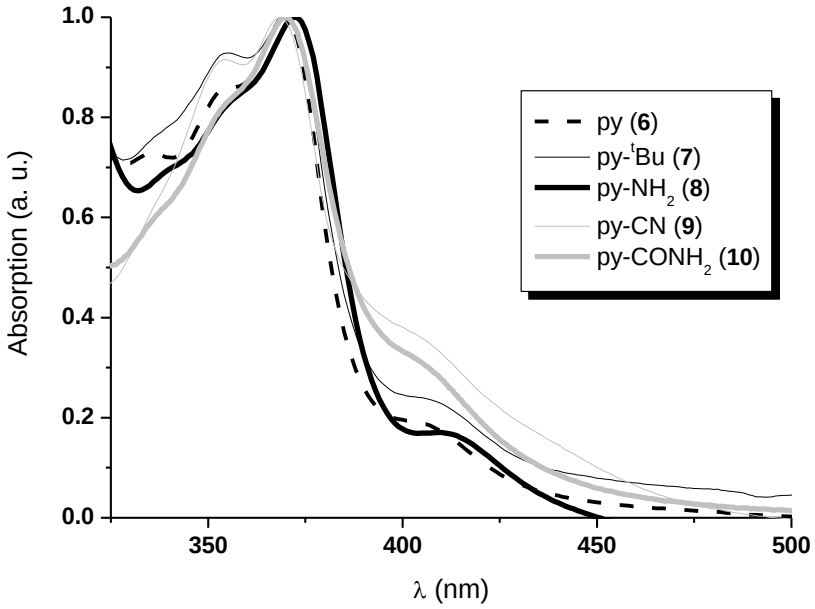


Figure S12. UV-Vis absorption spectra of **6**-**10** in CH_2Cl_2 (10^{-5} M) at 298 K.

Table S2. DFT-Optimized coordinates of [Pt(EtO_2C-C^N^C)(CN-^{t}Bu)] (**5**).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	78	1.059047	-0.006926	-0.017821
2	7	-0.974084	0.134601	-0.073395
3	7	4.127311	-0.212034	0.075386
4	6	0.553346	-2.035557	-0.043169
5	6	0.839026	2.071904	-0.013255
6	6	-1.524418	1.375301	-0.081921
7	6	-2.917710	1.486063	-0.119961
8	6	-3.692374	0.323547	-0.147739
9	6	-3.087230	-0.936599	-0.137350
10	6	-1.690594	-1.016835	-0.099443
11	6	-5.182479	0.488312	-0.187379
12	8	-5.740267	1.567910	-0.195313
13	6	2.956283	-0.135414	0.038155
14	6	5.567201	-0.287496	0.122248
15	6	-0.910827	3.816709	-0.050844
16	6	0.791924	-4.473781	-0.052873
17	6	-0.594149	-4.642568	-0.092667
18	6	5.975653	-1.770243	0.035510
19	6	-1.420349	-3.520937	-0.108110
20	6	-0.861497	-2.234766	-0.083803
21	6	0.062834	4.812688	-0.018434
22	6	1.412288	4.453419	0.016042
23	6	-0.534750	2.465559	-0.048554
24	6	1.786335	3.104826	0.018423
25	6	1.348796	-3.190110	-0.028756
26	6	6.125758	0.505102	-1.074987
27	8	-5.825240	-0.696188	-0.217796
28	6	-7.273447	-0.649174	-0.253605
29	1	-7.558953	-1.592573	-0.724836
30	1	-7.579708	0.184187	-0.890234
31	6	-7.857682	-0.521426	1.145382
32	1	-8.951665	-0.565240	1.093940
33	1	-7.573413	0.433468	1.595971
34	1	-7.510528	-1.336092	1.789272
35	6	6.033478	0.330732	1.454308
36	1	-1.960583	4.098945	-0.077826
37	1	2.431987	-3.092997	0.001431
38	1	-3.694997	-1.830832	-0.158361
39	1	-2.499031	-3.655219	-0.139367
40	1	-3.412190	2.448976	-0.128744
41	1	1.441870	-5.346425	-0.040819
42	1	-1.027919	-5.638662	-0.111654
43	1	-0.229259	5.859265	-0.020172
44	1	2.176560	5.227571	0.041262
45	1	2.845702	2.858290	0.045916
46	1	7.067017	-1.853897	0.069327
47	1	5.557490	-2.337305	0.873040
48	1	7.125855	0.285548	1.516633
49	1	5.613139	-0.215885	2.304155
50	1	5.723229	1.377658	1.526912
51	1	5.621646	-2.216190	-0.899172

52	1	5.815029	1.553314	-1.025908
53	1	7.220005	0.465070	-1.062890
54	1	5.772005	0.081956	-2.020240

Table S3. DFT-Optimized coordinates of [Pt(EtO_2C-C^N^C)(py-NH_2)] (**8**)

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	78	-1.017026	0.006578	-0.001986
2	6	0.795758	-4.564228	0.089194
3	6	-0.597076	-4.452827	0.106398
4	6	7.884739	-1.662912	0.023341
5	6	1.574522	-3.409266	0.053025
6	6	-5.218839	0.171015	1.019904
7	6	-1.206328	-3.193024	0.082262
8	6	-3.843670	0.313021	0.974244
9	6	0.960314	-2.148569	0.029628
10	6	-0.462487	-2.004334	0.037174
11	6	-5.881645	-0.548868	0.006869
12	6	7.297027	-0.264321	0.008371
13	6	1.733005	-0.894471	0.008657
14	6	3.124629	-0.752994	0.007753
15	6	5.159570	0.756380	-0.002833
16	6	3.679565	0.529958	-0.002719
17	6	-5.077656	-1.096423	-1.011582
18	6	1.466698	1.491256	-0.013968
19	6	2.854470	1.657196	-0.013205
20	6	-3.706475	-0.918025	-0.975035
21	6	-0.918952	2.089748	-0.041888
22	6	0.437135	2.543557	-0.034802
23	6	-1.906193	3.085377	-0.087166
24	6	0.759861	3.908308	-0.058742
25	6	-1.588329	4.448289	-0.111837
26	6	-0.254090	4.863348	-0.095027
27	7	-7.249430	-0.670921	-0.012028
28	7	-3.075941	-0.222324	-0.001753
29	7	0.963539	0.226840	-0.002529
30	8	5.857136	-0.397814	0.006964
31	8	5.678928	1.855155	-0.010698
32	1	1.270952	-5.541453	0.107237
33	1	7.567940	-2.211532	0.916227
34	1	-1.209441	-5.352121	0.141157
35	1	-5.775119	0.626018	1.833997
36	1	-7.753878	-0.497041	0.845857
37	1	8.978618	-1.604541	0.024974
38	1	-3.311432	0.872616	1.733923
39	1	2.658492	-3.499397	0.044821
40	1	-2.294554	-3.144433	0.103650
41	1	7.571538	-2.229193	-0.859739
42	1	7.593617	0.318172	0.886480
43	1	-7.654237	-1.387389	-0.598000
44	1	3.767885	-1.622412	0.016900
45	1	7.596966	0.300707	-0.879958
46	1	3.305919	2.641114	-0.022181
47	1	-5.520334	-1.660891	-1.826858
48	1	-2.957305	2.799658	-0.108670
49	1	-3.065200	-1.343629	-1.737559
50	1	1.797582	4.233809	-0.051005
51	1	-2.383564	5.190709	-0.146878

52	1	-0.005430	5.921088	-0.113568

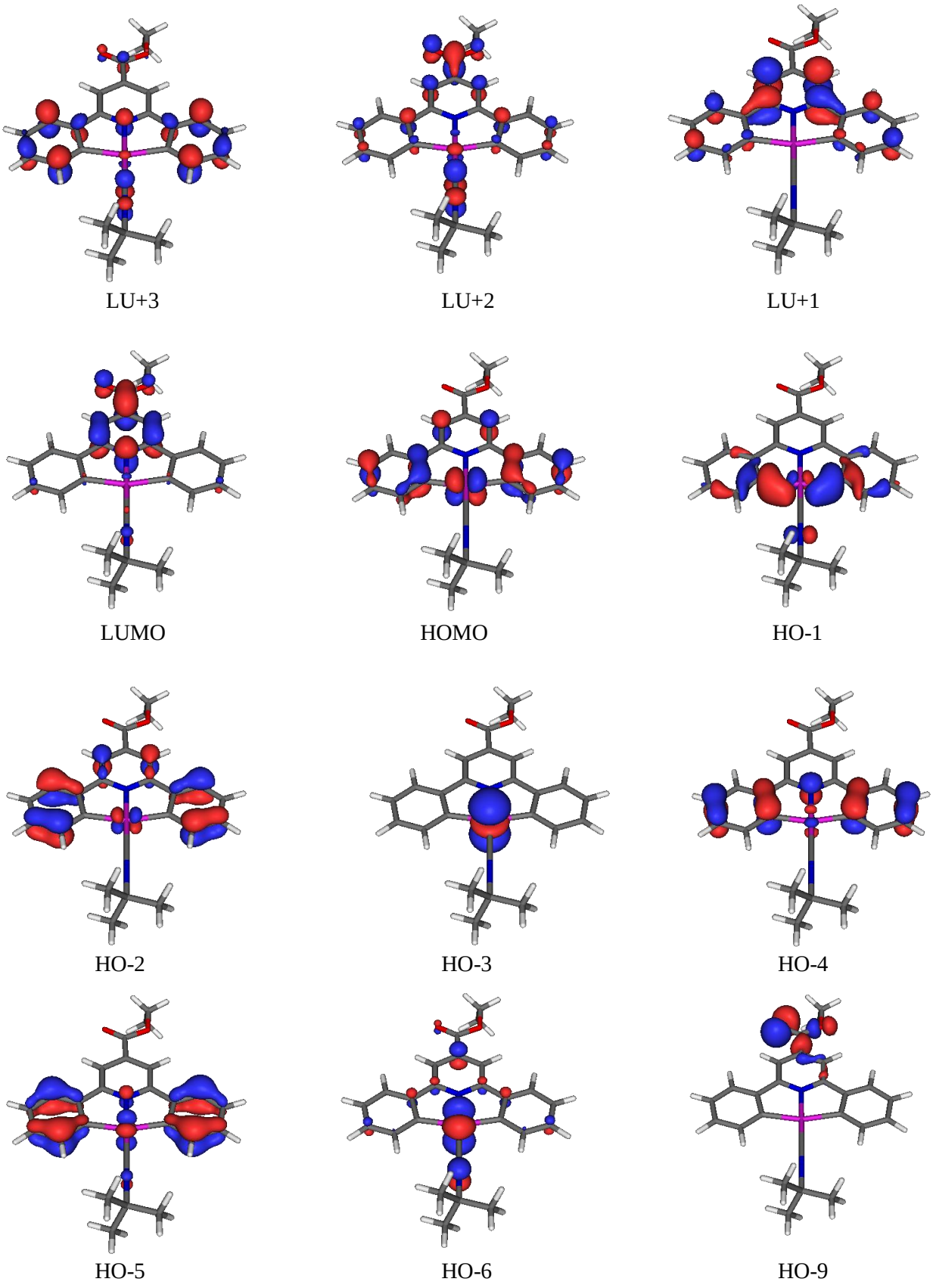


Figure S13. Representative frontier orbitals for (R-C^N^C)Pt(CN^{t}Bu) (**5**)

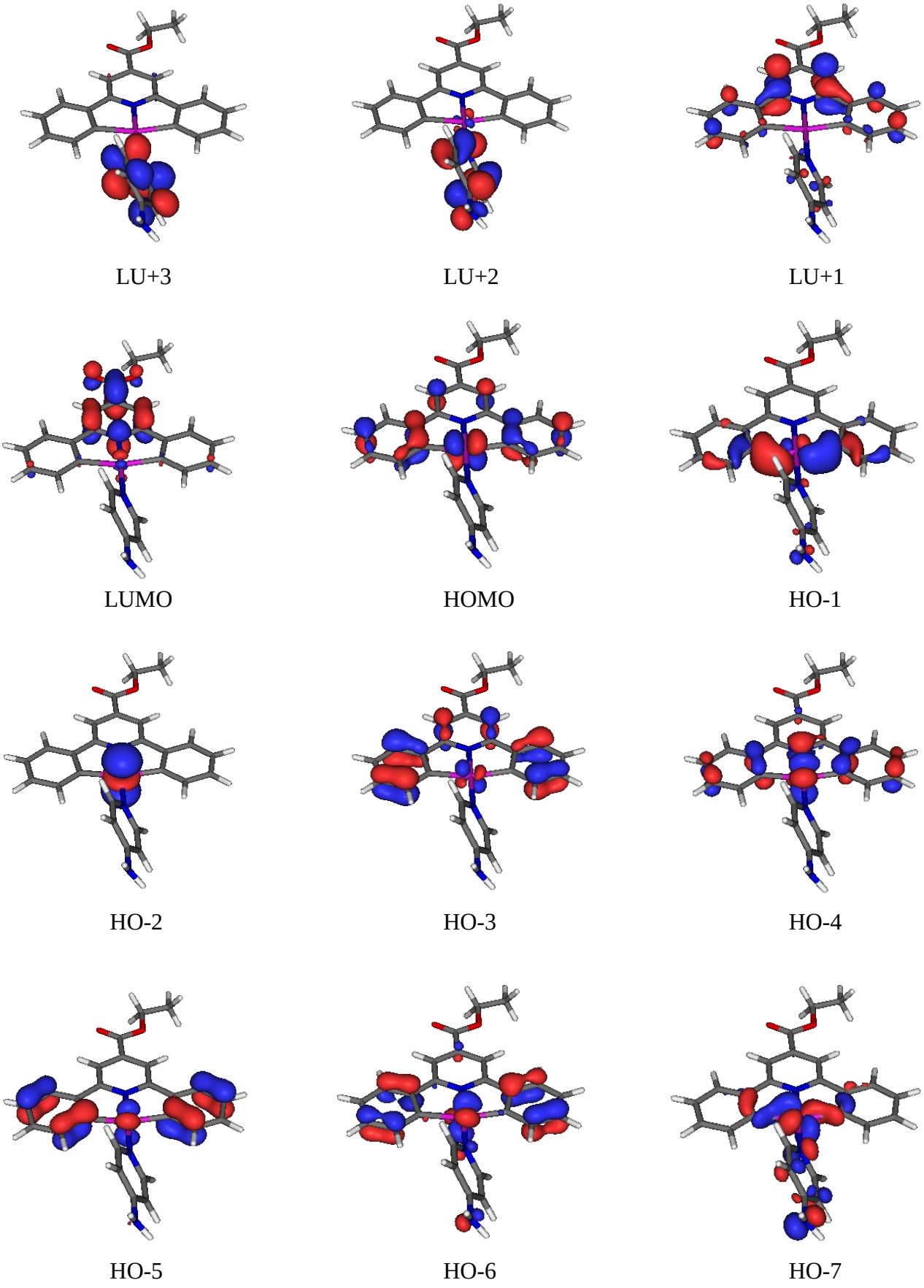


Figure S14. Representative frontier orbitals for (R-C^N^C)Pt(py-NH_2) (**8**)

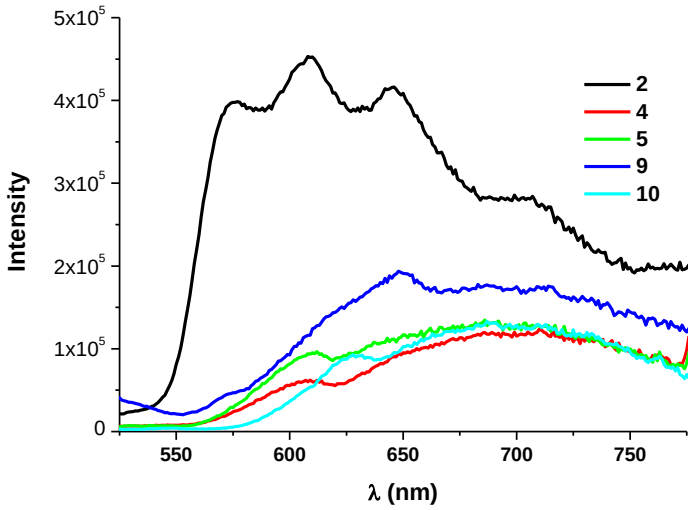


Figure S15. Solid state emission spectra at 298 K.

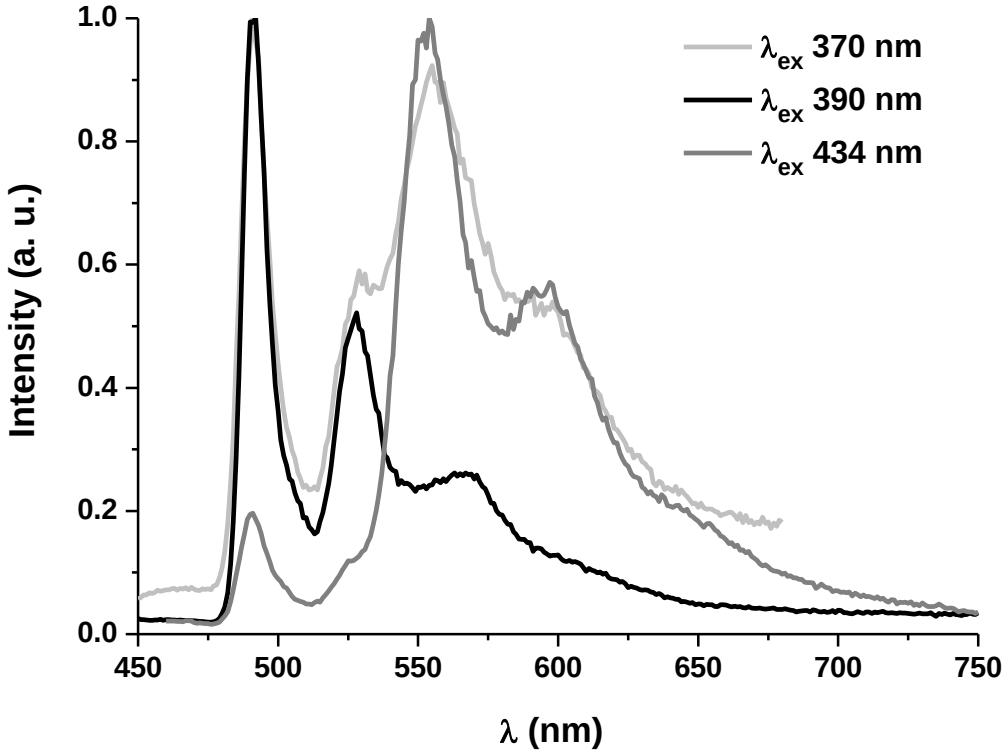


Figure S16. Normalized emission spectra of **6** in 2-MeTHF (5 x 10^{-5} M) at 77 K

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