

Supplementary data"

Synthesis, Characterization and Luminescence Properties of Homoleptic Platinum(II) Acetylide Complexes.

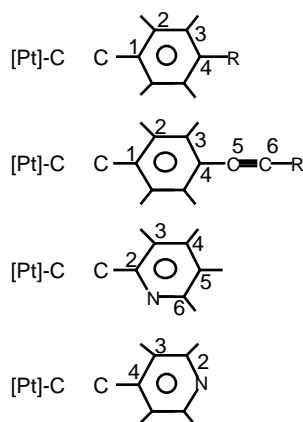
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Experimental

The NMR spectral assignments follow the numbering scheme shown in the following figure.



(NBu₄)₂[Pt(C≡CC₆H₅)₄] **1**

The synthesis of this complex has been previously reported.¹ $\delta_C\{^1\text{H}\}$ (CD₃COCD₃, 223K): 133.4 [s, ³J(Pt-C) ~ 25, ipso-C, Ph], 132.0 (s, ortho-C, Ph), 128.2 (s, meta-C, Ph), 123.3 (s, para-C, Ph),

120.9 [s, $^1J(\text{Pt-C})$ 989.8, C], 104.1 [s, $^2J(\text{Pt-C})$ 287.4, C], 60.3 (s, N-CH₂-, NBu₄), 25.5 (s, -CH₂-, NBu₄), 20.7 (s, -CH₂-, NBu₄) and 14.3 (s, -CH₃, NBu₄).

Synthesis of (NBu₄)₂[Pt{C≡C(4-CF₃)C₆H₄}]₄ **4**.

This complex was prepared, as a yellow solid, following a similar procedure to that described for **2**: [PtCl₂(tht)₂] (0.30 g, 0.68 mmol), LiC≡C(4-CF₃)C₆H₄ (5.42 mmol), (NBu₄)Br (0.55 g, 1.70 mmol); (0.68g, 74%) (Found: C, 59.86; H, 6.27; N, 2.37%. C₆₈H₈₈N₂F₁₂Pt requires: C, 60.21; H, 6.54; N, 2.07%); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (C≡C) 2084vs; δ_{H} (CD₃COCD₃, 293 K) 7.42, 7.36 [16H, AB system, $J(\text{H-H})$ 7.9, (4-CF₃)C₆H₄], 3.70 (16H, m, N-CH₂-, NBu₄), 1.88 (16H, m, -CH₂-, NBu₄), 1.54 (16H, q, -CH₂-, NBu₄) and 0.92 (24H, t, -CH₃, NBu₄); δ_{F} (CD₃COCD₃, 293 K) -145.72 [s, CF₃, (4-CF₃)C₆H₄]; $\delta_{\text{C}}\{^1\text{H}\}$ (CD₃COCD₃, 223K) 135.5 [q, $^5J(\text{C-F})$ 1.2, C¹], 130.7 (s, C²), 125.0 [s, $^1J(\text{C-Pt})$ 997.0, C], 124.9 [q, $^1J(\text{C-F})$ 270.0, CF₃, (4-CF₃)C₆H₄], 124.4 [q, $^3J(\text{C-F})$ 3.7, C³], 122.9 [q, $^2J(\text{C-F})$ 30.9, C⁴], 103.0 [s, $^2J(\text{C-Pt})$ 286.3, C], 58.4 (s, N-CH₂-, NBu₄), 23.9 (s, -CH₂-, NBu₄), 19.5 (s, -CH₂-, NBu₄) and 13.4 (s, -CH₃, NBu₄); m/z = 1405 ([Pt₂(C≡CC₆H₄CF₃)₆ + 1]⁻, 20%), 1236 ([Pt₂(C≡CC₆H₄CF₃)₅ + 1]⁻, 22%), 872 ([Pt(C≡CC₆H₄CF₃)₄ + 1]⁻, 8%), 703 ([Pt(C≡CC₆H₄CF₃)₃ + 1]⁻, 100%); $\mu_{\text{M}}(\text{CH}_3\text{NO}_2)$: 97 cm² mol⁻¹.

Synthesis of (NBu₄)₂[Pt{C≡C(4-OMe)C₆H₄}]₄·2H₂O **5a**·2H₂O

This complex has been used as precursor to a cluster Pt₂Cu₄ complex,² but its synthesis and spectroscopic data have not been reported. This complex was prepared, as a pale yellow solid, following an identical procedure to complex **2**, starting from [PtCl₂(tht)₂] (0.30 g, 0.68 mmol), LiC≡C(4-OMe)C₆H₄ (3.73 mmol) and (NBu₄)Br (0.55 g, 1.70 mmol); (0.67g, 82%) (Found: C, 66.02; H, 8.44; N, 2.02%. C₆₈H₁₀₄N₂O₆Pt requires: C, 65.83; H, 8.45; N, 2.26%); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (C≡C) 2085vs ; bands at 3455s br, 3422s br, 1651vs and 1640vs due to the presence of H₂O are also observed; δ_{H} (CD₃COCD₃, 293 K) 7.16 [8H, d, $J(\text{HH})$ 8.5], 6.67 [8H, d, $J(\text{H-H})$ 8.5, C₆H₄, (4-

OMe)C₆H₄], 3.75 (16H, m, N-CH₂-, NBu₄), 3.72 (12H, s, OMe, (4-OMe)C₆H₄), 1.85 (16H, m, -CH₂-, NBu₄), 1.53 (16H, m, -CH₂-, NBu₄) and 0.91 (24H, t, -CH₃, NBu₄); δ_C{¹H} (CD₃COCD₃, 223K) 155.1 (s, C^d), 131.3 (s, C^{2/3}), 123.8 (s, C¹), 115.8 [s, ¹J(C-Pt) 990.5, C], 112.4 (s, C^{2/3}), 101.2 [s, ²J(C-Pt) 286.0, C], 58.1 (s, N-CH₂-, NBu₄), 53.9 (s, OMe, (3-OMe)C₆H₄), 23.7 (s, -CH₂-, NBu₄), 19.3 (s, -CH₂-, NBu₄) and 13.3 (s, -CH₃, NBu₄); *m/z* 1201 ([Pt(C C₆H₄OMe)₄(NBu₄)₂-3]⁻, 63%); $\mu_{\text{M}}(\text{CH}_3\text{NO}_2)$: 91 ⁻¹ cm² mol⁻¹.

Synthesis of (NBu₄)₂[Pt{C≡C(3-OMe)C₆H₄}₄] 5b

This complex was prepared, as a very pale yellow solid, following the procedure described for **2**, using [PtCl₂(tht)₂] (0.30 g, 0.68 mmol), LiC C(3-OMe)C₆H₄ (3.73 mmol) and (NBu₄)Br (0.55 g, 1.70 mmol); (0.74g, 90%) (Found: C, 67.45; H, 8.47; N, 2.38%. C₆₈H₁₀₀N₂O₄Pt requires: C, 67.80; H, 8.37; N, 2.33%); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (C C) 2078 (s); ν_{H} (CD₃COCD₃, 293 K) 6.98 [4H, t, *J*(H-H) 8.0], 6.83 (8H, m), 6.51 [4H, dd, 7.4, *J*(H-H) 1.7, C₆H₄, (3-OMe)C₆H₄], 3.74 (16H, m, N-CH₂-, NBu₄), 3.72 (12H, s, OMe, (3-OMe)C₆H₄), 1.87 (16H, m, -CH₂-, NBu₄), 1.55 (16H, m, -CH₂-, NBu₄) and 0.92 (24H, t, -CH₃, NBu₄); δ_C{¹H} (CD₃COCD₃, 223K) 158.5 [s, C-OMe, (3-OMe)C₆H₄], 132.5 (s), 128.0 (s), 122.8 [s, C₆H₄, (3-OMe)C₆H₄], 119.4 [s, ¹J(C-Pt) 990.2, C], 114.8 (s), 108.4 [s, C₆H₄, (3-OMe)C₆H₄], 102.6 [s, ²J(C-Pt) 288.1, C], 58.2 (s, N-CH₂-, NBu₄), 53.7 [s, OMe, (3-OMe)C₆H₄], 23.7 (s, -CH₂-, NBu₄), 19.4 (s, -CH₂-, NBu₄) and 13.4 (s, -CH₃, NBu₄); *m/z* 1178 ([Pt₂(C C₆H₄OMe)₆+2]⁻, 15%), 1046 ([Pt₂(C C₆H₄OMe)₅+1]⁻, 10%), 720 ([Pt(C C₆H₄OMe)₄+1]⁻, 14%); $\mu_{\text{M}}(\text{CH}_3\text{NO}_2)$: 94 ⁻¹ cm² mol⁻¹.

Synthesis of (NBu₄)₂[Pt{C≡C(4-CN)C₆H₄}₄] 6

This complex was prepared as a lemon yellow solid following a similar procedure to that described for **2**, starting from [PtCl₂(tht)₂] (0.20 g, 0.45 mmol), LiC C(4-CN)C₆H₄ (2.71 mmol) and (NBu₄)Br (0.36 g, 1.13 mmol); (0.22g, 45%) (Found: C, 68.55; H, 7.51; N, 6.90%. C₆₈H₈₈N₆Pt requires: C,

68.95; H, 7.49; N, 7.10%); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (C N) 2218vs and (C C) 2080vs, 2041sh; δ_{H} (CDCl_3 , 293 K) 7.41, 7.29 [16H, AB system, $J(\text{H-H})$ 7.3, (4-CN) C_6H_4], 3.47 (16H, m, N- CH_2 -, NBu_4), 1.64 (16H, m, - CH_2 -, NBu_4), 1.44 (16H, m, - CH_2 -, NBu_4), 0.86 (24H, t, - CH_3 , NBu_4); $\delta_{\text{C}}\{^1\text{H}\}$ (CD_3COCD_3 , 223K) 135.8 (s), 131.1 (s, CH), 130.7 (s, CH), 128.46 [s, C_6H_4 , (4-CN) C_6H_4], 119.3 (tentatively assigned to C), 104.1 [s, $^2J(\text{C-Pt})$ 288.0, C], 58.0 (s, N- CH_2 -, NBu_4), 23.4 (s, - CH_2 -, NBu_4), 19.1 (s, - CH_2 -, NBu_4) and 13.2 (s, - CH_3 , NBu_4); m/z 696 ($[\text{Pt}(\text{C} \text{CC}_6\text{H}_4\text{CN})_4 - 3]^-$, 22%); $\mu_{\text{M}}(\text{CH}_3\text{NO}_2)$: 93 $\text{cm}^2 \text{mol}^{-1}$.

Synthesis of $(\text{NBu}_4)_2[\text{Pt}\{\text{C}\equiv\text{C}(4\text{-C}\equiv\text{CH})\text{C}_6\text{H}_4\}_4]\cdot 2\text{H}_2\text{O} \cdot 7\cdot 2\text{H}_2\text{O}$

To a fresh (-78°C) solution of $\text{LiC}\equiv\text{C}(4\text{-C}\equiv\text{CH})\text{C}_6\text{H}_4$ (4.35 mmol) in Et_2O (ca. 30 cm^3), $[\text{PtCl}_2(\text{tht})_2]$ (0.35 g, 0.80 mmol) was added, and the mixture stirred at this temperature for 2.5 hours. Then, it was slowly allowed to reach room temperature (ca. 2 h) and evaporated to dryness. The yellow residue was treated with cold deoxygenated H_2O (~ 40 cm^3) and filtered through celite. The resulting solution was treated with $(\text{NBu}_4)\text{Br}$ (0.51 g, 1.6 mmol) to yield $(\text{NBu}_4)_2[\text{Pt}\{\text{C}\equiv\text{C}(4\text{-C}\equiv\text{CH})\text{C}_6\text{H}_4\}_4]\cdot 2\text{H}_2\text{O} \cdot 7\cdot 2\text{H}_2\text{O}$ as a yellow solid. This complex is very unstable and must be kept under Ar at low temperature (-45°C); (0.55g, 57%) (Found: C, 70.34; H, 7.93; N, 2.06%. $\text{C}_{72}\text{H}_{96}\text{N}_2\text{O}_2\text{Pt} \cdot 7\cdot 2\text{H}_2\text{O}$) requires C, 71.08; H, 7.95; N, 2.30% and $\text{C}_{72}\text{H}_{98}\text{N}_2\text{O}_3\text{Pt} \cdot 7\cdot 3\text{H}_2\text{O}$) requires C, 70.04; H, 8.00; N, 2.27); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (CH) 3200s, (C C) 2073vs br, bands at 3450br and 1640br due to the presence of H_2O are also observed; δ_{H} (CDCl_3 , 293 K) 7.27, 7.21 [16H, AB system, $J(\text{H-H})$ 8.3, C_6H_4 , (4-C $\equiv\text{CH})\text{C}_6\text{H}_4$], 3.50 (16H, m, N- CH_2 -, NBu_4), 3.07 (4H, s, CH), 2.16 (4H, br, H_2O), 1.63 (16H, m, - CH_2 -, NBu_4), 1.45 (16H, m, - CH_2 -, NBu_4) and 0.87 (24H, t, - CH_3 , NBu_4); $\delta_{\text{C}}\{^1\text{H}\}$ (CD_3COCD_3 , 223K) 132.0 (s), 130.8 (s, CH), 130.2 [s, CH, C_6H_4 , (4-C $\equiv\text{CH})\text{C}_6\text{H}_4$], 124.0 [s, $^1J(\text{C-Pt})$ 993.0, C], 115.1 [s, C_6H_4 , (4-C $\equiv\text{CH})\text{C}_6\text{H}_4$], 103.2 [s, $^2J(\text{C-Pt})$ 289.0, C], 83.9 (s, C^6), 78.5 (s, C^5), 58.0 (s, N- CH_2 -, NBu_4), 23.4 (s, - CH_2 -, NBu_4), 19.2 (s, - CH_2 -, NBu_4) and 13.2 (s, - CH_3 , NBu_4); m/z 938 ($\{\text{Pt}(\text{C} \text{CC}_6\text{H}_4\text{C}\equiv\text{CH})_4\}(\text{NBu}_4) + 1^-$, 100%); $\mu_{\text{M}}(\text{CH}_3\text{NO}_2)$: 93 $\text{cm}^2 \text{mol}^{-1}$.

Synthesis of (NBu₄)₂[Pt{C≡C(4-C≡CPh)C₆H₄}₄] **8**

Complex **8** was prepared, as a yellow solid, by treating [PtCl₂(tht)₂] (0.25 g, 0.57 mmol) with LiC C(4-C CPh)C₆H₄ (3.39 mmol) and (NBu₄)Br (0.46 g, 1.41 mmol) in a similar way to that described above for complex **3**; (0.32g, 38%) (Found: C, 77.34; H, 7.37; N, 1.80%. C₉₆H₁₀₈N₂Pt requires: C, 77.65; H, 7.33; N, 1.89%); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (C C) 2209m (C CPh), 2075s br (PtC C); δ_{H} (CD₃COCD₃, 293 K) 7.52 (8H, m), 7.39 [12H, m, Ph, C C(4-C CPh)C₆H₄], 7.30, 7.25 [16H, AB system, *J*(H-H) 8.3, C₆H₄, (4-C CPh)C₆H₄], 3.68 (16H, m, N-CH₂-, NBu₄), 1.87 (16H, m, -CH₂-, NBu₄), 1.53 (16H, m, -CH₂-, NBu₄) and 0.95 (24H, t, -CH₃, NBu₄); $\delta_{\text{C}}\{^1\text{H}\}$ (CDCl₃, 223K) 132.2 (s), 131.0 (CH), 130.8 (overlapping of two CH carbons), 128.6 (s, CH), 128.1 [s, C₆H₄ and Ph, (4-CC CPh)C₆H₄], 124.6 [s, ¹*J*(C-Pt) 1003.0, C], 123.2 (s), 116.2 [s, C₆H₄ and Ph, (4-CC CPh)C₆H₄], 104.0 [s, ²*J*(C-Pt) 286.0, C], 90.3 (s), 88.9 (s, C⁵ and C⁶), 58.4 (s, N-CH₂-, NBu₄), 23.9 (s, -CH₂-, NBu₄), 19.6 (s, -CH₂-, NBu₄) and 13.6 (s, -CH₃, NBu₄); *m/z* 797 ([Pt(C CC₆H₄C₂Ph)₃ - 1]⁻, 83%), 598 ([Pt(C CC₆H₄C₂Ph)₂ + 1]⁻, 100%) and 396 ([Pt(C CC₆H₄C₂Ph)]⁻, 63%); $\mu_{\text{M}}(\text{CH}_3\text{NO}_2)$: 119 cm²mol⁻¹.

Synthesis of (NBu₄)₂[Pt(C≡CC₅H₄N-2)] **9a**

This complex was prepared following an identical procedure to that described for **2**, but, in this case, the temperature of the LiC CC₅H₄N-2 ethereal solution was -50°C. In addition, the final precipitate of **9a**, obtained after the addition of (NBu₄)Br, was extracted with CH₂Cl₂ and the solution dried with anhydrous MgSO₄ and evaporated to dryness. The addition of cold Et₂O (ca. 5 cm³) gives **9a** as a brown solid. The following amounts of the precursors were used: 0.50 g (1.13 mmol) of [PtCl₂(tht)₂], 7.9 mmol of LiC CC₅H₄N-2 and 0.73 g (2.26 mmol) of (NBu₄)Br; (0.33g, 27%). (Found: C, 65.93; H, 8.03; N, 7.45%. C₆₀H₈₈N₆Pt requires: C, 66.21; H, 8.15; N, 7.72%); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (C C) 2081vs, 2059 sh; δ_{H} (CDCl₃, 293 K) 8.24 [d, *J*(H-H) 4.2, 4H⁶], 7.34 [td, *J*(H-H) ~

7.6, $J(\text{H-H}) \sim 1.5$, 4H^4), 7.23 [d, $J(\text{H-H}) \sim 7.9$, 4H^3], 6.80 [t, $J(\text{H-H}) \sim 5.9$, 4H^5], 3.55 (16H, m, N- CH_2^- , NBu_4), 1.66 (16H, m, $-\text{CH}_2^-$, NBu_4), 1.42 (16H, m, $-\text{CH}_2^-$, NBu_4) and 0.83 (24H, t, $-\text{CH}_3$, NBu_4), assignment based on a ^1H - ^1H COSY. $\delta_{\text{C}}\{^1\text{H}\}$ (CDCl_3 , 298 K) 148.8 [s, $^3J(\text{Pt-C})$ 25.8, C^2], 147.9 (s, C^6), 134.3 (s, C^4), 126.1 (C^3), 120.5 [s, $^1J(\text{C-Pt})$ 991.7, C], 117.6 (C^5), 105.2 [s, $^2J(\text{C-Pt})$ 287.0, C], 58.8 (s, N- CH_2^- , NBu_4), 24.1 (s, $-\text{CH}_2^-$, NBu_4), 19.4 (s, $-\text{CH}_2^-$, NBu_4) and 13.5 (s, $-\text{CH}_3$, NBu_4), assignment based on a ^{13}C - ^1H correlation NMR spectrum; $m/z = 846$ ($[\{\text{Pt}(\text{C} \equiv \text{CC}_5\text{H}_4\text{N}-2)_4\}(\text{NBu}_4) + 1]^+$, 100%), 604 ($[\text{Pt}(\text{C} \equiv \text{CC}_5\text{H}_4\text{N}-2)_4 + 1]^+$, 81%); $\nu_{\text{M}}(\text{CH}_3\text{NO}_2)$: 123 $\text{cm}^{-1} \text{mol}^{-1}$.

Synthesis of $(\text{NBu}_4)_2[\text{Pt}(\text{C} \equiv \text{CC}_5\text{H}_4\text{N}-4)_4] \cdot 2\text{H}_2\text{O}$ **9b**·2H₂O

This complex has been prepared following a similar procedure to that used for complex **2**, using THF as the solvent and a reaction temperature of -50°C . The yellow solid thus obtained, which contains amounts of *para*-ethynylpyridine ($\sim 15\%$), is washed with hexane ($2 \times 5 \text{ cm}^3$) to give **9b** as a yellow solid. The following amounts of the starting materials were used: $[\text{PtCl}_2(\text{tht})_2]$ (0.30 g, 0.68 mmol), $\text{LiC} \equiv \text{CC}_5\text{H}_4\text{N}-4$ (4.75 mmol) and $(\text{NBu}_4)\text{Br}$ (0.55 g, 1.71 mmol) (0.22g, 29%) (Found: C, 63.84; H, 7.89; N, 7.28%. $\text{C}_{60}\text{H}_{92}\text{N}_6\text{PtO}_2$ requires: C, 64.09; H, 8.25; N, 7.47%); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (C-C) 2086s and 2039sh; δ_{H} (CD_3COCD_3 , 293 K) 8.22 [8H, d, $J(\text{H-H})$ 5.5, $\text{C}_5\text{H}_4\text{N}-4$], 7.04 [8H, d, $J(\text{H-H})$ 5.5, $\text{C}_5\text{H}_4\text{N}-4$], 3.66 (16H, m, N- CH_2^- , NBu_4), 1.88 (16H, m, $-\text{CH}_2^-$, NBu_4), 1.51 (16H, m, $-\text{CH}_2^-$, NBu_4) and 0.93 (24H, t, $-\text{CH}_3$, NBu_4); $\delta_{\text{C}}\{^1\text{H}\}$ (CDCl_3 , 298 K) 148.4 (s, C^2); 139.1 (s, C^4); 126.0 (s, C^3), 123.3 [s, $^1J(\text{C-Pt})$ 995.7, C], 102.6 [s, $^2J(\text{C-Pt}) = 297.7$, C], 58.6 (s, N- CH_2^- , NBu_4), 23.9 (s, $-\text{CH}_2^-$, NBu_4), 19.5 (s, $-\text{CH}_2^-$, NBu_4) and 13.8 (s, $-\text{CH}_3$, NBu_4); m/z 845 ($\{\text{Pt}(\text{C} \equiv \text{CC}_5\text{H}_4\text{N}-2)_4\}(\text{NBu}_4)^+$, 100%); $\nu_{\text{M}}(\text{CH}_3\text{NO}_2)$: 79 $\text{cm}^{-1} \text{mol}^{-1}$.

¹ A. Sebal, B. Wrackmeyer, C. R. Theocharis and W. Jones, *J. Chem. Soc., Dalton Trans.*, 1984, 747.

² V. W. W. Yam, K. -L. Yu and K. K. Cheung, *J. Chem. Soc., Dalton Trans.*, 1999, 2913.

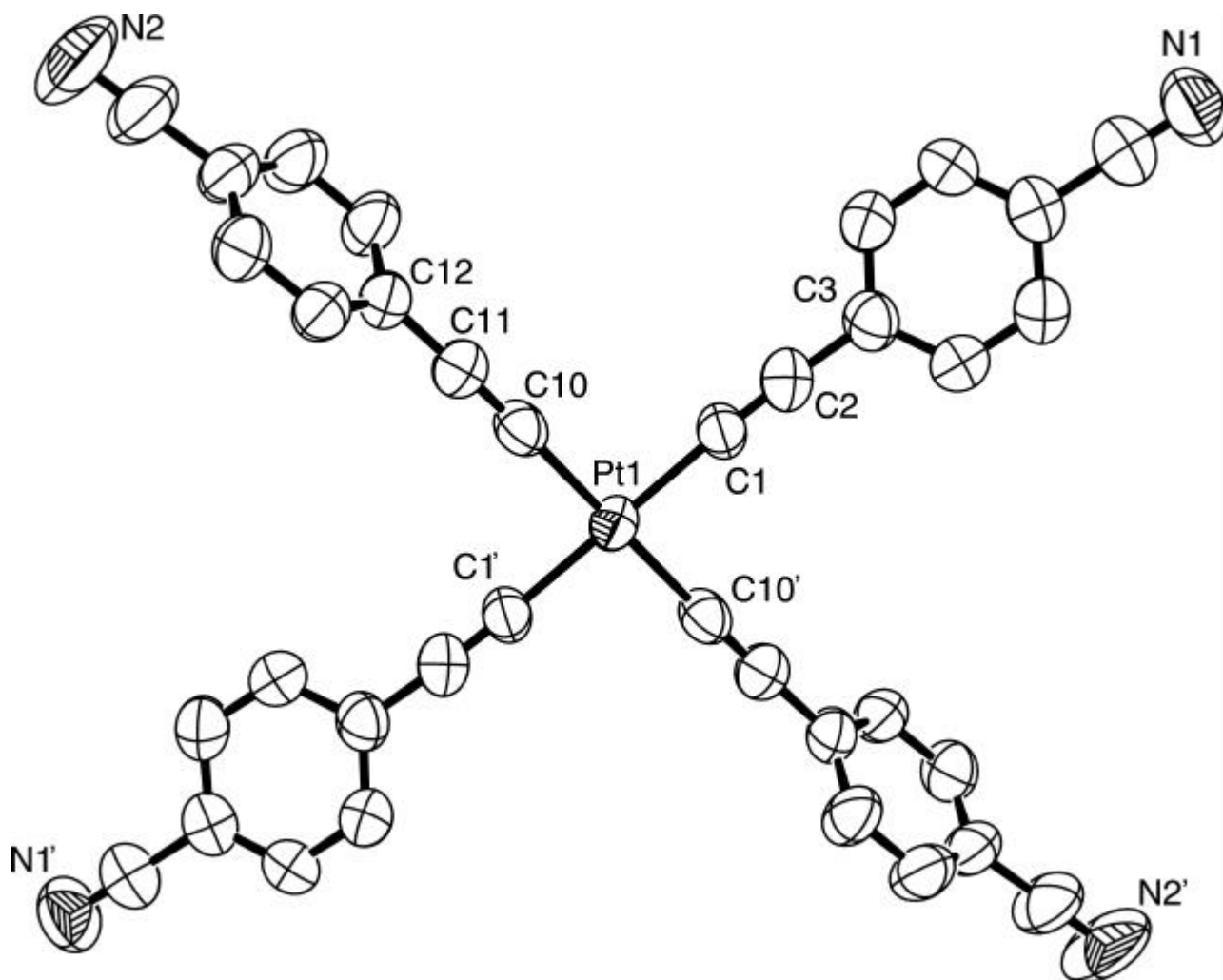


Figure S1 Molecular structure of the anion $[\text{Pt}\{\text{C}\equiv\text{C}(4\text{-CN})\text{C}_6\text{H}_4\}_4]^{2-}$ **6**. Ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity. Symmetry transformation used to generate equivalent atoms: $2-x, -y, -z$.

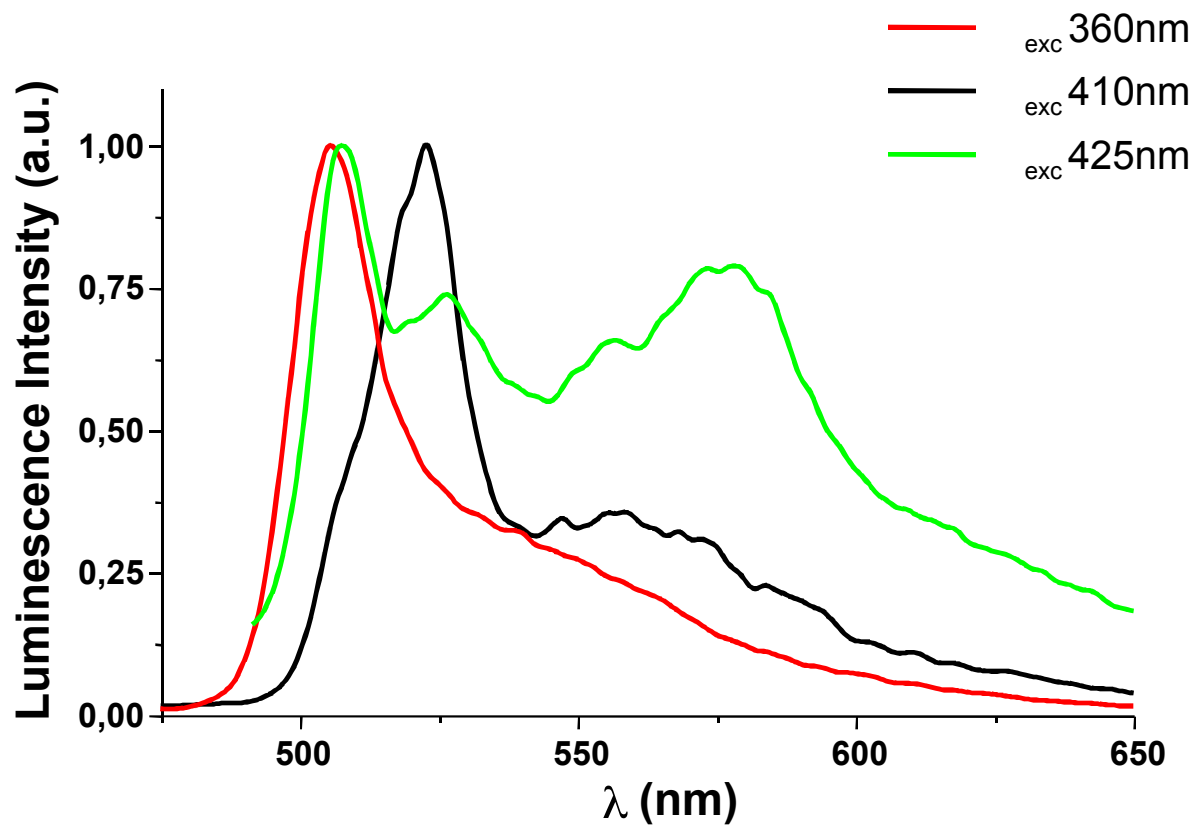


Figure S2 Emission spectra of complex **7** in CH₂Cl₂ at 77K by exciting at different (nm) (concentration 10⁻³ M).

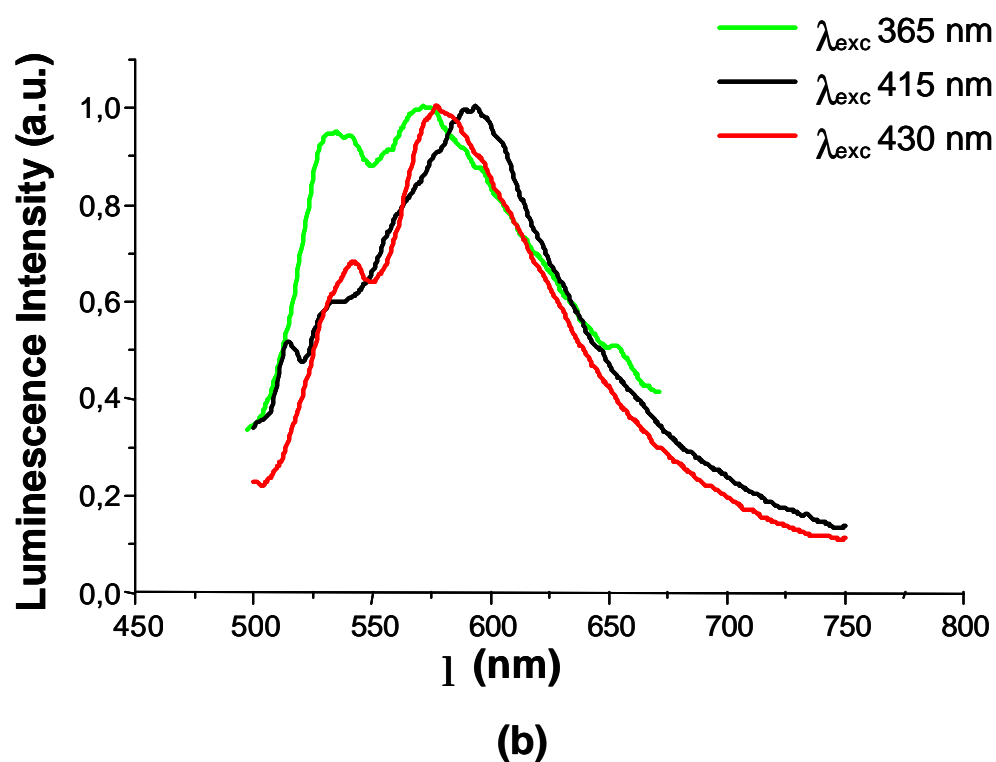
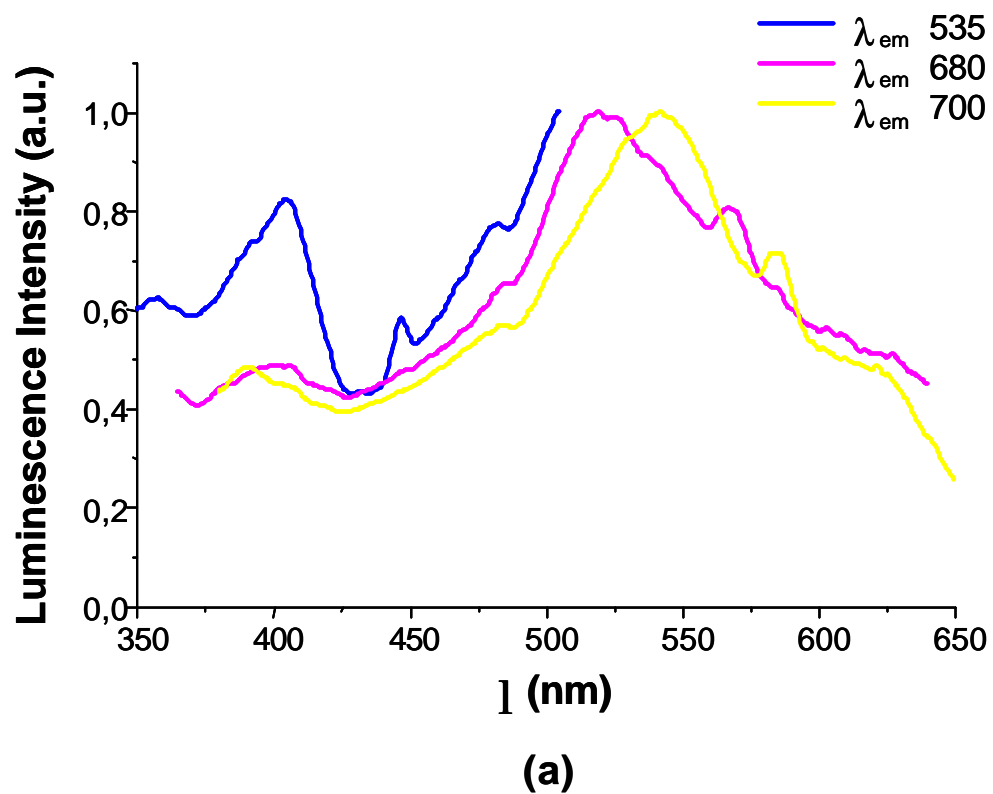


Figure S3 Excitation (a) and emission (b) spectra of complex **3** in KBr pellets at room temperature by exciting at different λ (nm).

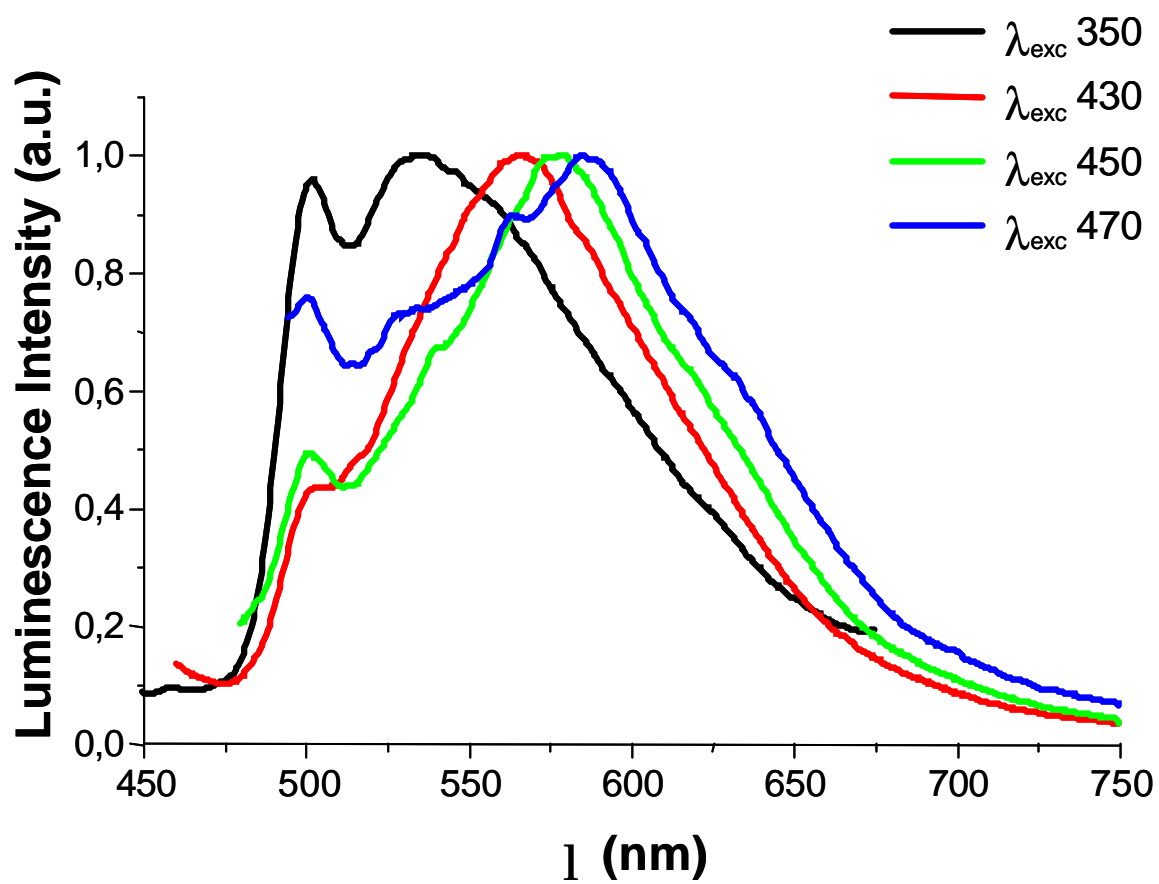


Figure S4. Emission spectra of complex **6** in KBr pellets at room temperature by exciting at different λ (nm).

Table S1. Population analysis (%) for the anion $[\text{Pt}\{\text{C} \text{ C}(4\text{-CN})\text{C}_6\text{H}_4\}_4]^{2-}$ of complex **6**

	Pt	C C	C CC ₆ H ₄ CN
HOMO-5	10.7	33.3	89.3
HOMO-4	2.2	49.7	97.8
HOMO-3	56.4	30.3	43.6
HOMO-2	11.1	38.3	89.9
HOMO-1	18.9	28.9	81.1
HOMO	19.7	29.7	80.3
LUMO	2.0	12.4	98.0
LUMO+1	1.1	13.4	98.9
LUMO+2	4.6	12.4	95.4
LUMO+3	3.3	12.8	96.7
LUMO+4	0.3	2.1	99.7

Table S2. Emission and excitation spectral data for complexes **1**, **2**, **3**, **4** and **6** in 10^{-3} M solutions of different solvents

Compound	λ_{exc}/nm	λ_{em}/nm	
1	acetone(298)	386	397, 422, 457
	acetone(77)	342, 354, 362	451, 472, 497
	acetonitrile(298)	382	396, 419, 430 (sh), 448
	acetonitrile(77)	360	451, 471, 486, 498
	toluene(298)	389	399, 425, 436, 455 (sh)
	toluene(77)	339, 360	451, 471, 485, 497
2	acetone(298)	388, 399, 408	459, 508
	acetone(77)	315, 334 (sh), 354	450, 469, 485, 495, 522
	acetonitrile(298)	385, 438 (sh), 453 (sh)	457, 479, 505
	acetonitrile(77)	333, 350	449, 470, 483, 495, 521
	toluene(298)	388, 392, 406	456, 502 (max)
	toluene(77)	333, 354 ^a 333, 357, 395 ^c	450 (max), 470 (sh), 500 ^b 450, 500 (max) ^d
3	Acetonitrile (77)	386	519, 555
4	acetone(298)	407, 426, 453	479
	acetone(77)	315, 334, 359, 381	468, 489, 504, 519
	acetonitrile(298)	394, 423, 437	472
	acetonitrile(77)	345, 365	462, 489 (sh), 511 (sh)
	toluene(298)	406, 424 (sh)	470, 502 (sh), 520 (sh)
	toluene(77)	358, 382, 400	468, 498, 520
6	acetone(298)	447, 464 (sh), 484 (sh), 497 (sh)	514
	acetone(77)	327, 343, 397	499, 526, 551
	acetonitrile(298)	423, 445	505, 542(sh)
	acetonitrile(77)	402	504, 598
	toluene(298)	430, 444, 474, 489	502
	toluene(77)	355, 377, 402	500, 525, 541, 555

a) $\lambda_{em} = 450nm$; b) $\lambda_{exc} = 350 nm$; c) $\lambda_{em} = 500 nm$; d) $\lambda_{exc} = 397 nm$;

Table S3. TD-DFT RPA (random phase approximation) singlet excitation calculations for the anion $[\text{Pt}\{\text{C C}(4\text{-CN})\text{C}_6\text{H}_4\}_4]^{2-}$ of complex **6**

Transition		Contributions	o.s.	$\lambda_{\text{exc}}(\text{calc})/\text{nm}$
HOMO	LUMO	0.63	0.071	470
HOMO	LUMO+1	0.23		
HOMO-2	LUMO	0.52	0.070	449
HOMO	LUMO+1	0.36		
HOMO-1	LUMO	0.61	0.682	428
HOMO-1	LUMO+1	0.23		
HOMO-1	LUMO+1	0.64	0.231	413
HOMO-1	LUMO	0.19		
HOMO-2	LUMO+1	0.60	0.753	399
HOMO	LUMO+1	0.25		
HOMO-5	LUMO	0.64	0.218	362
HOMO-5	LUMO+2	0.17		
HOMO-2	LUMO	0.12		