

Supporting Information

Spectacular Luminescent Behaviour of Tandem Terpyridyl Platinum(II) Acetylide Complexes Attributed to Solvent Effect on Ordering of Excited States, “Ion-Pair” Formation and Molecular Conformations.

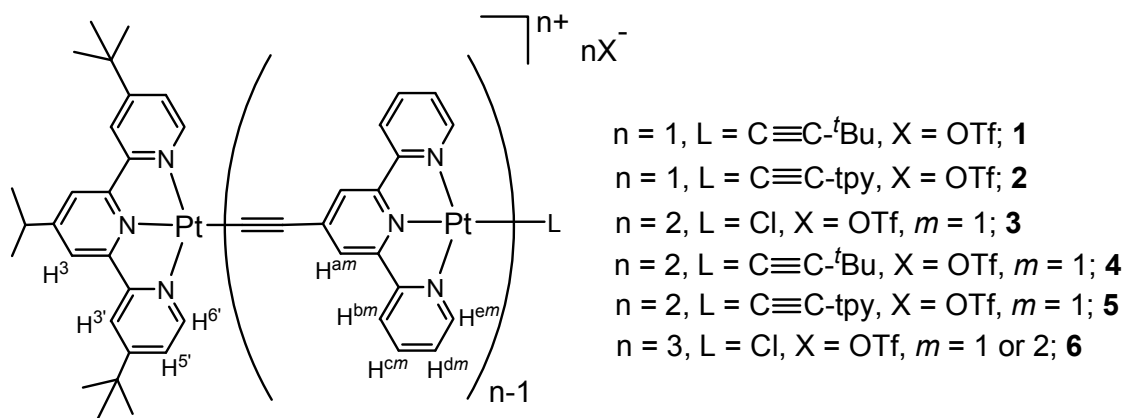
By

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(1) Detail Experimental



Syntheses.

[(^tBu₃tpy)PtC≡C^tBu](OTf) (1). Ligand HC≡C^tBu (18.9 mg, 0.23 mmol) was added to a solution of [(^tBu₃tpy)PtCl](OTf) (180 mg, 0.23 mmol), CuI (10 mg, 0.05 mmol), and diisopropylamine (1 mL) in dichloromethane (20 mL). The mixture, after stirring for 12 h at room temperature under an argon atmosphere, was evaporated to dryness *in vacuo*. The product was purified by chromatography on an alumina (neutral) column with (CH₂Cl₂/MeCN) (4/1, *v/v*) as eluent to afford a yellow solid. Yield: 158 mg, 83 %. Anal. Calcd for C₃₄H₄₄F₃N₃O₃PtS: C, 49.39; H, 5.36; N, 5.08. Found: C, 49.45; H, 5.35; N, 5.10. ¹H NMR (500 MHz, CD₃CN): δ 1.37 (s, 9H, ^tBu), 1.46 (s, 18H, ^tBu), 1.53 (s, 9H, ^tBu), 7.74 (dd, 2H, ³J_{HH} = 6.0 Hz, ⁴J_{HH} = 2.1 Hz, H^{5'}), 8.26 (d, 2H, ⁴J_{HH} = 1.9 Hz, H^{3'}), 8.29 (s, 2H, H₃), 8.97 (d with broad ¹⁹⁵Pt satellites, 2H, ³J_{HH} = 6.0 Hz, H^{6'}). ¹⁹⁵Pt NMR (107 MHz, CD₃CN): δ -3129 (s). FAB-MS (+ve NBA matrix): *m/z* 677 [M - OTf]⁺. IR (Nujol): $\tilde{\nu}$ (C≡C) 2119 cm⁻¹.

[(^tBu₃tpy)PtC≡Ctpy](OTf) (2). Ligand HC≡Ctpy (34 mg, 0.13 mmol) was added to a solution of [(^tBu₃tpy)PtCl](OTf) (94 mg, 0.12 mmol), CuI (10 mg, 0.05 mmol), and diisopropylamine (1 mL) in dichloromethane (20 mL). The mixture, after stirring for 5 days at room temperature under an argon atmosphere, was evaporated to dryness *in vacuo*. The product was purified by chromatography on an alumina (neutral) column with (CH₂Cl₂/MeCN) (5/1, *v/v*) as eluent to afford a bright yellow solid. Yield: 73 mg, 61 %. Anal. Calcd for C₄₅H₄₅N₆O₃SF₃Pt·2H₂O: C, 52.07; H, 4.76; N, 8.10. Found: C, 52.06; H, 4.46; N, 7.98. ¹H NMR (500 MHz, CD₃CN): δ 1.38 (s, 18H, ^tBu), 1.46 (s, 9H, ^tBu), 7.33 (qd, 2H, *J*_{HH} = 1.1, 7.4 Hz, H^{d1}), 7.65 (dd, 2H, *J*_{HH} = 2.1, 5.9 Hz, H^{5'}), 7.83 (td, 2H, *J*_{HH} =

1.7, 7.7 Hz, H^{c1}), 7.90 (d, 2H, $J_{\text{HH}} = 1.9$ Hz, H^{3'}), 7.97 (s, 2H, H³), 8.22 (s, 2H, H^{a1}), 8.27 (d, 2H, $J_{\text{HH}} = 7.9$ Hz, H^{b1}), 8.45 (d, 2H, $J_{\text{HH}} = 4.6$ Hz, H^{e1}), 8.97 (d with broad ¹⁹⁵Pt satellites, 2H, $J_{\text{HH}} = 5.9$ Hz, H^{6'}). ¹⁹⁵Pt{¹H} NMR (107 MHz, CD₃CN): δ -3108 (s). FAB-MS (+ve NBA matrix): m/z 853 [**2** - (OTf)]⁺; ESI-MS (MeCN): m/z 853 [**2** - (OTf)]⁺. IR (Nujol): $\tilde{\nu}$ (C≡C) 2091; 2124 cm⁻¹.

[(^tBu₃tpy)Pt(C≡Ctpy)PtCl](OTf)₂ (3). [(COD)PtCl₂] (5 mg, 0.04 mmol) and **2** (36 mg, 0.036 mmol) were dissolved in a mixture of H₂O/acetone (1/4, v/v, 25 mL). The solution was heated at 100 °C for 12 h to give a bright orange solution. Upon removal of solvent, the orange solid was dissolved in warm CH₃CN (10 mL) and the solution was filtered into an aqueous solution of NaOTf (34 mg, 2 mL). A reddish orange precipitate was collected on a sintered-glass funnel and air-dried. Yield: 35 mg, 70 %. Anal. Calcd for C₄₆H₄₅N₆ClO₆S₂F₆Pt₂·2H₂O: C, 38.97; H, 3.48; N, 5.93. Found: C, 38.90; H, 3.44; N, 5.93. ¹H NMR (500 MHz, DMF-*d*₇): δ 1.49 (s, 18H, ^tBu), 1.56 (s, 9H, ^tBu), 7.38 (br, 2H, H^{5'}), 7.54 (br, 2H, H^{d1}), 8.28 (br, s, 2H, H^{e1}), 8.41 (t, 2H, $J_{\text{HH}} = 7.4$ Hz, H^{c1}), 8.48 (br, s, 2H, H^{6'}), 8.61 (s, 2H, H³), 8.70 (d, 2H, $J_{\text{HH}} = 6.4$ Hz, H^{b1}), 8.80 (s, 2H, H^{3'}), 8.87 (s, 2H, H^{a1}). FAB-MS (+ve NBA matrix): m/z 1233 [**3** - (OTf)]⁺, 1083 [**3** - 2(OTf)]⁺; ESI-MS (MeCN): m/z 1233 [**3** - (OTf)]⁺, 542 [**3** - 2(OTf)]²⁺. IR (Nujol): $\tilde{\nu}$ (C≡C) 2097; 2122 cm⁻¹.

[(^tBu₃tpy)Pt(C≡Ctpy)PtC≡C^tBu](OTf)₂ (4). Ligand HC≡C^tBu (2.3 mg, 0.028 mmol) was added to a solution of **3** (35 mg, 0.025 mmol), CuI (1 mg, 0.005 mmol), and diisopropylamine (0.5 mL) in CH₂Cl₂/CH₃CN (1/1, v/v, 20 mL). The resultant solution, after stirring for 12 h at room temperature under an argon atmosphere, was evaporated to dryness *in vacuo*. The crude product was purified by chromatography on an alumina (neutral) column with (CH₂Cl₂/MeCN) (1/1, v/v) as eluent. Orange needles were obtained by vapor diffusion of diethyl ether into an acetonitrile solution. Yield: 20 mg, 56 %. Anal. Calcd for C₅₂H₅₄N₆O₆S₂F₆Pt₂·2H₂O: C, 42.68; H, 4.00; N, 5.74. Found: C, 42.61; H, 3.81; N, 6.10. ¹H NMR (500 MHz, CD₃CN): δ 1.10 (s, 9H, C≡C^tBu), 1.47 (s, 18H, ^tBu), 1.58 (s, 9H, ^tBu), 7.23 (br, s, 2H, H^{d1}), 7.39 (d, 2H, $J_{\text{HH}} = 4.2$ Hz, H^{5'}), 7.93 (t, 2H, $J_{\text{HH}} = 7.6$ Hz, H^{c1}), 8.13 (s, 2H, H³), 8.21 (br, s, 4H, H^{3'} and H^{b1}), 8.30 (s, 2H, $J_{\text{HH}} = 5.5$ Hz, H^{e1}), 8.32 (s, 2H, H^{a1}), 8.49 (d, 2H, $J_{\text{HH}} = 7.1$ Hz, H^{6'}). FAB-MS (+ve NBA matrix): m/z

1278 [4 - (OTf)]⁺, 1129 [4 - 2(OTf)]⁺; ESI-MS (MeCN): *m/z* 1278 [4 - (OTf)]⁺, 564 [4 - 2(OTf)]²⁺. IR (Nujol): $\tilde{\nu}$ (C≡C) 2093; 2124 cm⁻¹.

[(^tBu₃tpy)Pt(C≡Ctpy)PtC≡Ctpy](OTf)₂ (**5**). Ligand HC≡Ctpy (11 mg, 0.039 mmol) was added to a solution of **3** (35 mg, 0.025 mmol), CuI (1 mg, 0.005 mmol), and diisopropylamine (0.5 mL) in CH₂Cl₂/CH₃CN (1/1, *v/v*, 20 mL). After stirring for 12 h at room temperature under an argon atmosphere, the solution was evaporated to dryness *in vacuo*, and the solid was dissolved in a minimum amount of acetonitrile. The solution was filtered through celite and the filtrate was stored at 4 °C for 3 days. The light brown precipitate was washed with CH₂Cl₂ (5 mL) to afford a brownish orange solid. Yield: 30 mg, 52 %. Anal. Calcd for C₆₃H₅₅N₉O₆S₂F₆Pt₂·2H₂O: C, 46.18; H, 3.63; N, 7.81. Found: C, 45.78; H, 3.53; N, 7.86. ¹H NMR (500 MHz, 353 K, DMF-*d*₇): δ 1.16 (s, 9H, ^tBu), 1.51 (s, 18H, ^tBu), 7.46 (br, s, 2H, H^{d2}), 7.69–7.72 (m, 4H, H^{5'} and H^{d1}), 7.99 (s, 2H, H^{c2}), 8.30 (br, s, 2H, H^{a2}), 8.36 (t, 2H, *J*_{HH} = 7.4 Hz, H^{c1}), 8.59–8.61 (m, 6H, H³, H^{a1} and H^{b2}), 8.72 (br, s, 6H, H^{3'}, H^{b1} and H^{e2}), 8.78–8.85 (m, 4H, H^{6'} and H^{e1}). FAB-MS (+ve NBA matrix): *m/z* 1454 [5 - (OTf)]⁺, 1304 [5 - 2(OTf)]⁺; ESI-MS (MeCN): *m/z* 1454 [5 - (OTf)]⁺, 652 [5 - 2(OTf)]²⁺. IR (Nujol): $\tilde{\nu}$ (C≡C) 2095; 2124 cm⁻¹.

[(^tBu₃tpy)Pt(C≡Ctpy)Pt(C≡Ctpy)PtCl](OTf)₃ (**6**): [(COD)PtCl₂] (15 mg, 0.04 mmol) and **6** (50 mg, 0.030 mmol) were dissolved in H₂O/acetone (1/4, *v/v*, 25 mL). The solution was heated at 100 °C for 24 h to give a red solution, which was filtered into an aqueous solution of NaOTf (50 mg, 2 mL). The brownish orange precipitate was collected and air-dried. Yield: 32 mg, 52 %. Anal. Calcd for C₆₄H₅₅N₉ClO₉S₃F₉Pt₃: C, 38.78; H, 2.80; N, 6.36. Found: C, 38.74; H, 3.20; N, 6.00. ¹H NMR (500 MHz, 353 K, DMF-*d*₇): δ 1.67 (s, 18H, ^tBu), 1.71 (s, 9H, ^tBu), 7.97–7.99 (br, 2H, H^{5'}), 8.09–8.11 (br, fused with DMF-*d*₇ peak, 2H, H^{d2}), 8.18–8.21 (br, fused with DMF-*d*₇ peak, 2H, H^{d1}), 8.66 (t, *J* = 8.0 Hz, 2H, H^{c2}), 8.86–8.88 (m, 4H, H³ and H^{b2}), 8.90–8.95 (m, 8 H, H^{3'}, H^{a1}, H^{b1} and H^{c1}), 9.01 (s, 2H, H^{a2}), 9.06 (m, 2H, H^{e2}), 9.14 (d, *J* = 6.1 Hz, 2H, H^{e1}), 9.24 (m, 2H, H^{b1}). FAB-MS (+ve NBA matrix): *m/z* 1834 [6 - (OTf)]⁺, 1685 [6 - 2(OTf)]⁺, 1534 [6 - 3(OTf)]⁺; ESI-MS (MeCN): *m/z* 1833 [6 - (OTf)]⁺. IR (Nujol): $\tilde{\nu}$ (C≡C) 2097; 2124 cm⁻¹.

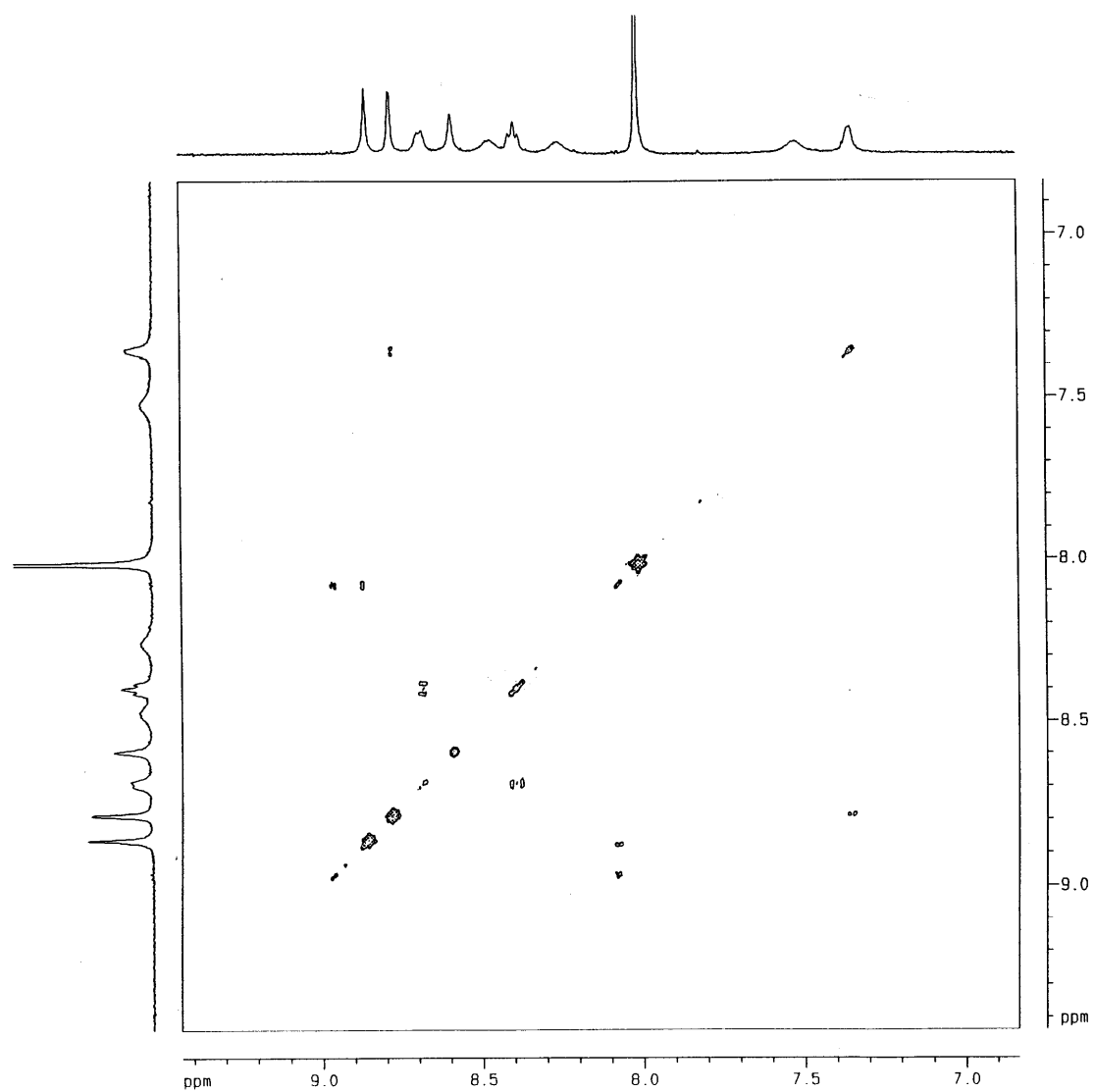


Figure S1. ¹H-¹H COSY spectrum of [(^tBu₃tpy)Pt(C≡Ctpy)PtCl](OTf)₂ (**3**) in DMF-*d*₇ at 299 K.

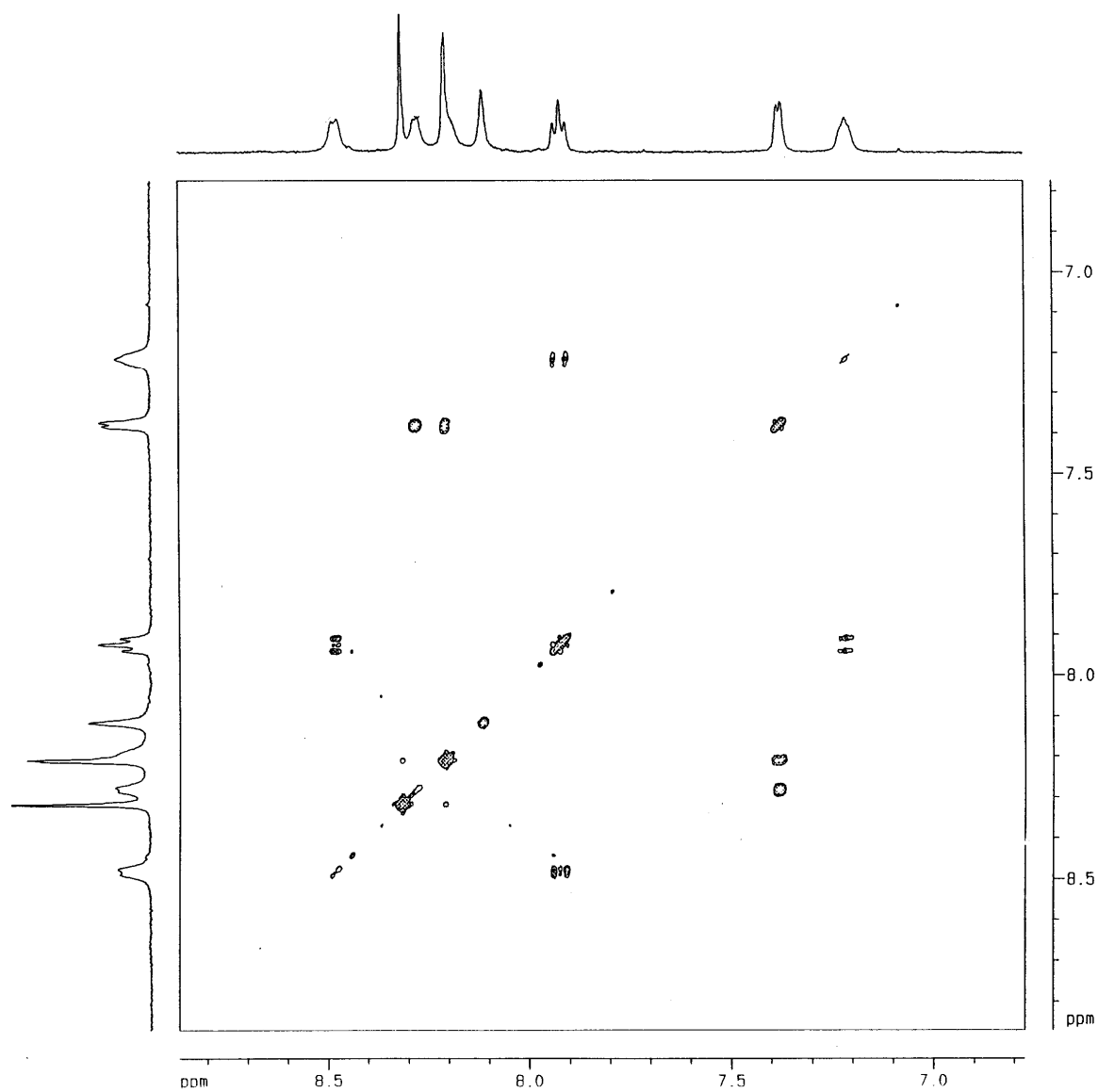


Figure S2. ^1H - ^1H COSY spectrum of $[(^t\text{Bu}_3\text{tpy})\text{Pt}(\text{C}\equiv\text{Ctpy})\text{PtC}\equiv\text{C}^t\text{Bu}](\text{OTf})_2$ (**4**) in CD_3CN at 298 K.

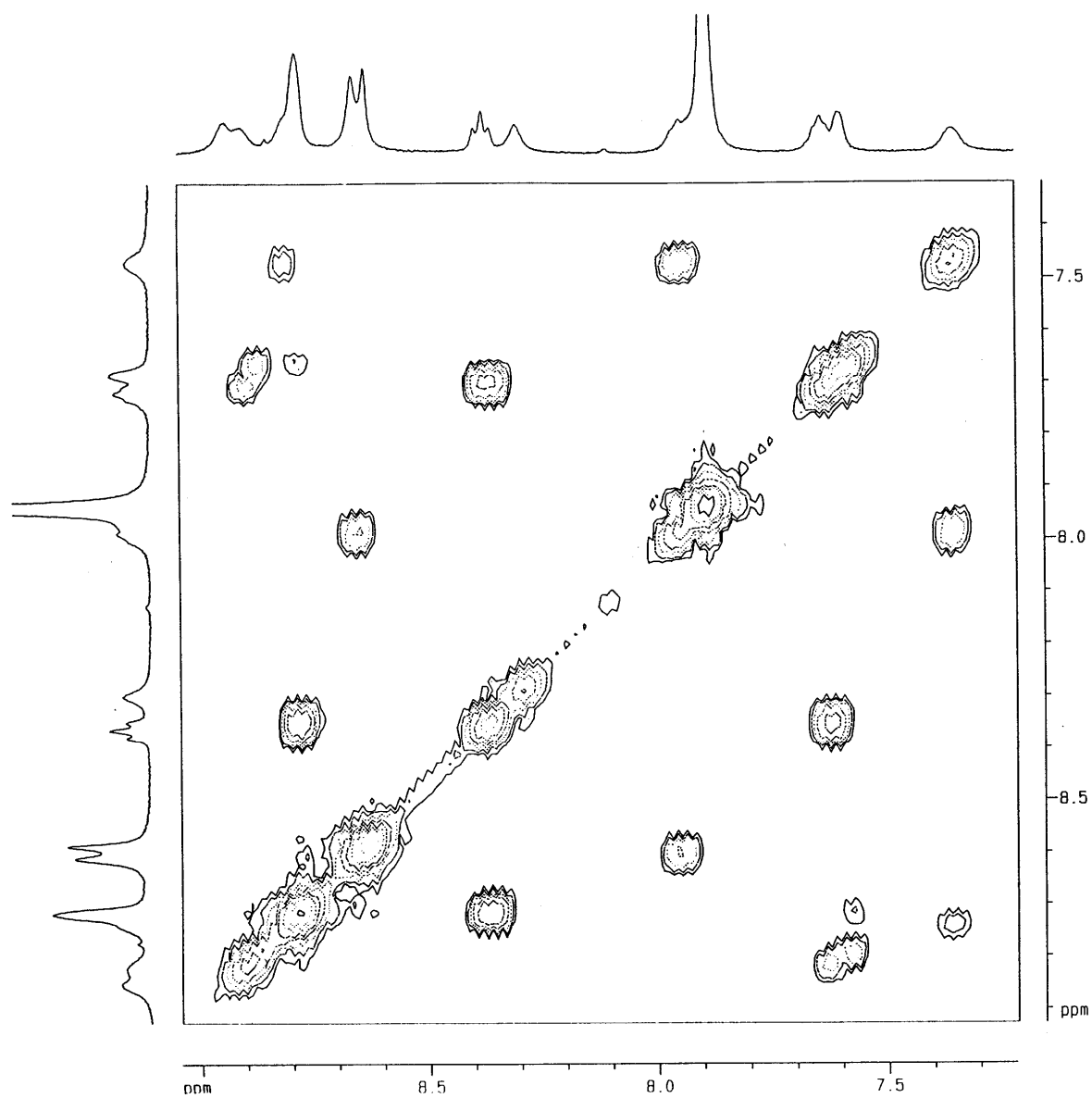


Figure S3. ^1H - ^1H COSY spectrum of $[(^i\text{Bu}_3\text{tpy})\text{Pt}(\text{C}\equiv\text{Ctpy})\text{PtC}\equiv\text{Ctpy}](\text{OTf})_2$ (**5**) in $\text{DMF-}d_7$ at 353 K.

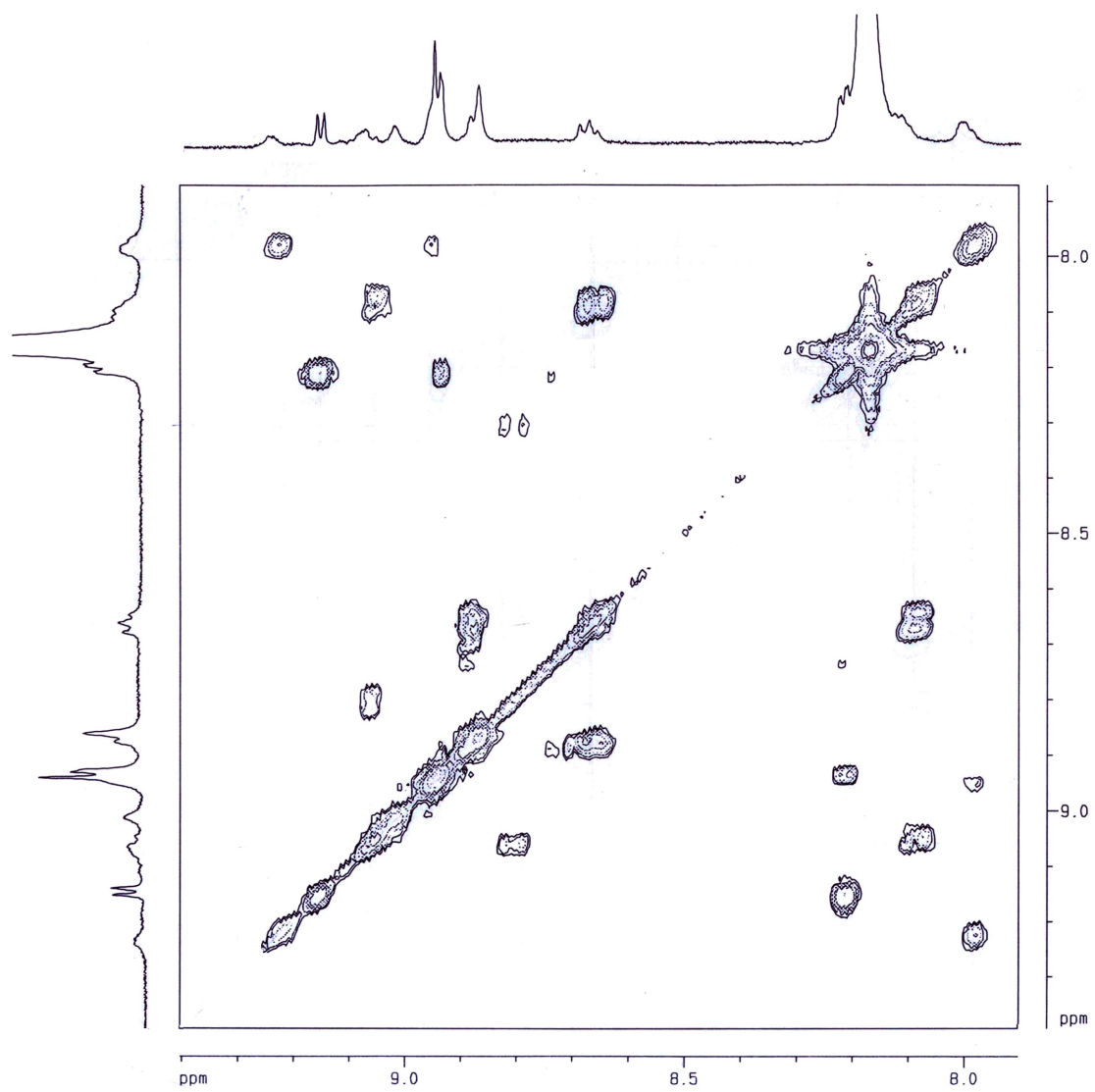


Figure S4. ¹H-¹H COSY spectrum of [(^tBu₃tpy)Pt(C≡Ctpy)Pt(C≡Ctpy)PtCl](OTf)₃ (**6**) in DMF-*d*₇ at 353

K.

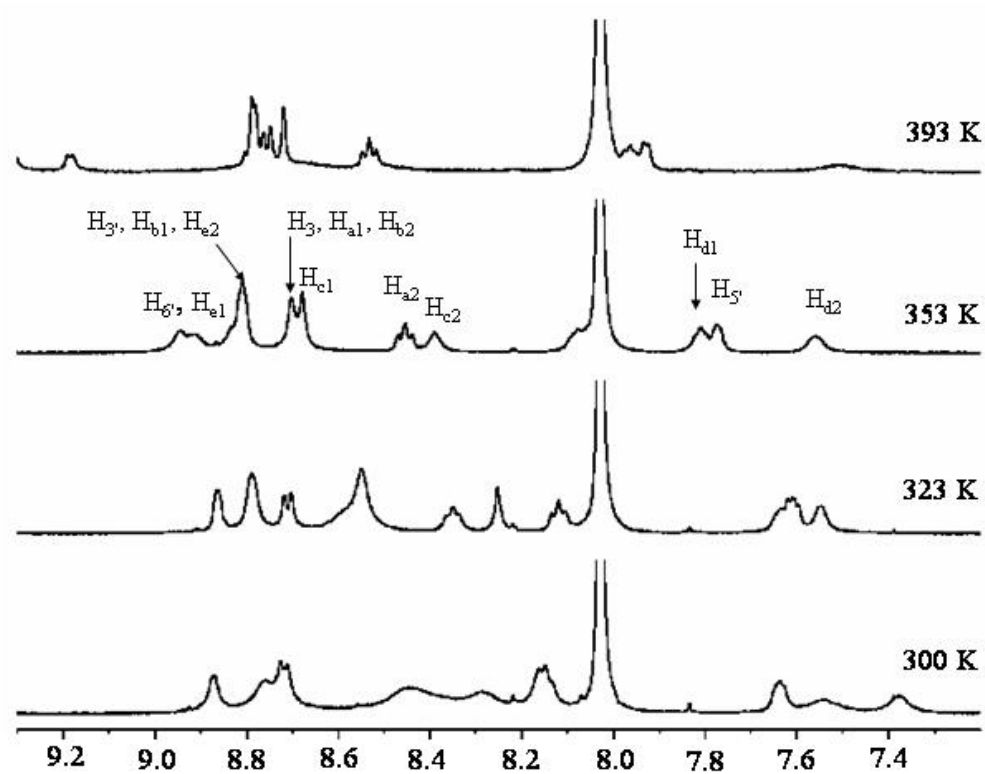


Figure S5. ^1H NMR spectra (500 MHz) of $[(^t\text{Bu}_3\text{tpy})\text{Pt}(\text{C}\equiv\text{Ctpy})\text{PtC}\equiv\text{Ctpy}](\text{OTf})_2$ (**5**) in $\text{DMF-}d_7$ at various temperature.

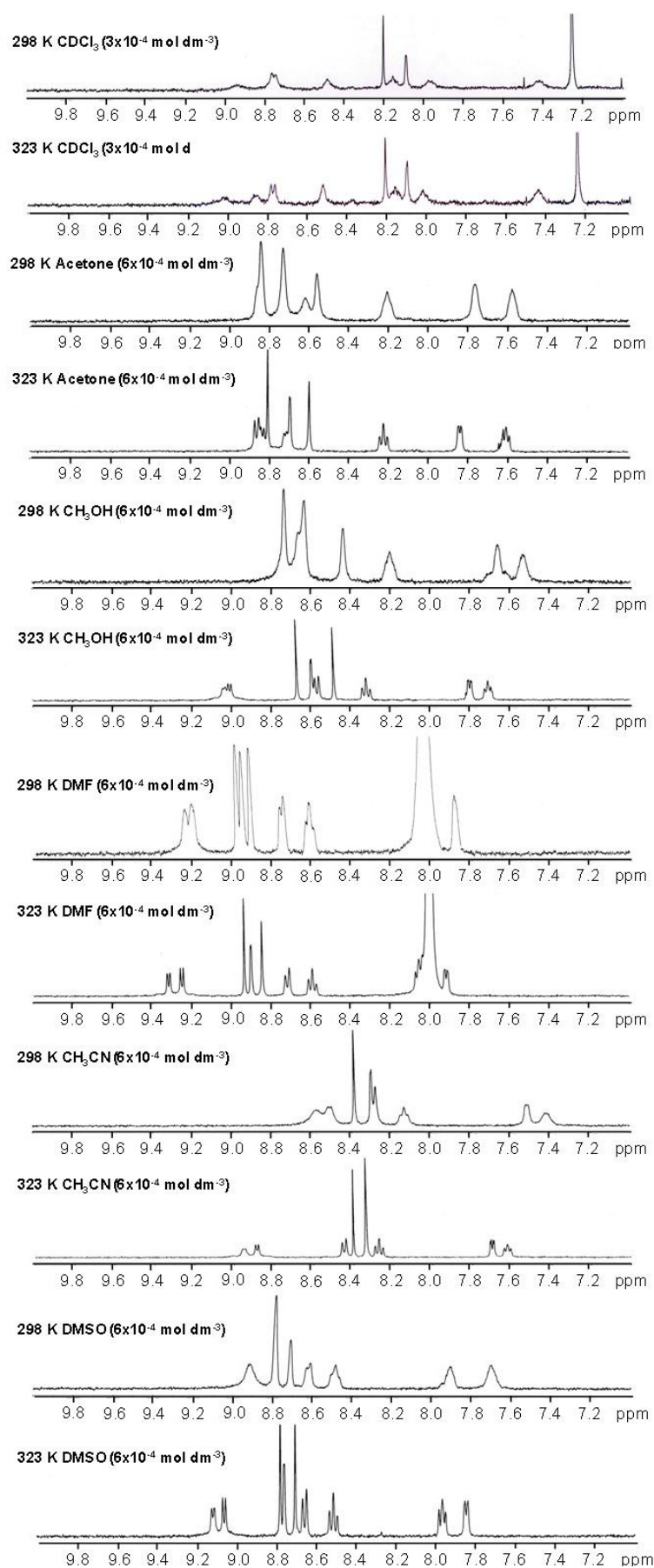


Figure S6. ^1H NMR spectra (400 MHz) of $[(^i\text{Bu}_3\text{tpy})\text{Pt}(\text{C}\equiv\text{Ctpy})\text{PtC}\equiv\text{C}^i\text{Bu}](\text{OTf})_2$ (**4**) in various NMR solvent at 298 K and 323 K.

Table S1. Spectroscopic and photophysical data of 1–6.

Complex	Medium	T / K	$\lambda_{\text{abs}}^{\text{a,b}} / \text{nm}$ ($\epsilon / \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{em}}^{\text{c,d}} / \text{nm}$ ($\tau / \mu\text{s}$)	$\phi_{\text{em}}^{\text{e}}$
1	CH ₃ CN	298	285 (2.71), 312 (1.81), 322 (1.65), 338 (1.86), 414 (0.44)	537 (0.02)	<0.01
	CH ₂ Cl ₂	298	287 (2.77), 317 (1.99), 325 (1.70), 341 (1.74), 400 (sh, 0.54), 429 (0.64)	547 (3.2)	0.41
	ⁿ BuCN	77		498 (8.4), 530 (8.0)	
	Solid	298		545 (1.3), 583 (sh, 4.0)	
	Solid	77		507 (1.1), 540 (1.9), 583 (4.0)	
2	CH ₃ CN	298	245 (4.03), 277 (sh, 4.39), 286 (5.10), 308 (1.84), 319 (1.65), 334 (1.62), 382 (sh, 0.49), 405 (br, 0.59)	519 (0.3)	<0.01
	CH ₂ Cl ₂	298	248 (5.28), 278 (sh, 5.50), 287 (5.98), 313 (2.30), 323 (sh, 1.94), 338 (1.75), 416 (br, 0.70)	530 (0.7)	0.07
	ⁿ BuCN	77		478 (7), 510 (7), 540 (sh, 7), 613 (sh, 2)	
	Solid	298		520 (1), 545 (sh, 1)	
	Solid	77		524 (4), 565 (sh, 4), 610 (sh, 5)	
3	CH ₃ CN	298	254 (3.91), 284 (3.66), 308 (sh, 2.05), 331 (2.49), 423 (1.66)	544, 587 (<0.01)	<0.01
	CH ₂ Cl ₂	298	254 (sh, 3.48), 285 (3.14), 333 (1.84), 440 (1.36)	549, 586 (sh, 1)	0.04
	ⁿ BuCN	77		559 (9), 607 (sh, 9), 648 (sh, 3)	
	Solid	298		641 (0.1)	
	Solid	77		669 (1)	
4	CH ₃ CN	298	262 (5.59), 273 (sh, 5.48), 286 (6.41), 313 (3.52), 330 (3.74), 340 (3.74), 376 (sh, 1.21), 398 (sh, 1.33), 439 (1.92), 462 (sh, 1.39)	570 (0.1)	0.03
	CH ₂ Cl ₂	298	264 (sh, 3.21), 275 (3.13), 288 (3.67), 315 (2.05), 338 (3.26), 384 (sh, 0.64), 409 (sh, 0.75), 446 (1.12), 463 (sh, 0.96)	576 (11)	0.43
	ⁿ BuCN	77		557 (sh, 15), 572 (12), 612 (sh, 12)	
	Solid (evaporation from CH ₃ CN)	298		585 (0.2), 627 (0.2), 666 (0.3)	
	Solid (evaporation from CH ₂ Cl ₂)	298		585 (1.3), 627 (1.1), 666 (sh, 1.1)	
	Solid	77		591 (3), 643 (sh, 3), 671 (sh, 2)	
5	CH ₃ CN	298	253 (5.98), 287 (7.42), 330 (sh, 3.04), 434 (br, 1.96), 459 (sh, 1.43)	549 (0.1), 593 (sh, 0.1), 635 (sh, 0.2), 671 (0.2)	<0.01
	CH ₂ Cl ₂	298	289 (3.59), 335 (sh, 1.40), 441 (1.03), 456 (1.00)	560 (3.4);	0.20
	ⁿ BuCN	77		538 (19), 580 (13), 641 (sh, 2), 665 (sh, 2)	
	Solid	298		639 (sh) ^f , 669 ^f	
	Solid	77		536 (sh, 0.3), 589 (0.8), 640 (sh, 0.7), 676 (0.5)	
6	CH ₃ CN	298	285 (4.97), 304 (sh, 3.27), 331 (3.01), 426 (2.00)	546, 671 (<0.01)	<0.01
	ⁿ BuCN	77		541 (8), 584 (sh, 8), 660 (2)	
	Solid	298		Non-emissive	
	Solid	77		Non-emissive	

^a Absorption maxima; br = broad. ^b At $1 \times 10^{-5} \text{ mol dm}^{-3}$; ^c Emission maxima; the most intense emission in italic; sh = shoulder. ^d At $1 \times 10^{-5} \text{ mol dm}^{-3}$. ^e Emission quantum yield.

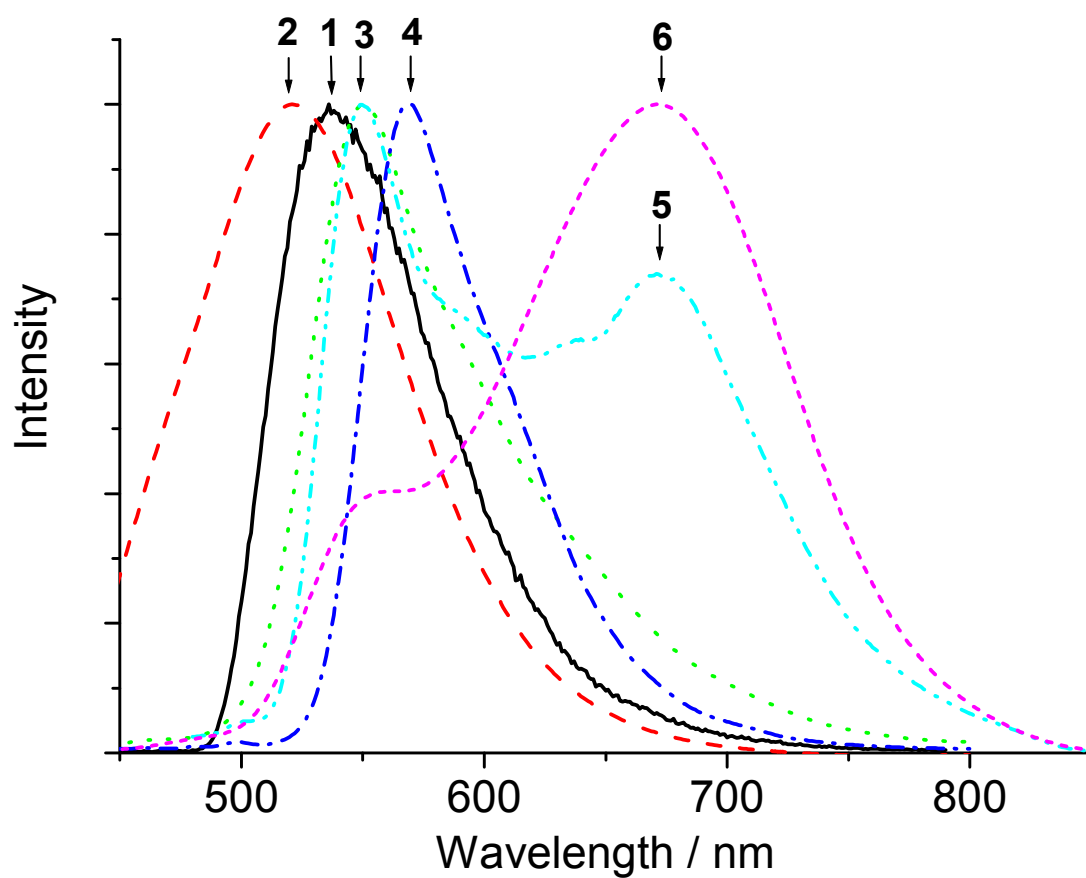
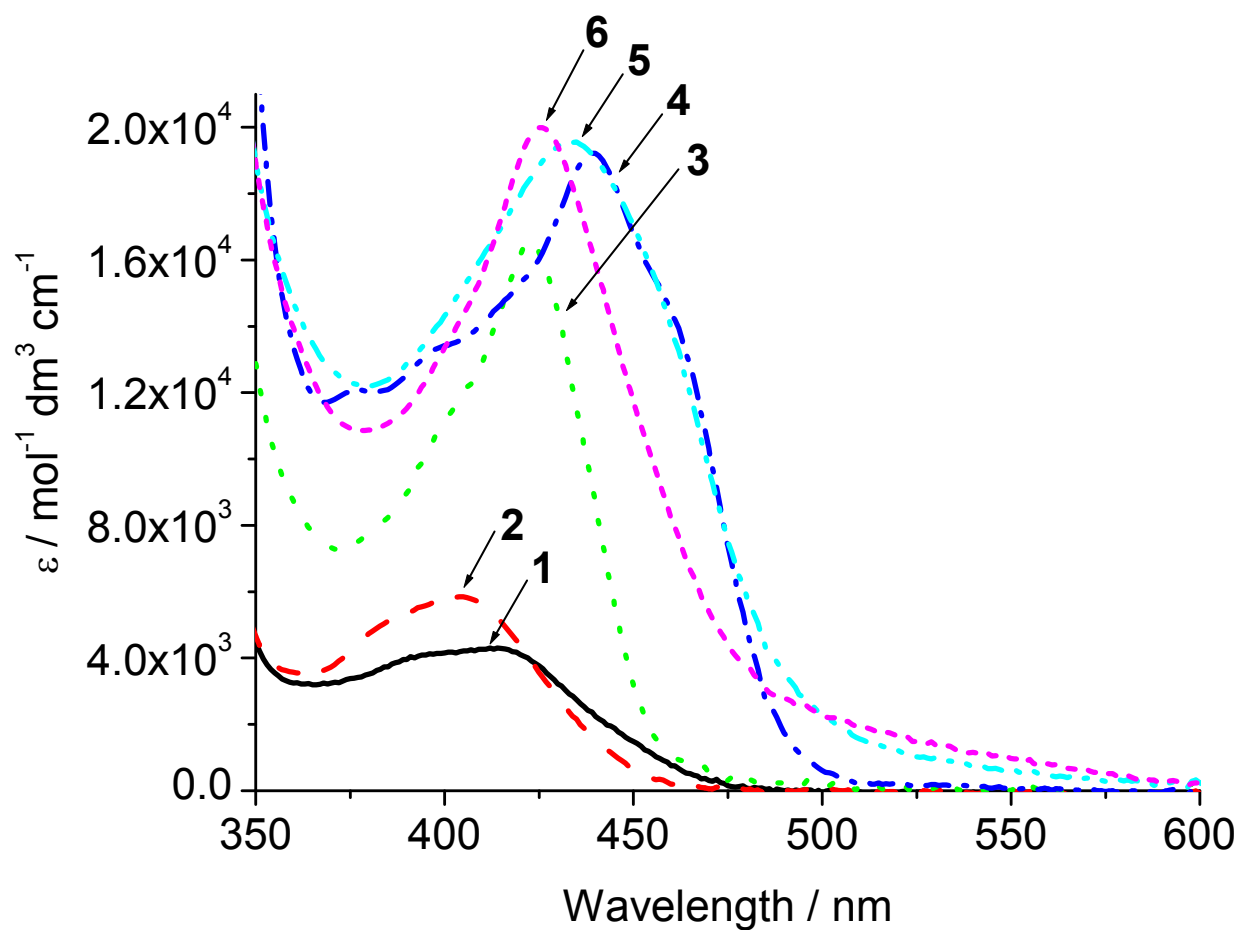


Figure S7. Upper: Absorption spectra of **1-6** in CH₃CN solutions ($1 \times 10^{-5} \text{ mol dm}^{-3}$) at 298 K. Bottom: Normalized emission spectra of **1-6** in CH₃CN solutions ($1 \times 10^{-5} \text{ mol dm}^{-3}$) at 298 K.

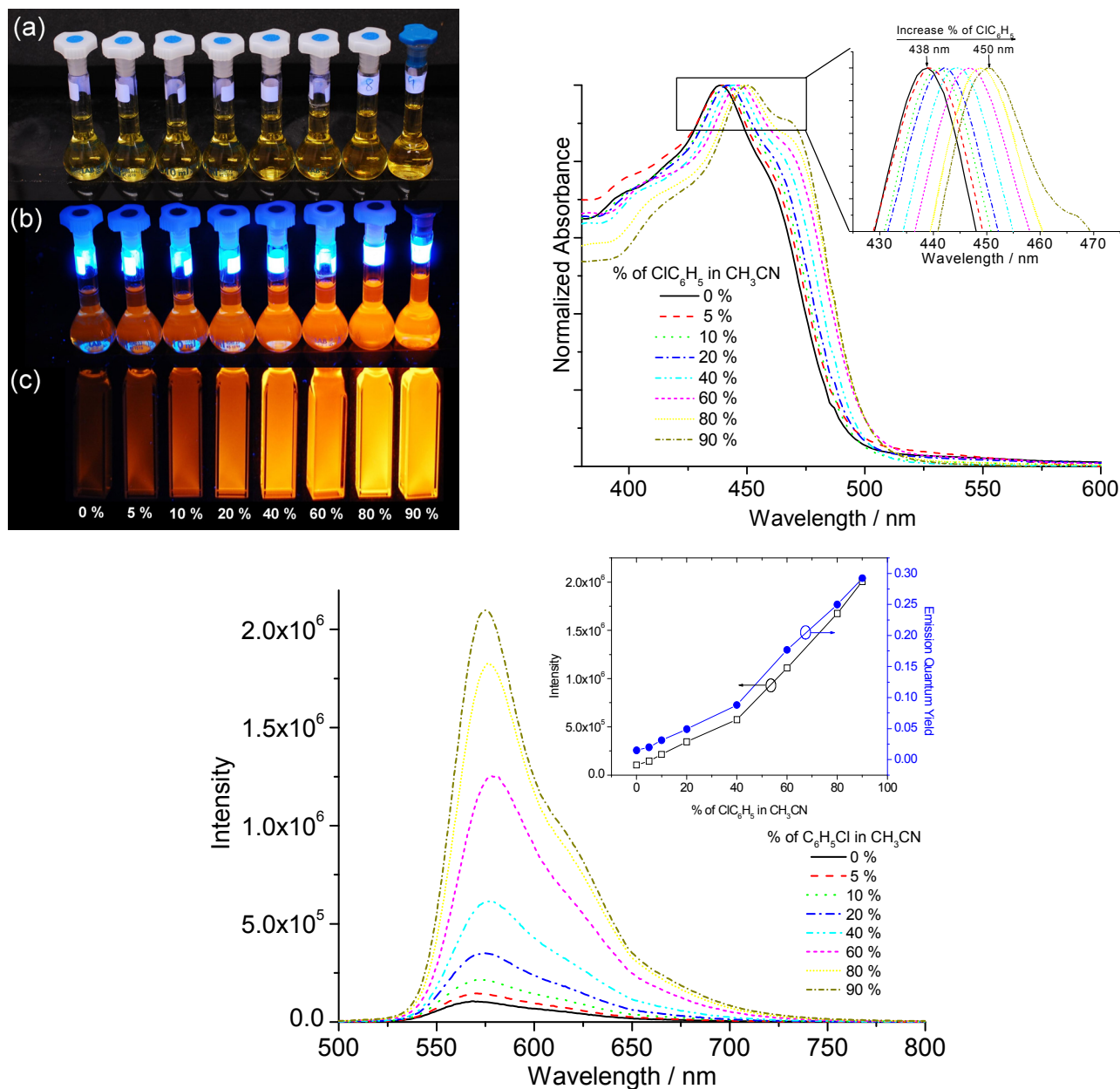


Figure S8. Upper Left: Photographs of complex **4** (concentration = 2×10^{-5} mol dm⁻³) in CH₃CN mixed with 0–90 % ClC₆H₅; (a) under ambient light (in air), (b) under UV light irradiation (350 nm; in air) and (c) under UV light irradiation (350 nm; in degassed environment). Upper Right: Normalized UV-vis spectra of complex **4** (concentration = 2×10^{-5} mol dm⁻³) in CH₃CN mixed with 0–90 % ClC₆H₅ depicted from 380 nm to 600 nm. Bottom: Emission Spectra of complex **4** (concentration = 2×10^{-5} mol dm⁻³) in CH₃CN mixed with 0–90 % ClC₆H₅ (Inset: plots of intensity at 570 nm and emission quantum yield versus % of ClC₆H₅ in CH₃CN).

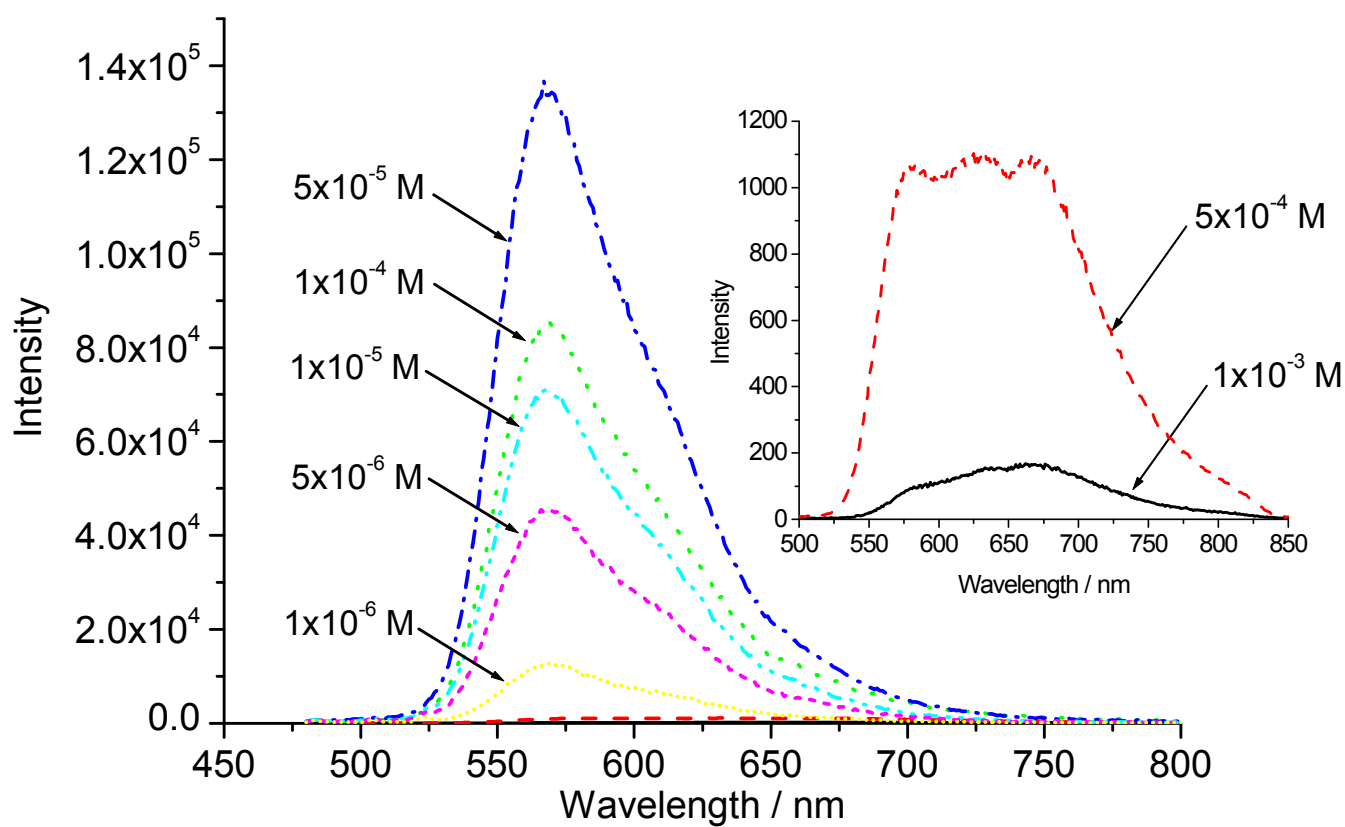


Figure S9. Emission spectra of complex 4 in CH_3CN at different concentration.

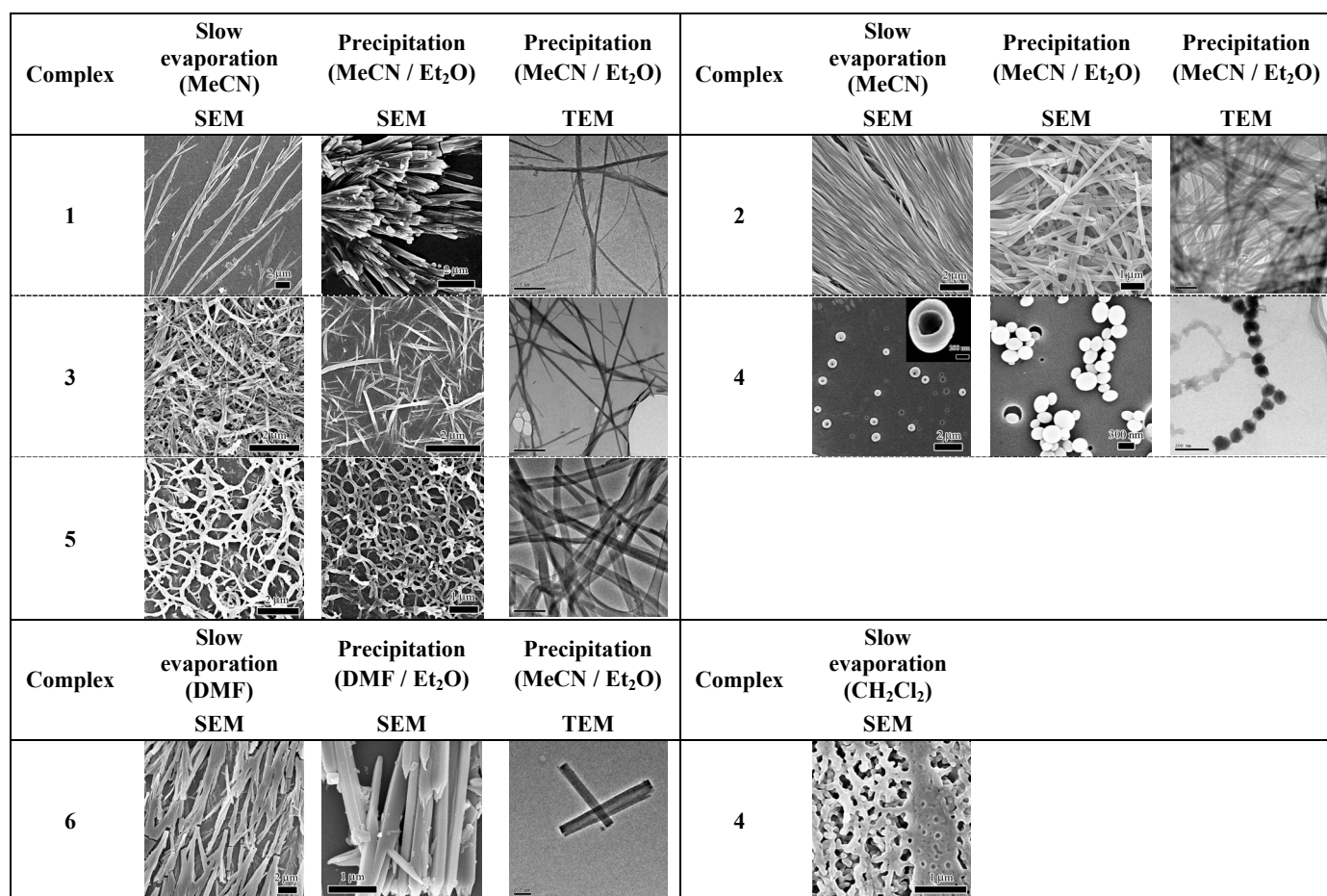


Figure S10. SEM and TEM images of complexes 1–6.

Computational Details. Density Functional Theory (DFT) was employed to study the photophysics of the model complex, $[(\text{Me}_3\text{tpy})\text{Pt}(\text{C}\equiv\text{Ctpy})\text{PtC}\equiv\text{CMe}]^{2+}$ (**4'**) with the *t*Bu groups of **4** replaced by smaller Me groups. All calculations were performed using the G03 software^[1] with the density functional PBE1PBE.^[2] Stuttgart small core relativistic pseudopotentials and its accompanying basis set was employed for Pt^[3] while the 6-31G* basis set was used for all other atoms.^[4] Two configurations were considered in the present work, coplanar and perpendicular, in which the tpy moieties are respectively coplanar and perpendicular to each other. Geometry optimizations were performed on both singlet ground state (S_0) and the first triplet excited state (T_1). The excited states were then calculated using time-dependent DFT (TDDFT) with solvent effect included using the polarizable continuum model (PCM) and conductor-like PCM (CPCM) as implemented in G03.^[1]

- [1] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
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