

Supporting Information

Dual-AIEgens in One Organoplatinum(II) Metallaprism: Photoluminescence Exploration

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Experimental Procedures

1. Materials and methods

The $[\text{Pt}(\text{dpy})(\text{dms})]$ (H_2dpy = 2,6-diphenylpyridine, dms = dimethylsulfoxide) were prepared according to the reported procedures.¹ All other reagents (4,4'-bipyridine, Bpy; 1,2-bis(4-pyridyl)ethyne, Bpe; 1,1,2,2-tetrakis(4-pyridin-4-yl)phenyl)ethane, TPPE, etc) were commercially available and used as received. All reactions and manipulations were performed under a nitrogen atmosphere, using standard Schlenk techniques. ^1H NMR spectra were recorded on a Bruker Avance III HD 400 spectrometer using the residual protonated solvent as internal standard. Infrared spectra were recorded on IRAffinity-1S spectrometer (IRAffinity-1S). UV-vis spectra were recorded on TU-1901 spectrophotometer. The photoluminescence (PL) spectra were performed on a Hitachi F-7000 spectrophotometer equipped with a 150W xenon lamp as the excitation source at room temperature. The fluorescence spectra at various temperatures were recorded on an Edinburgh Instruments FLS980 spectrophotometer. ESI-MS spectra were recorded on Agilent Q-TOF 6520 mass spectrometer.

2. Synthesis and characterization of complexes

2.1 Synthesis of $\{[\text{Pt}(\text{dpy})]_2(\text{Bpy})\}$

A mixture of $[\text{Pt}(\text{dpy})(\text{dms})]$ (1.0 mmol, 503 mg) and Bpy (0.5 mmol, 78.0 mg) were dissolved in 15 ml dry dichloromethane and stirred at room temperature for 12 h. Gradually, orange solids precipitated from solution. These solids were subsequently collected by filtration and then washed with 10 mL ethyl ether to give orange solids. Yield: 456mg, 90%; ^1H NMR (400 MHz, DMSO-d_6 , 298 K) δ (ppm): 8.73 (d, J = 4 Hz, 4H, H_b), 7.84 (m, 6H, H_{a+h}), 7.78 (d, J = 8 Hz, 4H, H_c), 7.66-7.63 (m, 8H, H_{f+g}), 7.22 (t, J = 8 Hz, 4H, H_d), 7.10 (t, J = 4 Hz, 4H, H_e).

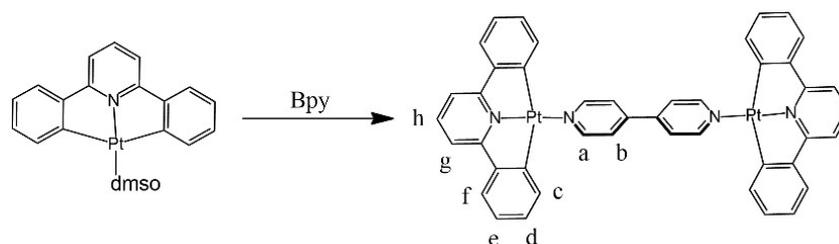


Fig S1. Synthesis of $\{[\text{Pt}(\text{dpy})]_2(\text{Bpy})\}$.

2.2 Synthesis of $\{[\text{Pt}(\text{dpy})]_2(\text{Bpe})\}$

A mixture of $[\text{Pt}(\text{dpy})(\text{dms})]$ (1.0 mmol, 503 mg) and Bpe (0.5 mmol, 90.0 mg) were dissolved in 15 ml dry dichloromethane and stirred at room temperature for 12 h. The solvent was removed under vacuum and then these solids were washed with 10 mL ethyl ether to give red solids. Yield: 471mg, 92%; ^1H NMR (400 MHz, CDCl_3 , 298 K) δ (ppm): 9.16 (d, J = 8 Hz, 4H, H_b), 7.58 (m, 6H, H_{a+h}), 7.53 (d, J = 4 Hz, 4H, H_c), 7.49-7.47 (m, 8H, H_{f+g}), 7.11 (t, J = 8 Hz, 4H, H_d), 7.00 (t, J = 12 Hz, 4H, H_e).

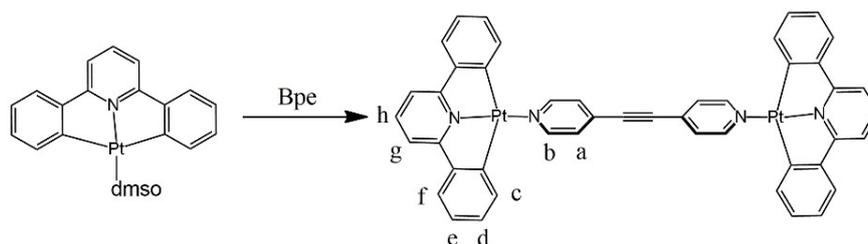


Fig S2. Synthesis of $\{[\text{Pt}(\text{dpy})]_2(\text{Bpe})\}$.

2.3 Synthesis of $\{[\text{Pt}(\text{dpy})]_4(\text{TPPE})\}$

The $\{[\text{Pt}(\text{dpy})]_4(\text{TPPE})\}$ was synthesized in a procedure analogous to that of $\{[\text{Pt}(\text{dpy})]_2(\text{Bpy})\}$ except that Bpy was took the place of TPPE (0.25 mmol, 160.1 mg). The yellow solids were obtained. Yield: 539 mg, 92%; ^1H NMR (400 MHz, DMSO-d_6 , 298 K) δ (ppm): 8.59 (d, J = 4 Hz, 8H, H_b), 7.86 (t, J = 8 Hz, 4H, H_h), 7.76 (d, J = 20 Hz, 8H, H_f), 7.69

(d, J = 4 Hz, 8H, H_a), 7.67 (d, J = 4 Hz, 8H, H_i), 7.65-7.63 (m, 16H, H_{c+g}), 7.24-7.18 (m, 16H, H_{d+j}), 7.10 (t, J = 4 Hz, 8H, H_e).

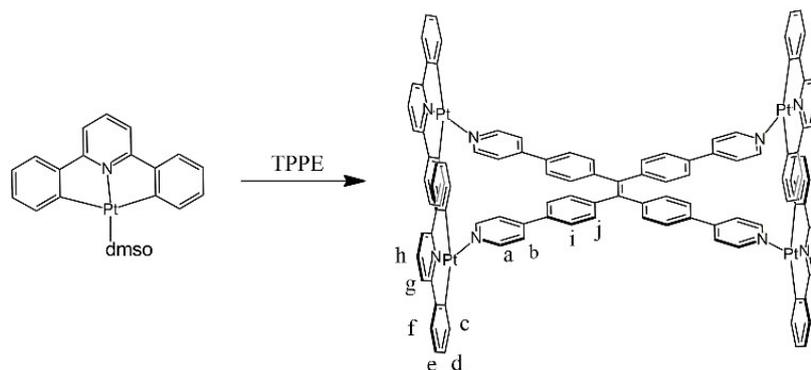


Fig S3. Synthesis of $\{[Pt(dpy)]_4(TPPE)\}$.

2.4 Synthesis of $\{cis-[Pt(Hdpy)]_8(Bpy)_4(TPPE)_2\}(OTf)_8\}$ (*cis-1*)

$[Pt(dpy)(dmsO)]$ (1.0 mmol, 503 mg) and Bpy (0.5 mmol, 78.0 mg) was dissolved in 15 ml dry dichloromethane and stirred at room temperature for 6 h. Followed by the addition of camphorsulfonic acid (1.0 mmol, 234 mg), the solution became clear. 30 minutes later, TPPE (0.25 mmol, 160 mg) was added and the solution was stirred at room temperature for 12h, the solvents was concentrated to about 5 ml. 3 ml DCM solution of Tetrabutylammonium Triflate (3.0 mmol, 1.18 g) was added and stirred at room temperature for 3 h, Then, diethyl ether was added, giving *cis-1* as yellow solid. Yield: 650 mg, 80%; IR spectrum (ν , cm^{-1}): $\nu = 3059$ (w), 2357 (w), 2314 (w), 1608 (s), 1558 (m), 1473 (m), 1438 (s), 1419 (m), 1253 (s), 1219 (s), 1153 (s), 1064 (m), 1029 (s), 813 (s), 759 (s), 694 (m), 636 (s), 570 (m), 516 (s) cm^{-1} . 1H NMR (400 MHz, CD_2Cl_2 , 298 K) δ (ppm): 8.90 (d, J = 8 Hz, 16H, H_c), 8.08 (t, J = 8 Hz, 8H, H_g), 7.97 (s, 8 H, H_f), 7.94 (d, J = 4 Hz, 16H, H_{k+b}), 7.80 (d, J = 8 Hz, 16H, H_d), 7.73 (d, J = 8 Hz, 8H, H_e), 7.48 (d, J = 8 Hz, 16H, H_a), 7.33 (d, J = 8 Hz, 16H, H_p), 7.29 (s, 8 H, H_k), 7.26-7.22 (m, 32H, H_{n+o}), 7.19 (d, J = 8 Hz, 16H, H_l), 7.12 (d, J = 8 Hz, 16H, H_m), 7.08 (t, J = 8 Hz, 8H, H_j), 6.51 (d, J = 8 Hz, 8H, H_i). ESI-MS: 2018.02 $[(cis-1) - 5OTf]^{3+}$.

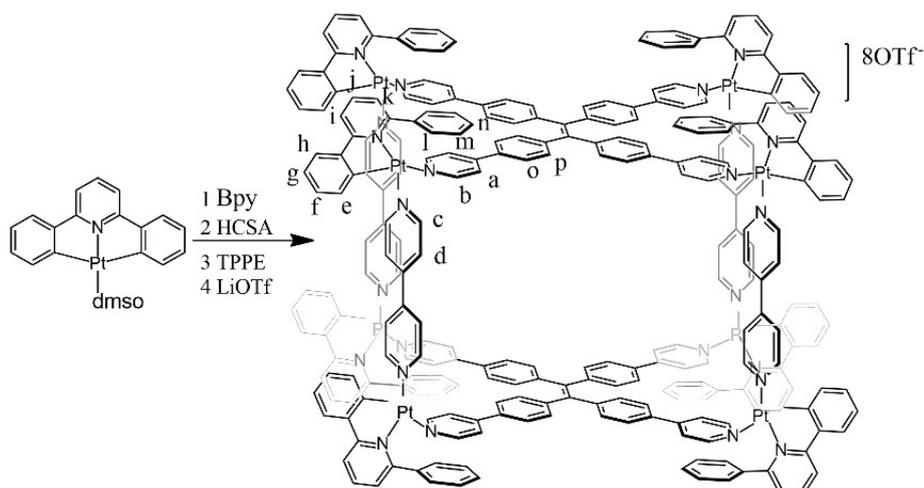


Fig S4. Synthesis of *cis-1*.

2.5 Synthesis of $\{trans-[Pt(Hdpy)]_8(TPPE)_2(Bpy)_4\}(OTf)_8\}$ (*trans-1*)

$[Pt(dpy)(dmsO)]$ (1.0 mmol, 503 mg) and TPPE (0.25 mmol, 160 mg) was dissolved in 15 ml dry dichloromethane and stirred at room temperature for 6 h. Followed by the addition of camphorsulfonic acid (1.0 mmol, 234 mg), the solution became clear. 30 minutes later, Bpy (0.5 mmol, 78.0 mg) was added and the solution was stirred at room temperature for 12h, the solvents was concentrated to about 5 ml. 3 ml DCM solution of Tetrabutylammonium Triflate (3.0 mmol, 1.18 g) was added and stirred at room temperature for 3 h, Then, diethyl ether was added, giving *trans-1* as yellow solid. Yield: 666 mg, 82%; IR spectrum (ν , cm^{-1}): $\nu = 3059$ (w), 2349 (w), 2310 (w), 1604 (s), 1558 (m), 1473 (m), 1438 (s), 1411 (m), 1253 (s), 1222 (s), 1145 (s), 1064 (m), 1029 (s), 813 (s), 759 (s), 698 (s), 636 (s), 570 (m), 516 (s) cm^{-1} . 1H NMR (400 MHz, CD_2Cl_2 , 298 K) δ (ppm): 8.67 (d, J = 8 Hz, 16H, H_b),

8.12 (d, J = 8 Hz, 16H, H_c), 8.06 (t, J = 8 Hz, 8H, H_g), 7.95 (d, J = 8 Hz, 8H, H_k), 7.70 (d, J = 8 Hz, 8H, H_e), 7.53 (d, J = 8 Hz, 16H, H_d), 7.49 (d, J = 4 Hz, 16H, H_a), 7.39 (d, J = 8 Hz, 16H, H_o), 7.32-7.28 (m, 32H, H_{l+m}), 7.26 (d, J = 8 Hz, 8H, H_f), 7.23 (t, J = 8 Hz, 16H, H_{n+h}), 7.12 (d, J = 8 Hz, 16 H, H_p), 7.03 (t, J = 8 Hz, 8H, H_j), 6.45 (d, J = 8 Hz, 8H, H_i). ESI-MS: 934.53 [(*trans*-1) – 2OTf]⁶⁺.

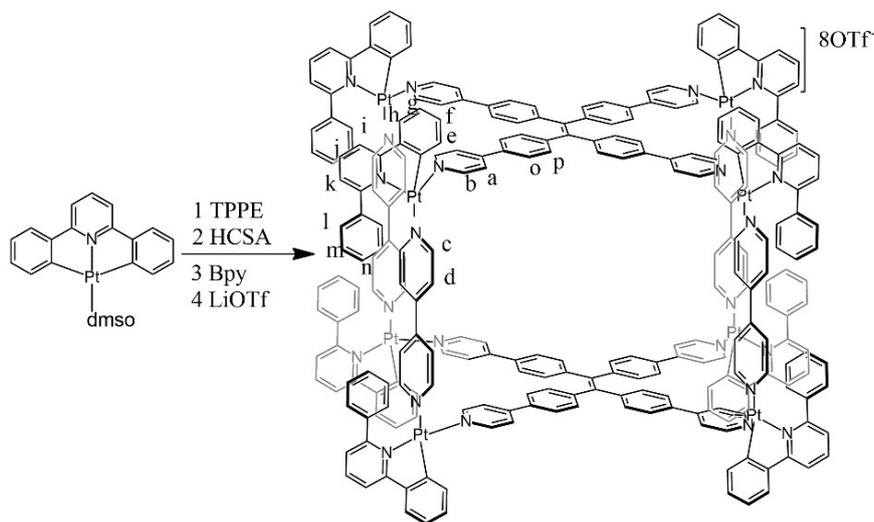


Fig S5. Synthesis of *trans*-1.

2.6 Synthesis of {*cis*-[Pt-Hdpy]₈(Bpe)₄(TPPE)₂}(OTf)₈ (*cis*-2)

[Pt(dppe)(dmsol)] (1.0 mmol, 503 mg) and Bpe (0.5 mmol, 90.0 mg) was dissolved in 15 ml dry dichloromethane and stirred at room temperature for 6 h. The camphorsulfonic acid (1.0 mmol, 234 mg) was added, 30 minutes later, TPPE (0.25 mmol, 160 mg) was added and the solution was stirred at room temperature for 12h, the solvents was concentrated to about 5 ml. 3 ml DCM solution of Tetrabutylammonium Triflate (3.0 mmol, 1.18 g) was added and stirred at room temperature for 3 h, Then, diethyl ether was added, giving *cis*-2 as yellow solid. Yield: 617 mg, 75%; IR spectrum (ν , cm⁻¹): ν = 3051 (w), 2376 (w), 2353 (w), 2322 (w), 1608 (s), 1554 (m), 1473 (m), 1438 (s), 1257 (s), 1219 (s), 1145 (s), 1064 (m), 1029 (s), 821 (s), 756 (s), 698 (s), 632 (s), 574 (m), 547 (m), 513 (s) cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂, 298 K) δ (ppm): 8.80 (d, J = 8 Hz, 16H, H_c), 8.05 (t, J = 8 Hz, 8H, H_g), 7.93 (d, J = 8 Hz, 8H, H_k), 7.88 (d, J = 4 Hz, 16H, H_b), 7.70 (d, J = 8 Hz, 8H, H_n), 7.48 (d, J = 8 Hz, 16H, H_p), 7.44 (d, J = 8 Hz, 16H, H_d), 7.37 (d, J = 8 Hz, 16H, H_{e+f}), 7.26-7.24 (m, 32H, H_{a+o}), 7.23 - 7.21 (d, J = 8 Hz, 16H, H_m), 7.19 (d, J = 4 Hz, 16H, H_l), 7.17 (d, J = 4 Hz, 8H, H_n), 7.09 (t, J = 4 Hz, 8H, H_j), 6.58 (d, J = 8 Hz, 8H, H_i). ESI-MS: 2050.01 [(*cis*-2) – 5OTf]³⁺.

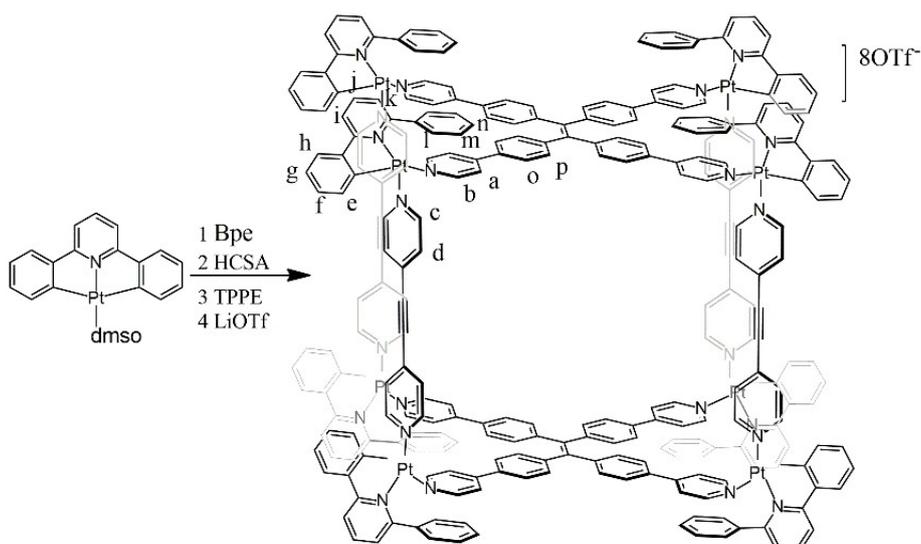


Fig S6. Synthesis of *cis*-2.

2.7 Synthesis of $\{trans-[(Pt-Hdpy)_8(TPPE)_2(Bpe)_4](OTf)_8\}$ (*trans-2*)

[Pt(dpy)(dmsO)] (1.0 mmol, 503 mg) and Bpe (0.5 mmol, 90.0 mg) was dissolved in 15 ml dry dichloromethane and stirred at room temperature for 6 h. The camphorsulfonic acid (1.0 mmol, 234 mg) was added, 30 minutes later, TPPE (0.25 mmol, 160 mg) was added and the solution was stirred at room temperature for 12h, the solvents was concentrated to about 5 ml. 3 ml DCM solution of Tetrabutylammonium Triflate (3.0 mmol, 1.18 g) was added and stirred at room temperature for 3 h, Then, diethyl ether was added, giving *cis-2* as yellow solid. Yield: 617 mg, 75%; IR spectrum (ν , cm^{-1}): $\nu = 3051$ (w), 2376 (w), 2353 (w), 2322 (w), 1608 (s), 1554 (m), 1473 (m), 1438 (s), 1257 (s), 1219 (s), 1145 (s), 1064 (m), 1029 (s), 821 (s), 756 (s), 698 (s), 632 (s), 574 (m), 547 (m), 513 (s) cm^{-1} . 1H NMR (400 MHz, CD_2Cl_2 , 298 K) δ (ppm): 8.80 (d, $J = 8$ Hz, 16H, H_b), 8.05 (t, $J = 8$ Hz, 8H, H_g), 7.93 (d, $J = 8$ Hz, 8H, H_k), 7.88 (d, $J = 4$ Hz, 16H, H_c), 7.70 (d, $J = 8$ Hz, 8H, H_n), 7.48 (d, $J = 8$ Hz, 16H, H_a), 7.44 (d, $J = 8$ Hz, 16H, H_p), 7.37 (d, $J = 8$ Hz, 16H, H_{e+f}), 7.26 (d, $J = 4$ Hz, H_o), 7.24 (d, $J = 4$ Hz, 16H, H_d), 7.23 (d, $J = 4$ Hz, 16H, H_l), 7.19 (d, $J = 4$ Hz, 16H, H_m), 7.17 (d, $J = 4$ Hz, 8H, H_i), 7.09 (t, $J = 4$ Hz, 8H, H_j), 6.58 (d, $J = 8$ Hz, 8H, H_i). ESI-MS: 2050.01 [*cis-2* - 5OTf] $^{3+}$.

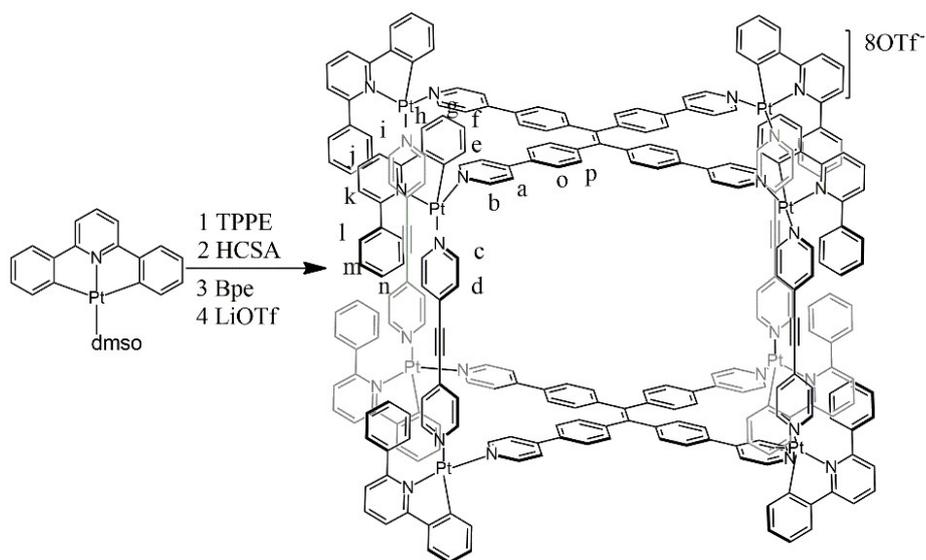


Fig S7. Synthesis of *trans-2*.

3. 1H NMR and 2D COSY spectra

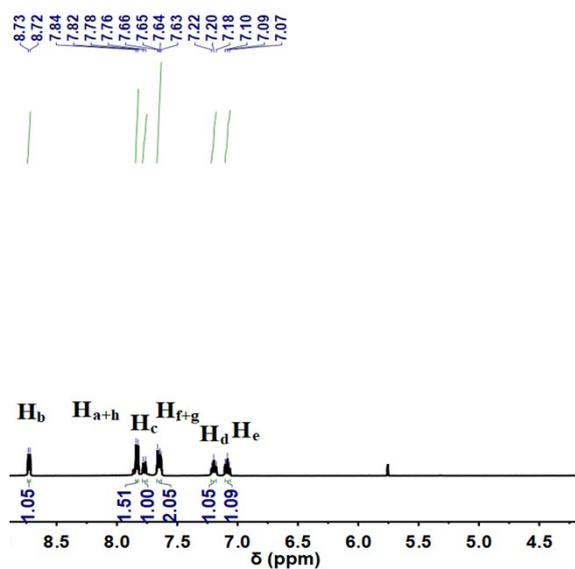


Fig S8. 1H NMR spectra (400 MHz, $DMSO-d_6$, 298 K, TMS as an external standard) of $\{[Pt(Hdpy)]_2(Bpy)\}_2$.

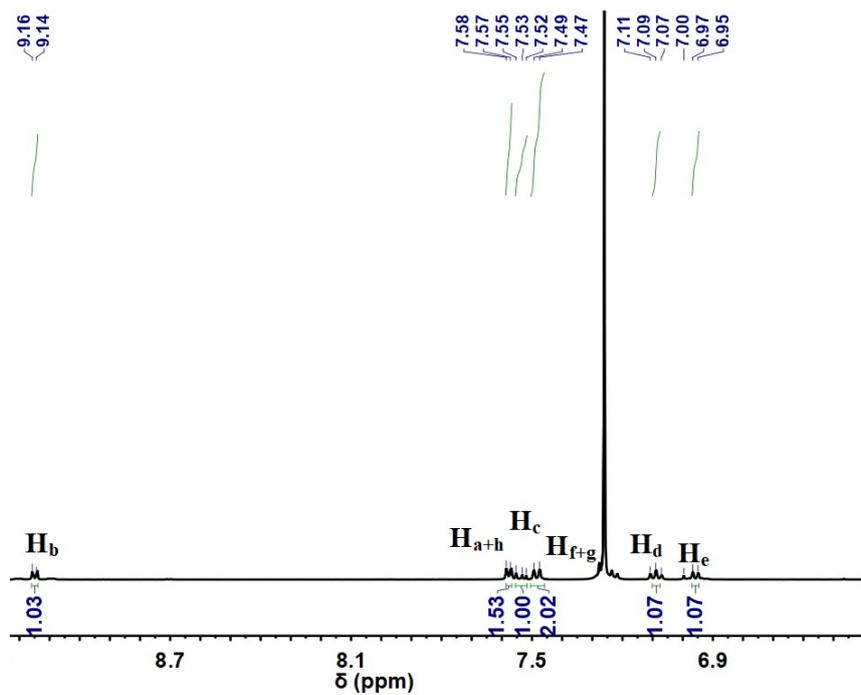


Fig S9. ^1H NMR spectra (400 MHz, CDCl_3 , 298 K, TMS as an external standard) of $\{[\text{Pt}(\text{Hdpy})_2]_2(\text{Bpe})\}$.

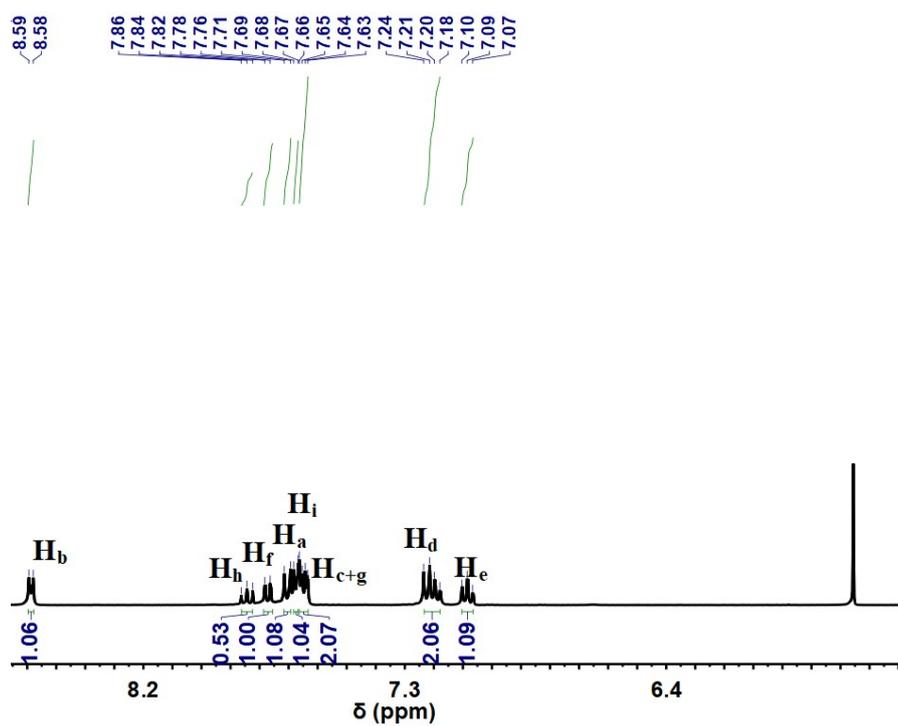


Fig S10. ^1H NMR spectra (400 MHz, DMSO-d_6 , 298 K, TMS as an external standard) of $\{[\text{Pt}(\text{Hdpy})_4](\text{TPPE})\}$.

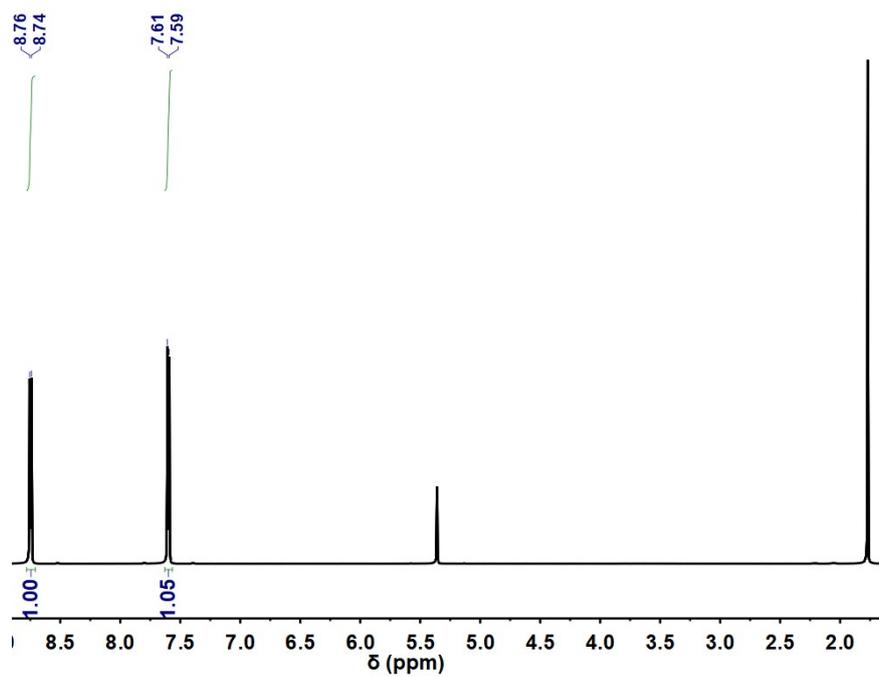


Fig S11. ^1H NMR spectra (400 MHz, CD_2Cl_2 , 298 K, TMS as an external standard) of Bpy.

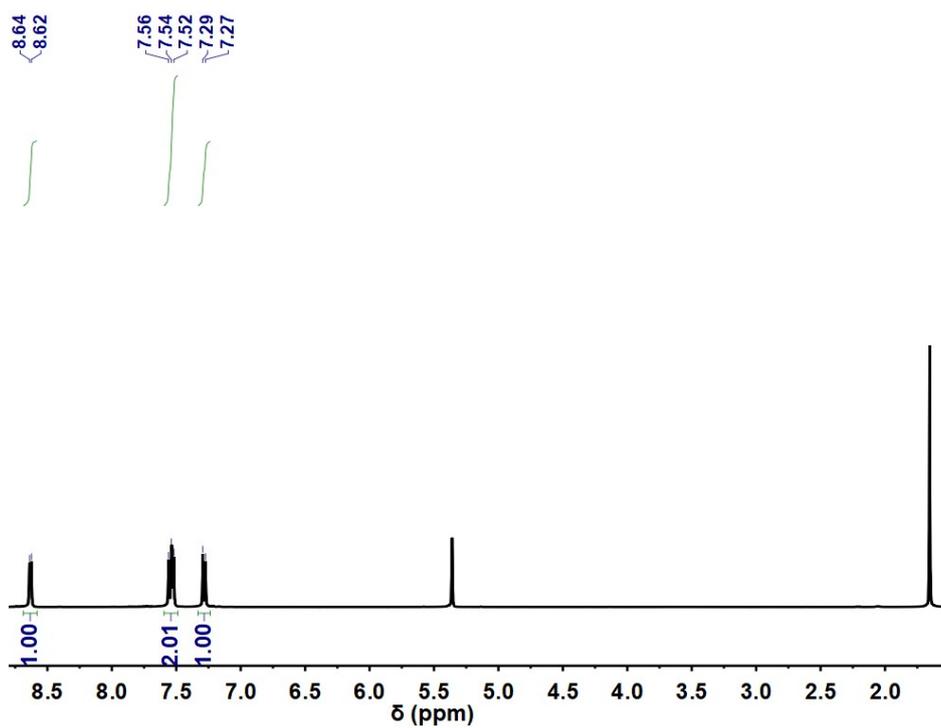


Fig S12. ^1H NMR spectra (400 MHz, CD_2Cl_2 , 298 K, TMS as an external standard) of TPPE.

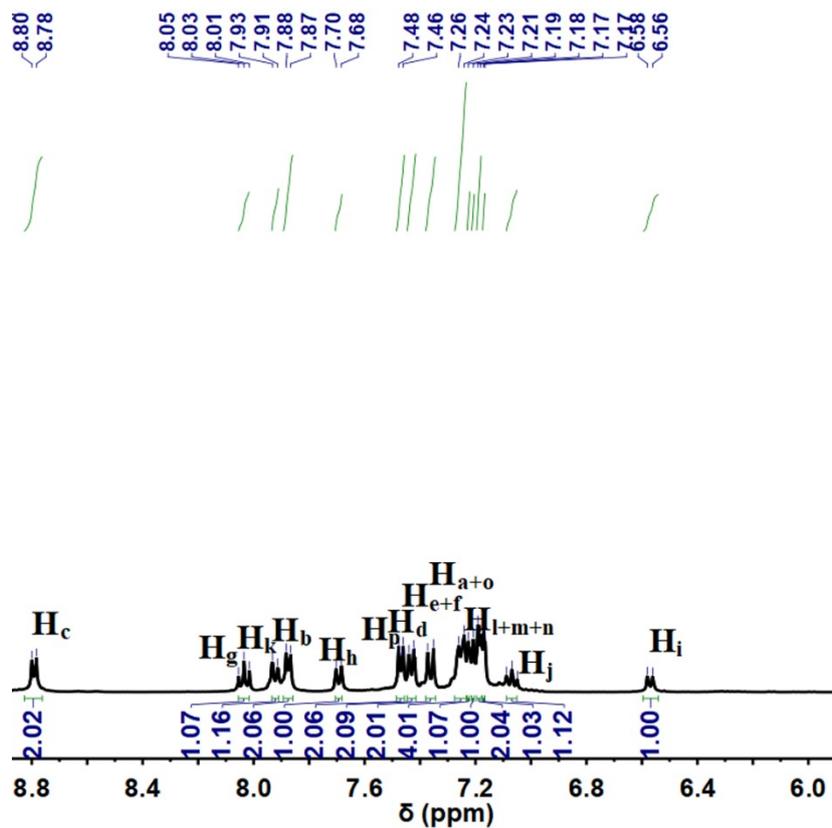


Fig S13. 1H NMR spectra (400 MHz, DMSO- d_6 , 298 K, TMS as an external standard) of *cis*-2.

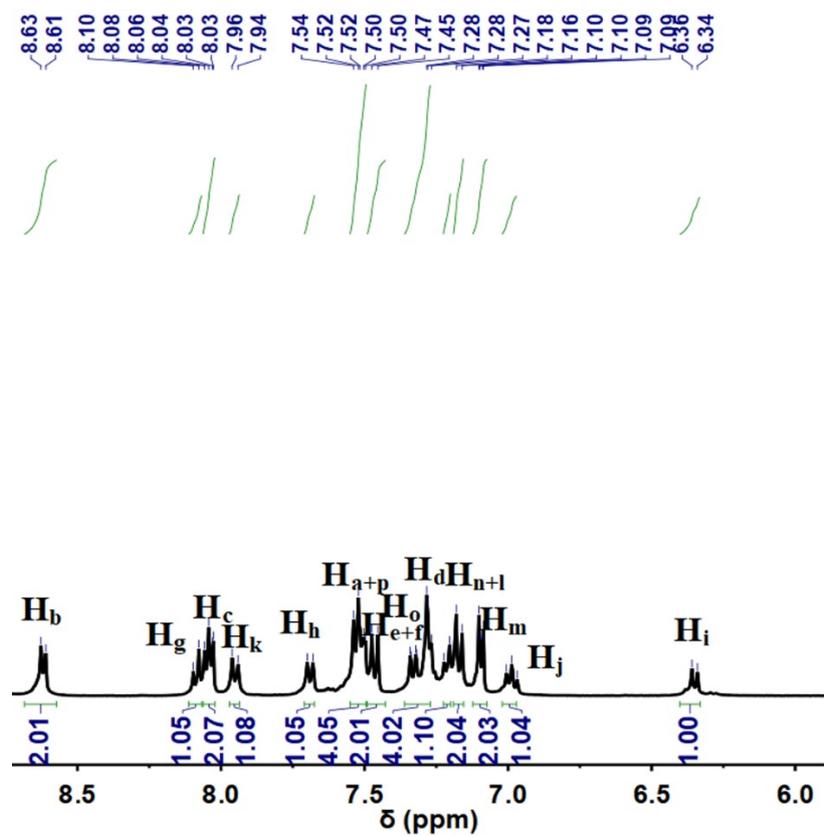


Fig S14. 1H NMR spectra (400 MHz, DMSO- d_6 , 298 K, TMS as an external standard) of *trans*-2.

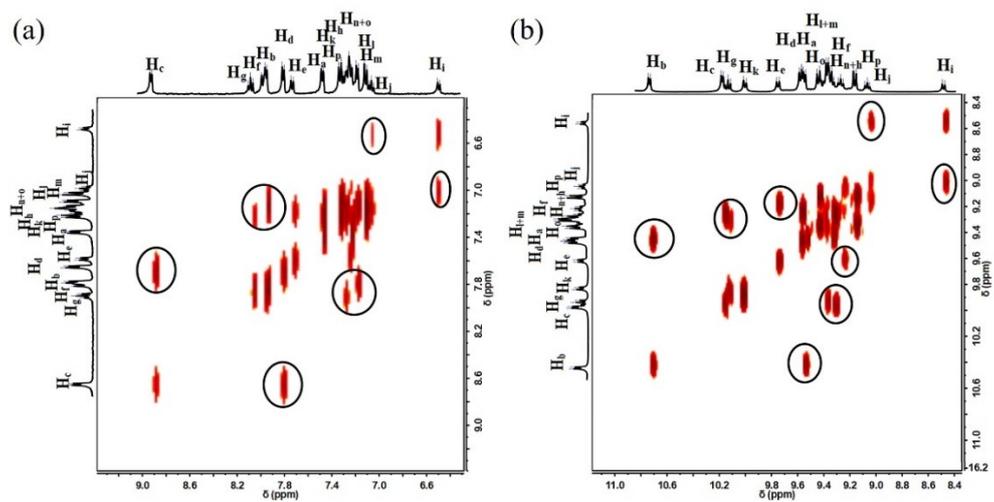


Fig S15. 2D COSY spectra of *cis-1* (a) and *trans-1* (b).

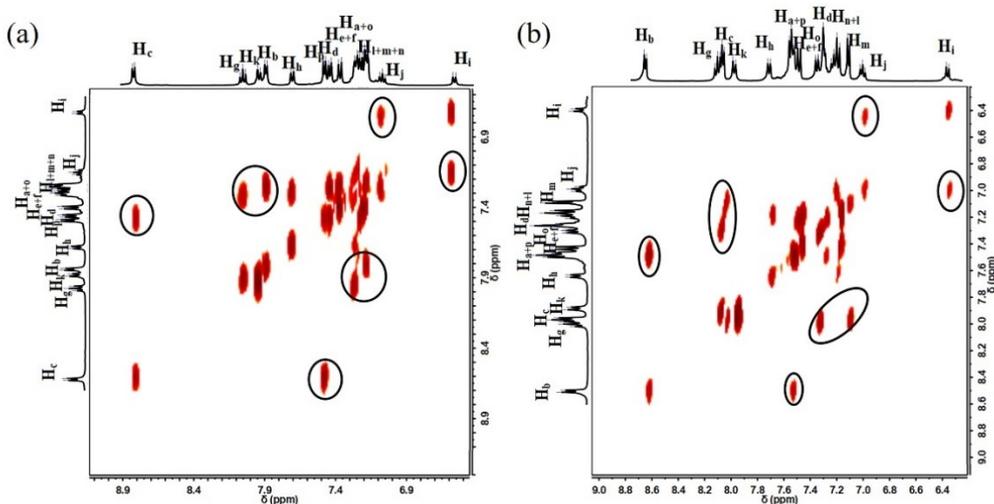


Fig S16. 2D COSY spectra of *cis-2* (a) and *trans-2* (b).

4. ESI-MS spectra of *cis-2* and *trans-2*

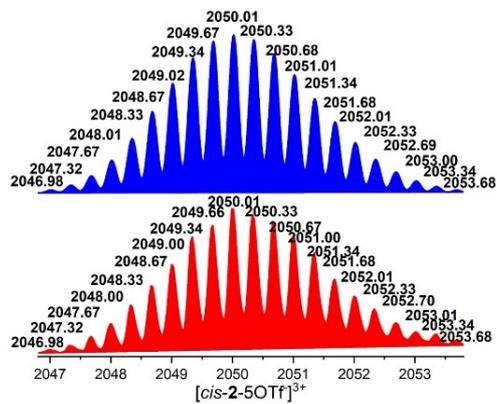


Fig S17. Experimental (below, red) and calculated (above, blue) ESI-MS spectra (3+) of *cis-2*

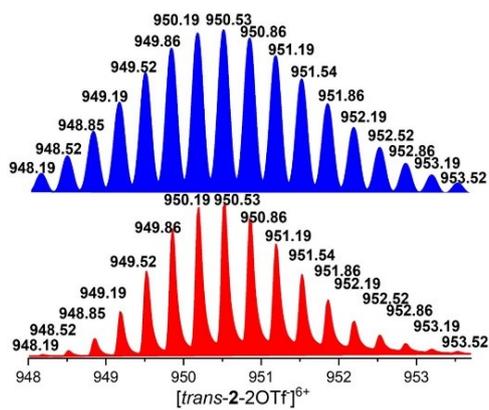


Fig S18. Experimental (below, red) and calculated (above, blue) ESI-MS spectra (6+) of *trans-2*

5. IR spectra of *cis-1*, *trans-1*, *cis-2* and *trans-2*

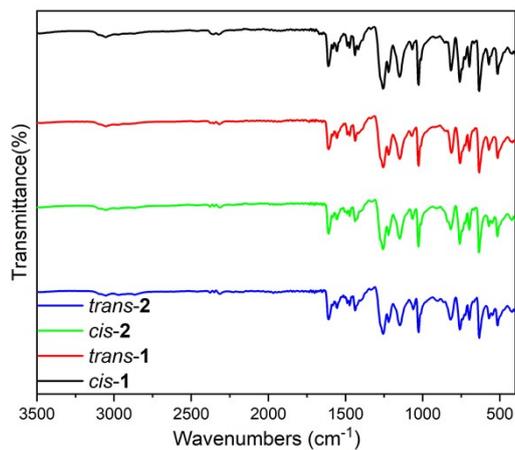


Fig S19. IR spectra of *cis-1*, *trans-1*, *cis-2* and *trans-2*.

6. Absorption spectra of ligands and complexes

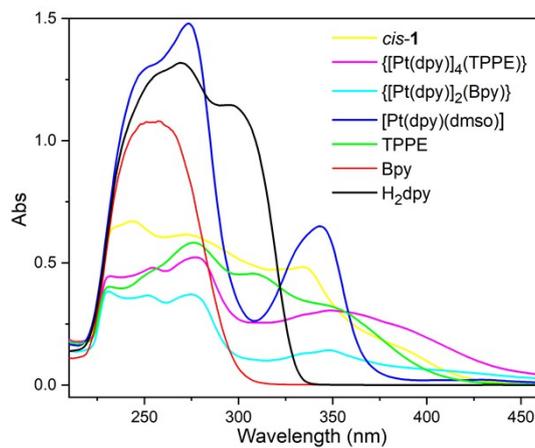


Fig S20. Absorption spectra of *cis-1*, {[Pt(dpy)]₄(TPPE)}, {[Pt(dpy)]₂(Bpy)}, [Pt(dpy)(dmsO)], TPPE, Bpy and H₂dpy in CH₂Cl₂ (C = 20.0 μM).

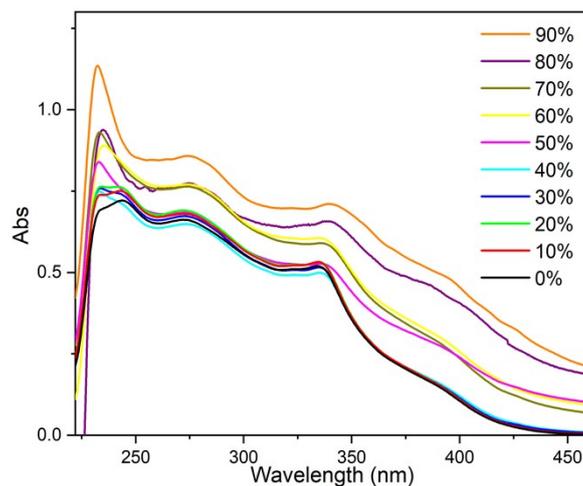


Fig S21. Absorption spectra of *cis-1* versus hexane fraction in CH_2Cl_2 /hexane mixtures ($C = 20.0 \mu\text{M}$).

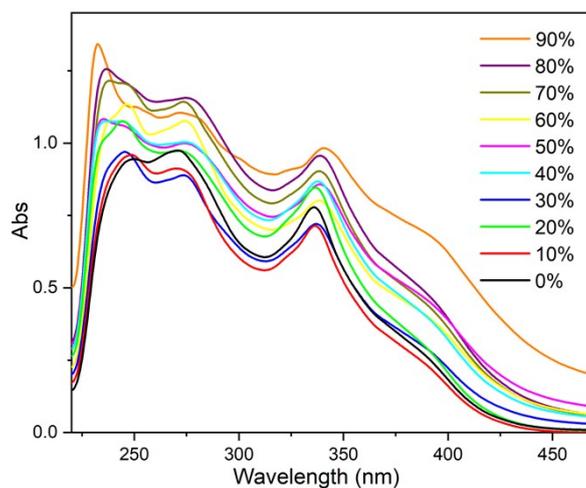


Fig S22. Absorption spectra of *trans-1* versus hexane fraction in CH_2Cl_2 /hexane mixtures ($C = 20.0 \mu\text{M}$).

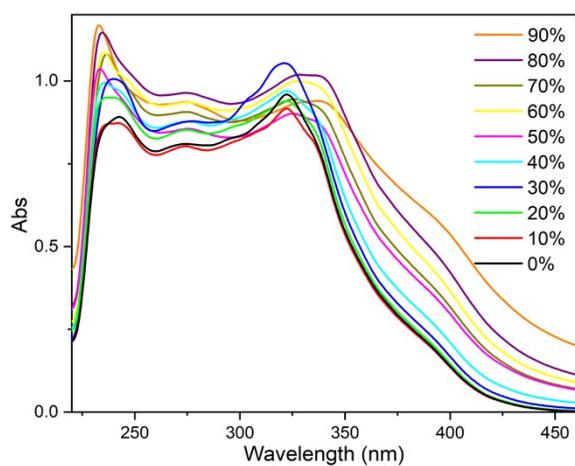


Fig S23. Absorption spectra of *cis-2* versus hexane fraction in CH_2Cl_2 /hexane mixtures ($C = 20.0 \mu\text{M}$).

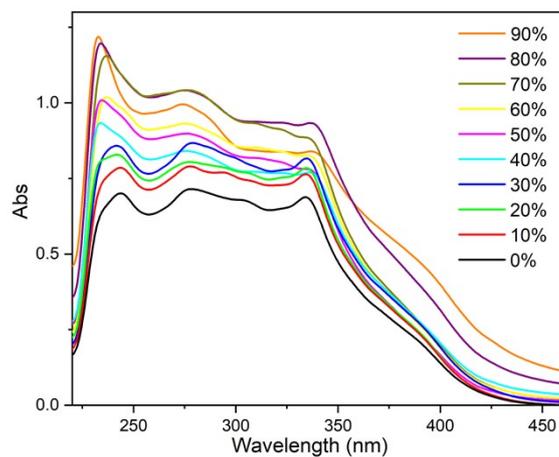


Fig S24. Absorption spectra of *trans-2* versus hexane fraction in CH_2Cl_2 /hexane mixtures ($C = 20.0 \mu\text{M}$).

7. The photoluminescence (PL) emission spectra, Fluorescence quantum yield (Φ_f) and lifetime (τ)

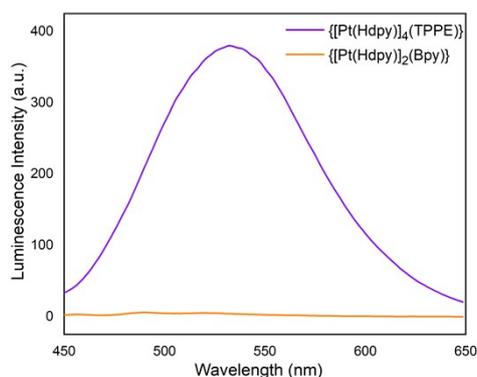


Fig S25. Emission spectra of $[\text{Pt}(\text{Hdpy})_4](\text{TPPE})$ and $[\text{Pt}(\text{Hdpy})_2](\text{Bpy})$ in CH_2Cl_2 ($C = 20.0 \mu\text{M}$).

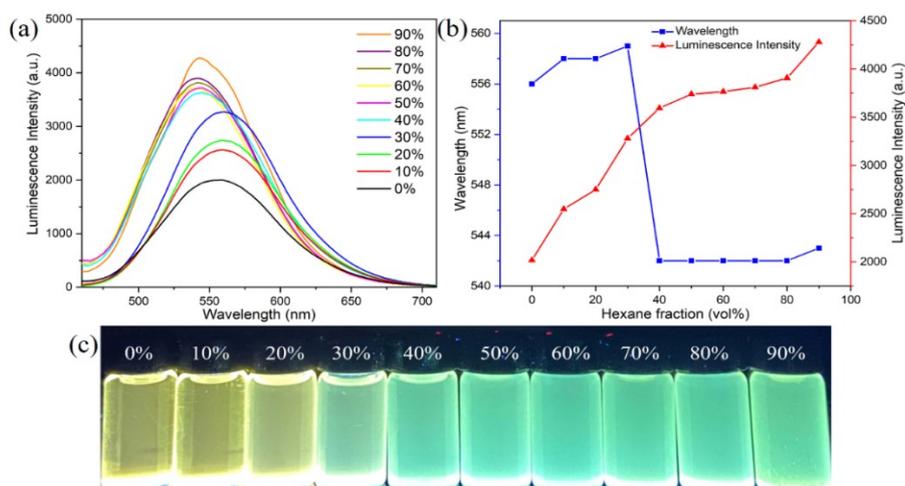


Fig S26. Fluorescence emission spectra and plots of maximum emission intensity and wavelength of *trans-1* versus hexane fraction in CH_2Cl_2 /hexane mixtures ($\lambda_{\text{ex}} = 366 \text{ nm}$, $C = 20.0 \mu\text{M}$) (a and b); The photographs show the CH_2Cl_2 solution of *trans-1* with increasing hexane content from 0% to 90% under 365 nm UV light (c).

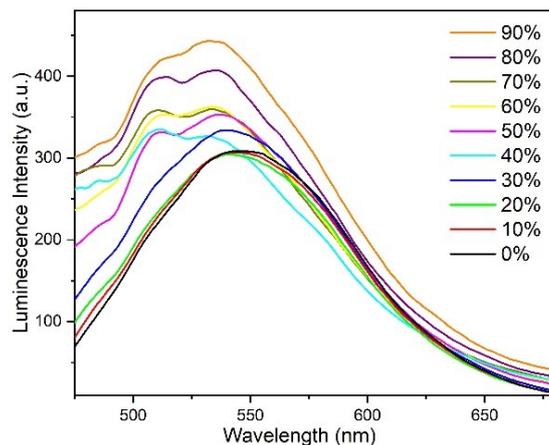


Fig S27. Emission spectra of *cis-2* versus hexane fraction in CH_2Cl_2 /hexane mixtures ($\lambda_{\text{ex}} = 366 \text{ nm}$, $C = 20.0 \mu\text{M}$).

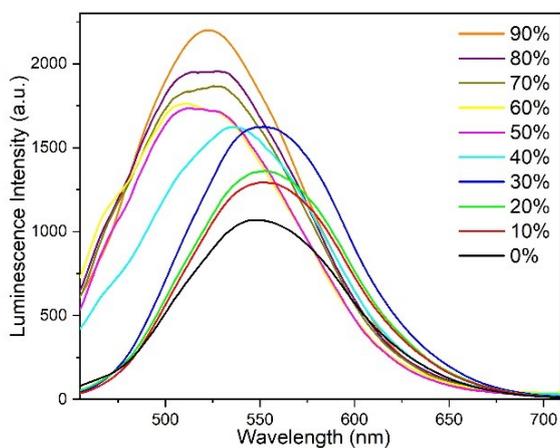


Fig S28. Emission spectra of *trans-2* versus hexane fraction in CH_2Cl_2 /hexane mixtures ($\lambda_{\text{ex}} = 366 \text{ nm}$, $C = 20.0 \mu\text{M}$).

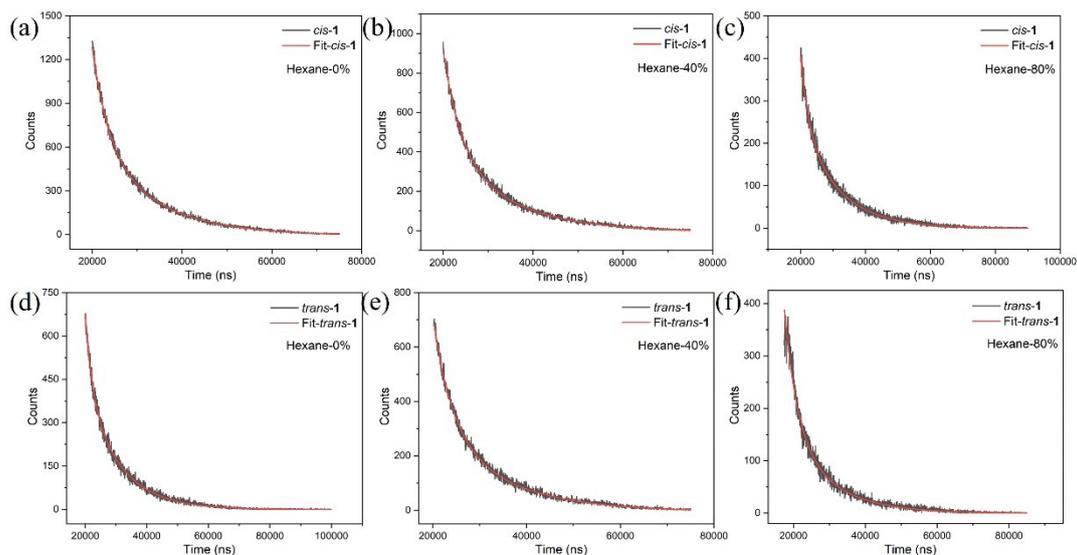


Fig S29. Fluorescence lifetime decay traces of *cis-1* (a-c) and *trans-1* (d-f) versus hexane fraction in CH_2Cl_2 /hexane mixtures ($\lambda_{\text{ex}} = 366 \text{ nm}$, $C = 20.0 \mu\text{M}$).

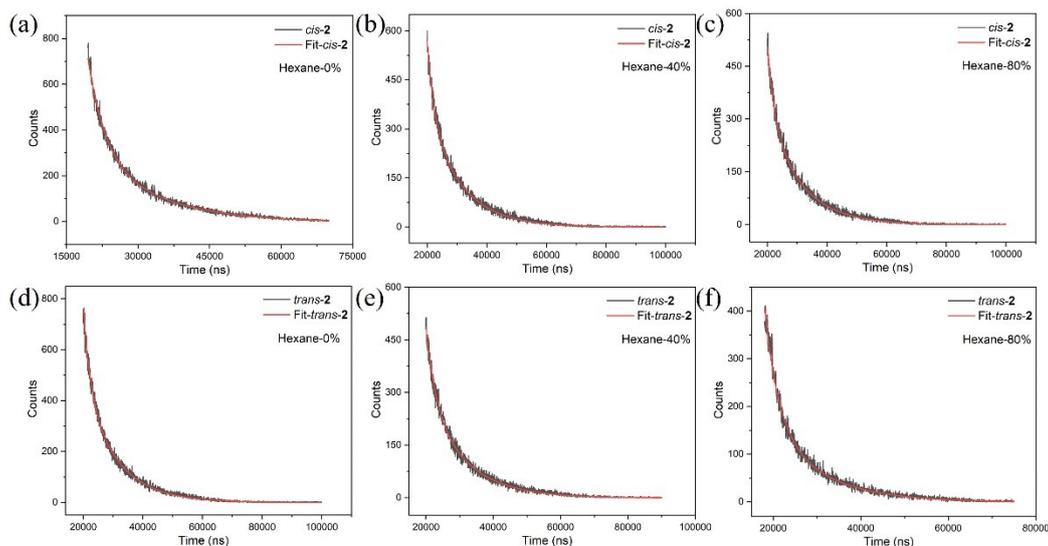


Fig S30. Fluorescence lifetime decay traces of *cis-2* (a-c) and *trans-2* (d-f) versus hexane fraction in CH_2Cl_2 /hexane mixtures ($\lambda_{\text{ex}} = 366 \text{ nm}$, $C = 20.0 \mu\text{M}$).

Table S1 Fluorescence quantum yield (Φ_F) and lifetime (τ) of complexes in CH_2Cl_2 /hexane mixtures.

sample	Hexane%	Φ_F	$\tau_1/\mu\text{s}$	Rel (τ_1)/%	$\tau_2/\mu\text{s}$	Rel (τ_2)/%	χ^2
<i>cis-1</i>	0	0.80	3.77	22.74	14.00	77.26	1.07
	40	1.00	3.86	23.62	14.57	76.38	1.07
	80	1.50	2.54	12.28	11.59	87.72	1.02
<i>trans-1</i>	0	1.90	2.28	11.01	11.07	88.99	1.01
	40	2.30	4.07	25.49	15.00	74.51	1.09
	80	2.80	3.60	29.48	12.32	70.52	1.01
<i>cis-2</i>	0	0.40	3.60	25.14	14.66	74.86	1.09
	40	0.70	2.30	10.99	11.30	89.01	1.03
	80	1.30	2.37	11.28	11.20	88.72	1.00
<i>trans-2</i>	0	1.20	2.52	12.98	11.23	87.02	1.08
	40	1.60	2.87	14.96	11.63	85.04	1.07
	80	2.20	3.15	26.78	12.52	73.22	1.03

8. The scanning electron microscopy (SEM) of *cis-1* and *cis-2* nanostructures

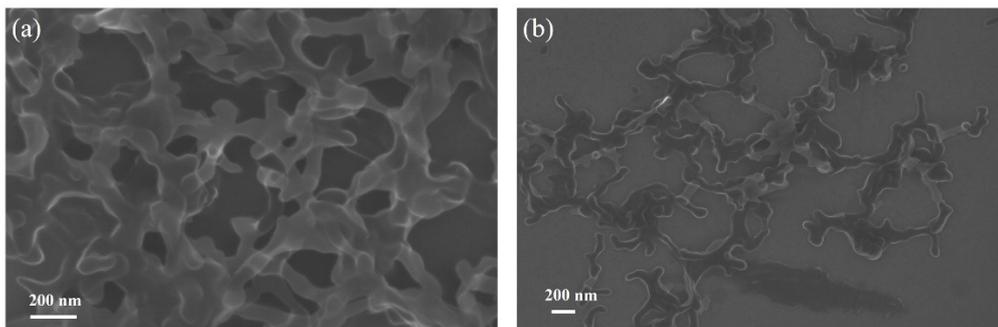


Fig S31. TEM images prepared from a solution of *cis-1* (a) and *cis-2* (b) in 70% hexane/ CH_2Cl_2 mixture.

9. The photoluminescence (PL) emission spectra and CIE coordinate diagram of *cis-2* and *trans-2* in CH_2Cl_2 at various temperatures

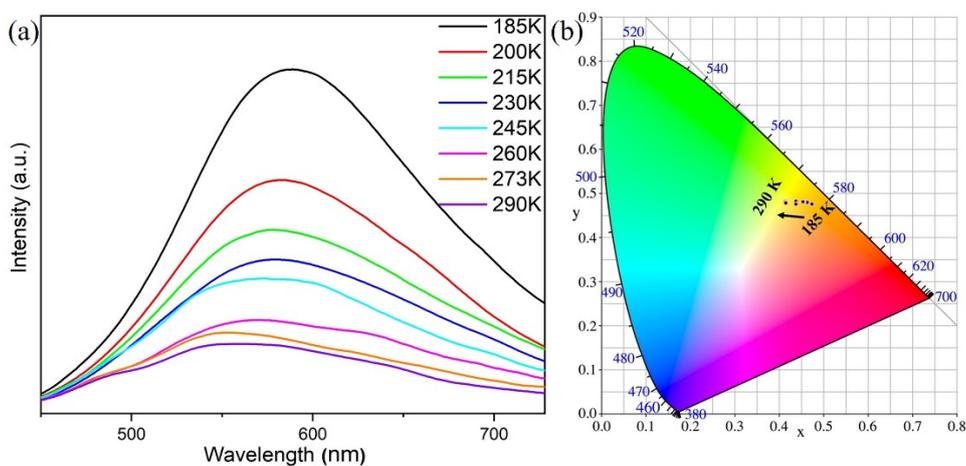


Fig S32. Fluorescence emission spectra (a) and CIE coordinate diagram (b) of *cis-2* in CH_2Cl_2 ($C = 20.0 \mu\text{M}$) at various temperatures.

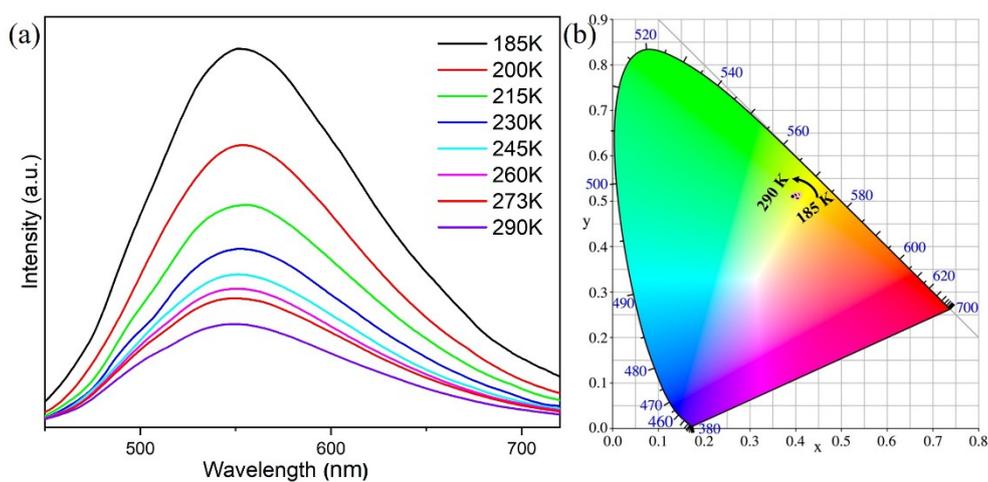


Fig S33. Fluorescence emission spectra (a) and CIE coordinate diagram (b) of *trans-2* in CH_2Cl_2 ($C = 20.0 \mu\text{M}$) at various temperatures.

References

- [1] C. White, A. Yates, P. M. Maitles, *Inorg. Synth.*, 1992, **29**, 228-234.
- [2] J. Bolger, A. Gourdon, E. Ishow, J. P. Launay, *Inorg. Chem.*, 1996, **35**, 2937-2944.