Electronic Supplementary Information (ESI)

Platinadithiolene-conjugated Pyrylium Salt with Strong Intramolecular Donor-Acceptor Interaction

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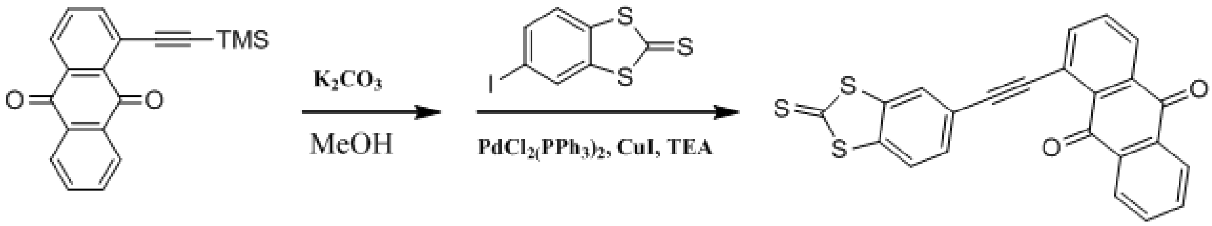
Experimental Section

Synthesis:

1) **1-pdtAq:**



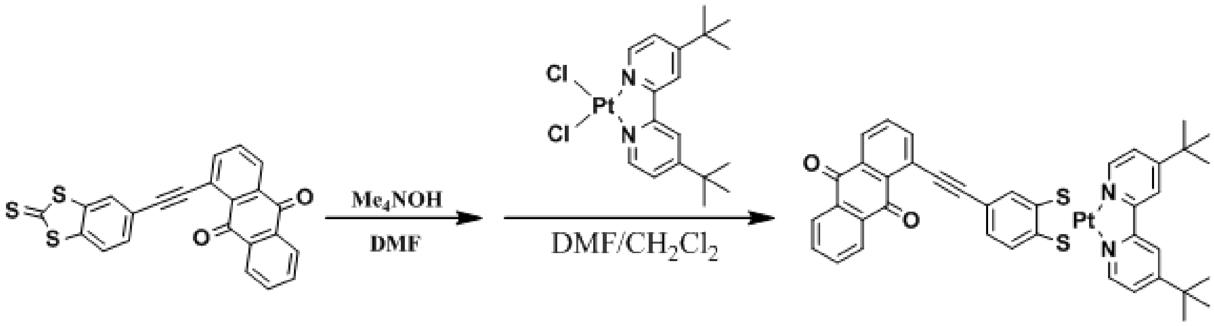
Under N_2, a mixture of 1-((trimethylsilyl)ethynyl)anthraquinone (0.350 g, 1.15 mmol), and K_2CO_3 (0.318 g, 2.31 mmol), in MeOH (40 mL) was stirred for 12 hrs. The solvent was removed under vacuum and added a mixture of 5-iodobenzo[*d*][1,3]dithiole-2-thione (0.357 g, 1.15 mmol) was prepared according to the reported procedure[1,2], bis(triphenylphosphine)palladium(II) dichloride (0.161 g, 0.23 mmol) and cuprous iodide (0.088 g, 0.46 mmol) in triethylamine (50 mL, 358.73 mmol) was refluxed at 90 °C overnight. The color of the reaction mixture was changed from yellow to dark brown. After cooling to room temperature, the solvent was removed under vacuum. The residue was dissolved in chloroform and washed with water and dried with Na_2SO_4. The product was purified by silica gel column chromatography eluted with CH_2Cl_2: hexane = 3 : 1. **1-pdtAq**, was obtained in 40% yield. Anal. Calcd for $C_{23}H_{10}O_2S_3.0.4(H_2O)$: C, 65.50; H, 2.58. Found: C, 65.49; H, 2.81. ^1H NMR ($CDCl_3$ 400 MHz): δ 7.51(d, 1H, J = 8.3 Hz), 7.72 (d, 1H, J = 8.3 Hz), 7.80 (m, 4H), 7.98 (d, 1H, J = 7.8 Hz), 8.31 (d, 1H, J = 6.8 Hz), 8.37 (m, 2H).

References

(1) J. Nakayama, E. Seki, M. Hoshino, *J. Chem. Soc., Perkin Trans. 1*, **1978**, 468 – 471.

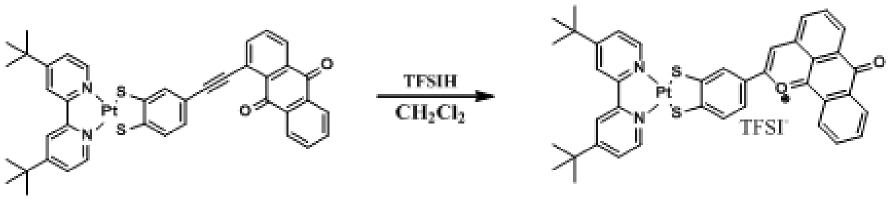
(2) J. Nakayama, H. Sugiura, M. Hoshino, *Tetrahedron Lett*, **1983**, *24*, 2585-2588.

2) **Pt(1-pdtAq)(^{t}Bu$_2$bpy):**



Under N$_2$, a mixture of **1-pdtAq** (0.140 g, 0.34 mmol), and tetramethylammonium hydroxide (1.15 mL, 2.71 mmol), in DMF (25 mL) was stirred for 3 h. The color of the reaction mixture was changed from yellow to dark red. To this reaction a mixture (^{t}Bu$_2$bpy)PtCl$_2$ (0.216 g, 0.41 mmol) in DMF/ CH$_2$Cl$_2$ (15/10 mL) was added and stirred at room temperature for 6 h. The color of the reaction mixture was changed from dark red to violet. The solvent was removed under vacuum. The residue was dissolved in CH$_2$Cl$_2$ and washed with water and dried with Na$_2$SO$_4$. The product was purified by basic Al$_2$O$_3$ column chromatography eluted with CH$_2$Cl$_2$: hexane = 5:1. **Pt(1-pdtAq)(^{t}Bu$_2$bpy)** was obtained in 29% yield. Anal. Calcd for $C_{40}H_{34}N_2O_2PtS_2{\cdot}0.55(CH_2Cl_2)$: C, 55.31; H, 4.02; N, 3.18. Found: C, 55.38; H, 4.14; N, 3.01. HRMS (ESI-TOF): *m/z* = 833.1716 (calcd M$^+$ 833.1713). 1H NMR (400 MHz, CDCl$_3$): δ 7.21(dd, 1H, J = 9.0 Hz, 1.5Hz), 7.44 (d, 1H, J = 8.0 Hz), 7.50 (m, 2H), 7.73 (t, 1H, J = 7.8 Hz), 7.79 (m, 2H), 7.97 (m, 4H), 8.28 (m, 2H), 8.39 (d, 1H, J = 7.6 Hz), 9.17 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$): δ(ppm) 30.3, 35.9, 88.5, 98.2, 115.9, 119.7, 124.8, 125.9, 125.6, 126.7, 126.9, 127.7, 128.1, 131.8, 132.7, 132.8, 132.9, 133.7 134.5, 134.6, 140.3, 148.4, 155.7, 163.0, 183.3.

3) **[Pt(1-pdtPyl)(^{t}Bu$_2$bpy)](TFSI)**:



Under an argon atmosphere, **Pt(1-pdtAq)(^{t}Bu$_2$bpy)** (0.050 g, 0.12 mmol) was dissolved in 10 mL CH_2Cl_2 and stirred. To this was added bis(trifluoromethanesulfone)imide (0.040 g, 1.19 in 3 mL CH_2Cl_2. The color of solution changed from violet to dark red. After stirring for 30 min, 20 mL hexane was added. The mixture was allowed to crystallize overnight. The dark precipitate was filtered off using a membrane filter and washed with hexane. **[Pt(1-pdtPyl)(^{t}Bu$_2$bpy)](TFSI)** was obtained in 85% yield. Anal. Calcd for $C_{42}H_{35}N_3O_6S_4F_6Pt.2(H_2O)$: C, 43.82; H, 3.41; N, 3.65 %. Found: C, 43.86; H, 3.30; N, 3.44 %. HRMS (ESI-TOF): m/z = 834.1794 (calcd M^+ 834.1791).

NMR Measurements and Mass Spectrometry: ^{1}H NMR and ^{13}C spectra of samples in chloroform-d_1 were collected with AL-400 (JEOL) NMR and DRX500 NMR (Bruker) spectrometer, respectively. ESI-TOF mass spectra were recorded with a LCT time-of-flight mass spectrometer (Micromass).

UV-vis-near-IR Spectroscopy in Solution: Samples for UV-vis-near-IR spectroscopy in solution were prepared under an argon atmosphere. UV-vis-NIR spectra were recorded with a V-570 spectrometer (JASCO). Quartz cells with a path length of 0.1 cm were utilized to observe absorption in the UV region.

DFT calculations: The geometries of **1-pdtAq, Pt(1-pdtAq)(^{t}Bu$_2$bpy)** and **[Pt(1-pdtPyl)(^{t}Bu$_2$bpy)]$^+$** were fully optimized using the DFT methods. The three-parametrized Becke-Lee-Yang-Parr (B3LYP) hybrid exchange-correlation functional was employed. The 6-31G** basis set was used for all atoms and LanL2DZ(Hay-Wadt ECP) basis set was used for Pt atom. Based on the optimized structure, the TD-DFT method was applied to calculate the excited states relevant to the absorption spectra of each compound. The solvent effect (CH_2Cl_2) was considered using the PCM model. The present calculations were implemented using the Gaussian03 program package.[1]

References

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian03, Revision C.02*, Gaussian, Inc., Pittsburgh PA, **2003**.

EPR measurements: The spin susceptibility of the samples was measured using a JEOL FA 200. The sample solution was introduced in the sample tube and degassed by three freeze–pump–thaw cycles. Finally, the tube was sealed under vacuum.

Magnetic susceptibility measurements: The magnetic susceptibilities were measured using an MPMS-5S superconducting quantum interference device spectrometer (SQUID) at a field length of 2 T (Quantum Design) in the temperature range of 1.8–300 K. The scan rate of the temperature was fixed to 3.0 K/min and each measurement was performed 30 seconds after the temperature had stabilized. Aluminum foil purchased from Nippaku Co. was used for the sample containers, the magnetic contributions of which were subtracted as background by measuring their individual magnetic susceptibilities at each experiment.

Table S1. Experimental and calculated excitation energies to the lowest excited state for, **[Pt(1-pdtPyl)(^{t}Bu$_2$bpy)]$^+$**

Excitation energy / eV		**Oscillator strength (Calcd.)**	**Assignment (CI Coefficient)**
Exptl.	**Calcd.**		
1.28	1.09	0.0723	177→178 (0.67890)
1.75	1.55	0.1591	176→178 (0.68168)
2.34	2.33	0.5644	174→178 (-0.13730) 177→179 (0.60566) 177→180 (-0.29292)
2.34	2.47	0.0188	174→178 (-0.12093) 177→179 (0.25248) 177→180 (0.60833)
2.82	2.58	0.1571	174→178 (0.62562) 176→179 (-0.15754) 177→180 (0.14954)
2.82	2.72	0.0412	176→179 (0.49118) 176→180 (-0.47889)
2.82	2.85	0.2803	174→178 (0.10019) 176→179 (0.43007) 176→180 (0.47649) 177→181 (-0.11317)
2.82	2.85	0.0019	177→183 (0.67476)
2.82	3.01	0.0100	172→178 (0.34991) 173→178 (0.60335)
2.82	3.10	0.0127	166→178 (0.30580) 168→178 (0.55981) 171→178 (-0.14825) 177→181 (0.16757)
2.82	3.13	0.0819	166→178 (-0.15594) 171→178 (-0.26578) 172→178 (0.11937) 173→181 (-0.11792) 177→181 (0.59362)

Table S1. (continued)

3.65	3.20	0.0071	172→178 (0.58997) 173→178 (-0.33151) 177→181 (-0.14926) 177→182 (0.10373)
3.65	3.21	0.0046	177→182 (0.68469)
3.65	3.22	0.0008	174→183 (0.11068) 175→179 (-0.16224) 175→180 (0.32736) 176→183 (0.55880)
3.65	3.28	0.0029	175→179 (-0.27170) 175→180 (0.52548) 176→183 (-0.33340)
3.65	3.28	0.1332	166→178 (-0.21879) 169→178 (0.31668) 171→178 (0.45715) 177→181 (-0.24321)
3.65	3.39	0.0386	177→184 (0.68016)
3.65	3.43	0.0156	166→178 (0.52041) 169→178 (-0.16596) 171→178 (0.37441)
3.65	3.59	0.0586	175→183 (0.35915) 176→181 (0.53748) 176→182 (0.19154)
3.65	3.67	0.0286	175→183 (-0.24011) 176→182 (0.63299)
3.82	3.81	0.1462	174→179 (0.57775) 176→184 (0.29992) 177→185 (-0.13718)
3.82	3.84	0.0094	177→185 (0.68085)
3.82	3.87	0.0135	165→178 (-0.24011) 174→179 (-0.27840) 174→180 (-0.26442) 176→184 (0.53566)
3.82	3.93	0.0031	165→178 (0.67480) 174→179 (-0.11970)

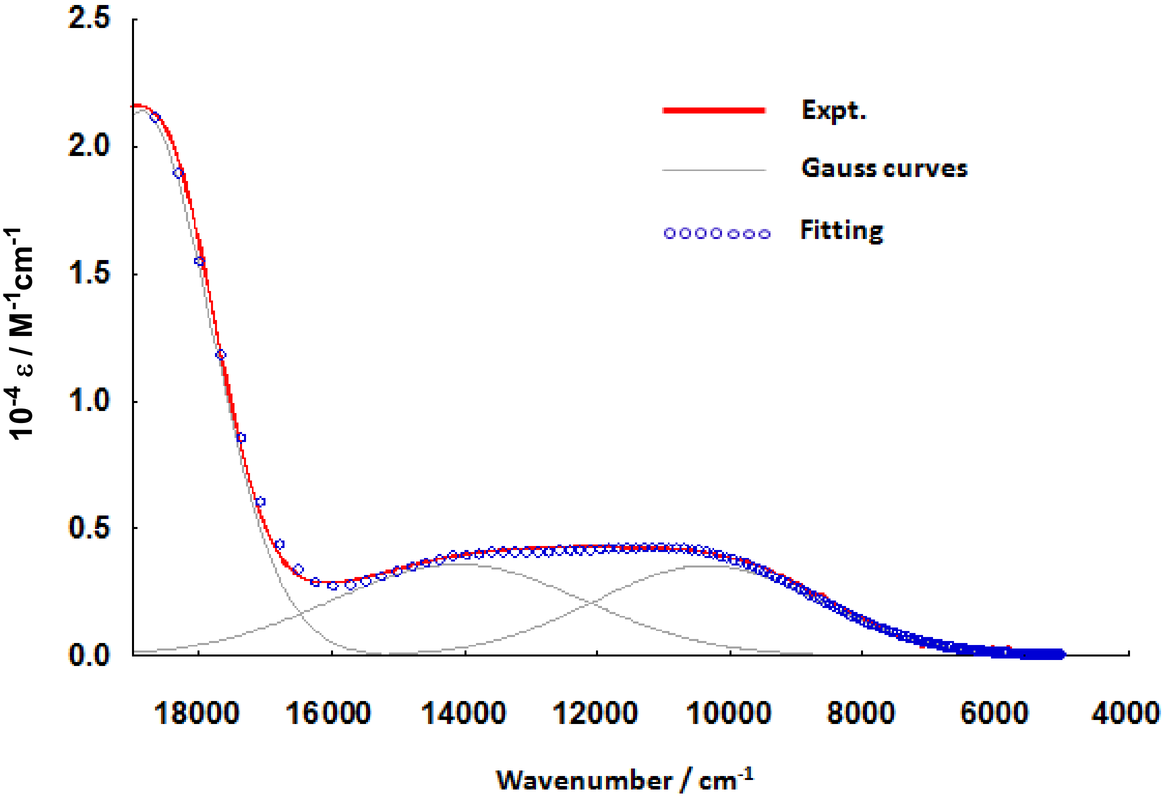


Fig. S1. Deconvolution of the IVCT band for **[Pt(1-pdtPyl)(^{t}Bu$_2$bpy)](TFSI)**.

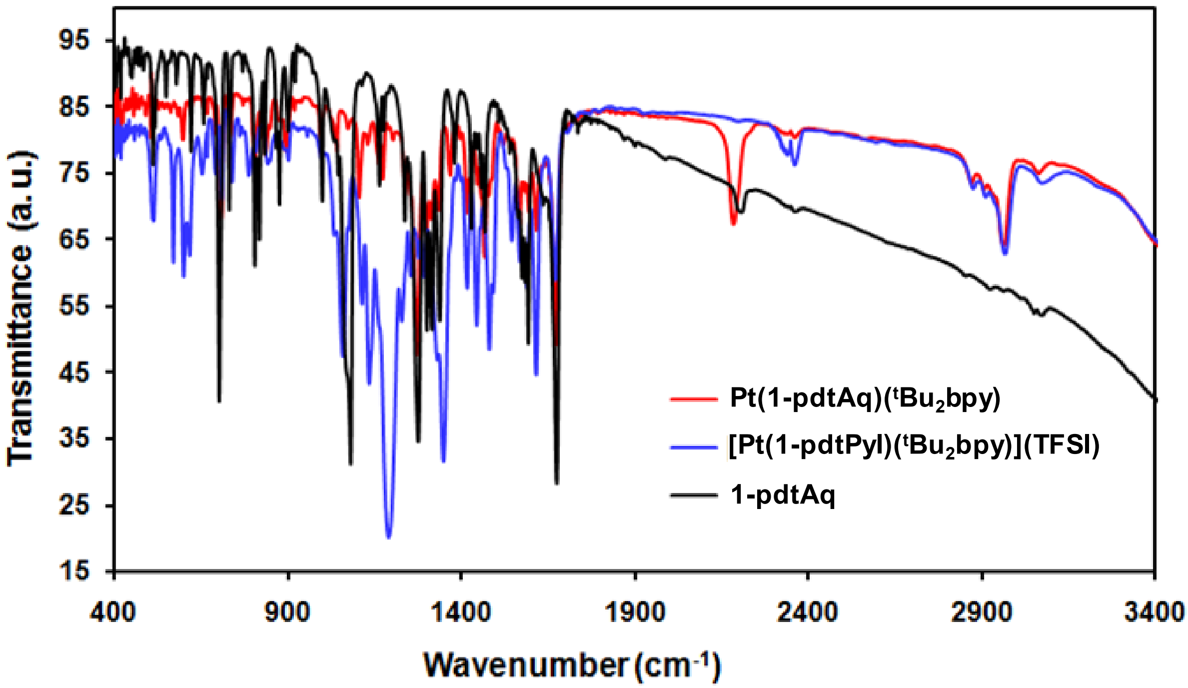


Fig. S2. FT-IR spectra of **1-pdtAq** (black), **Pt(1-pdtAq)(^{t}Bu$_2$bpy)** (red) and **[Pt(1-pdtPyl)(^{t}Bu$_2$bpy)](TFSI)** (blue).

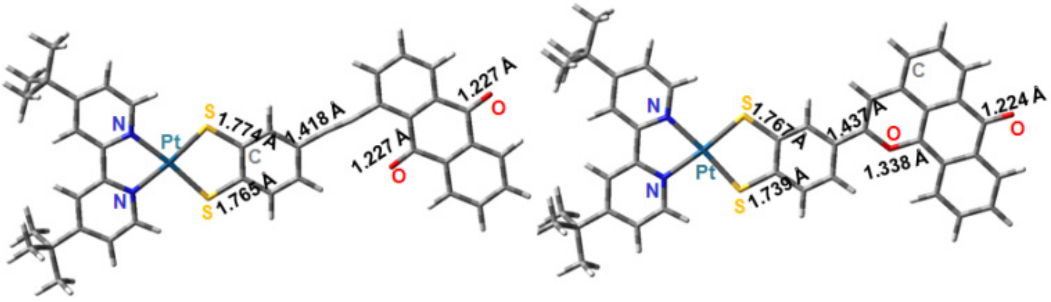


Fig. S3. Optimized structures of **Pt(1-pdtAq)(^{t}Bu$_2$bpy)** (left) and **[Pt(1-pdtPyl)(^{t}Bu$_2$bpy)]$^+$** (right) by the DFT (B3LYP) method.

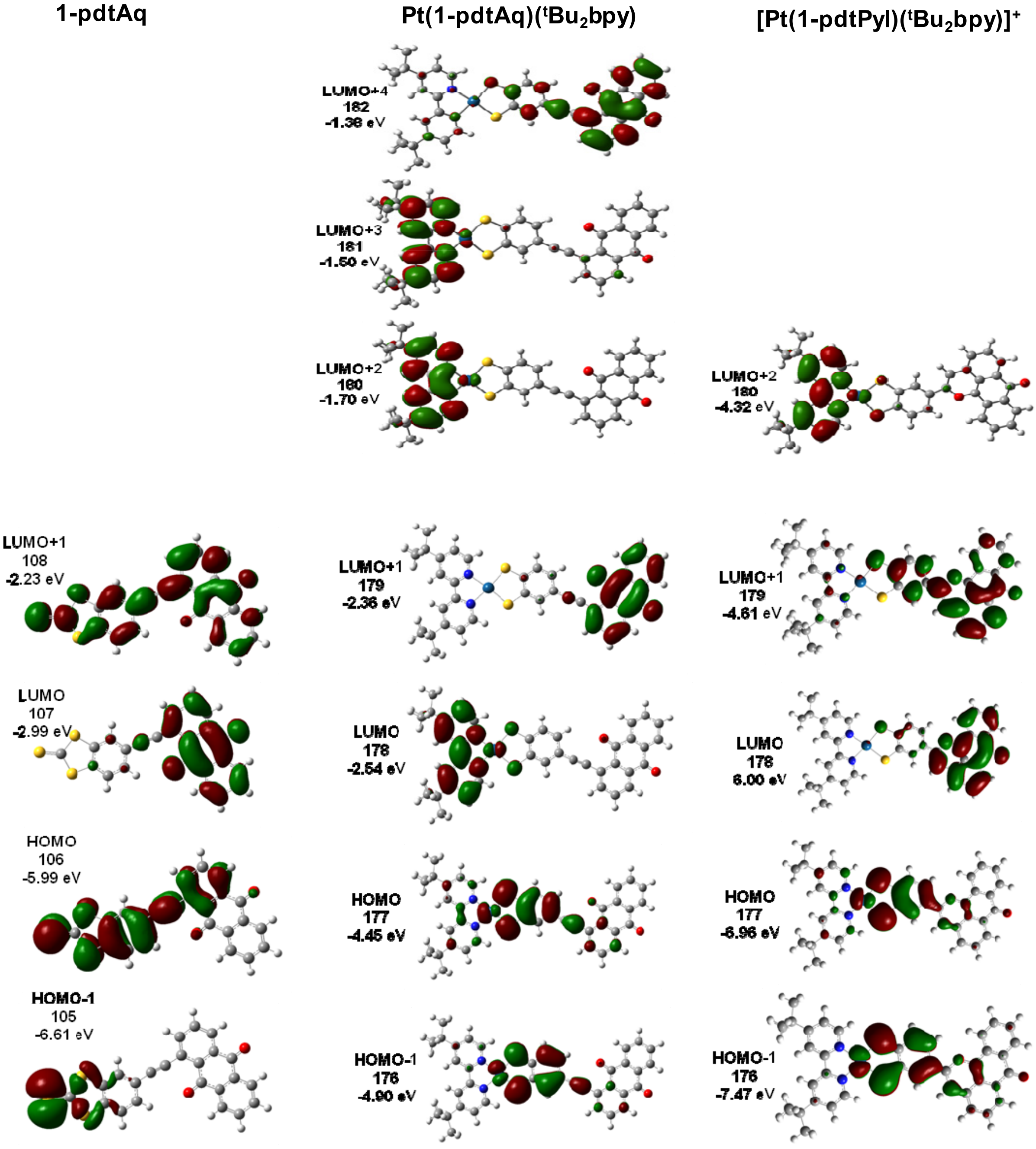


Fig. S4. Molecular orbitals calculated by the DFT method for **1-pdtAq**, **Pt(1-pdtAq)(^{t}Bu$_2$bpy)** and **[Pt(1-pdtPyl)(^{t}Bu$_2$bpy)]$^+$**.

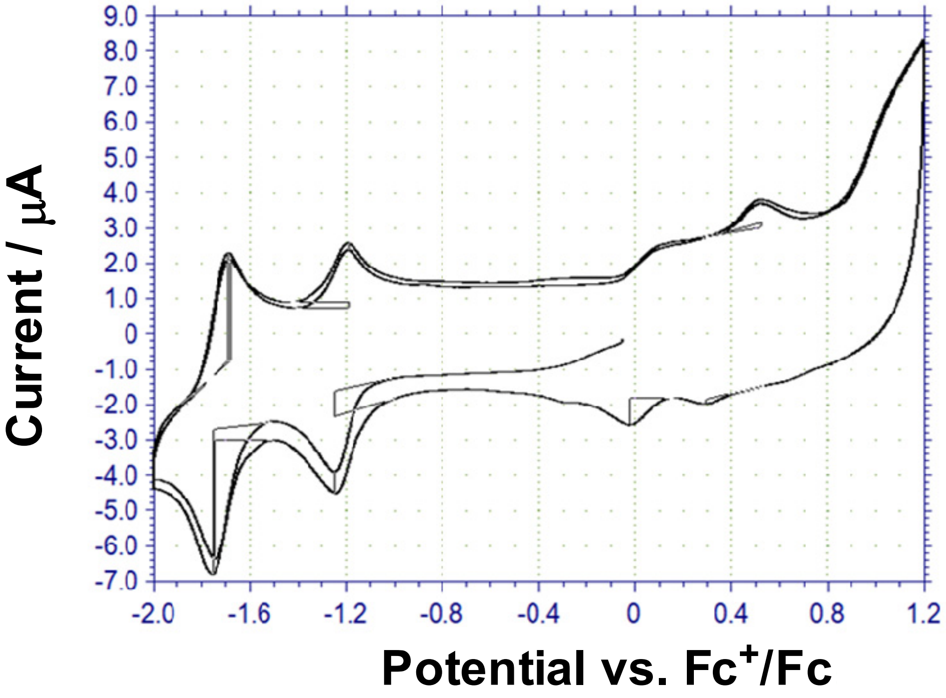


Fig. S5. A cyclic voltammogram of (**Pt(1-pdtAq)(^{t}Bu$_2$bpy)**) at 0.1 Vs^{-1} in 0.1 M Bu_4NClO_4-CH_2Cl_2 at 293 K.

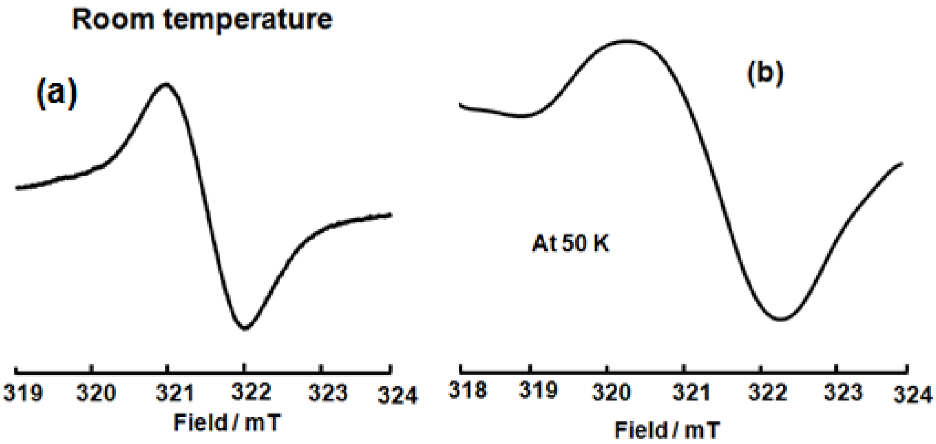


Fig. S6. EPR spectra of **[Pt(1-pdtPyl)(^{t}Bu$_2$bpy)](TFSI)** in the solid state at room temperature (a), and in a CH_2Cl_2 frozen solution (2.0×10^{-4} M) at 50 K (b).

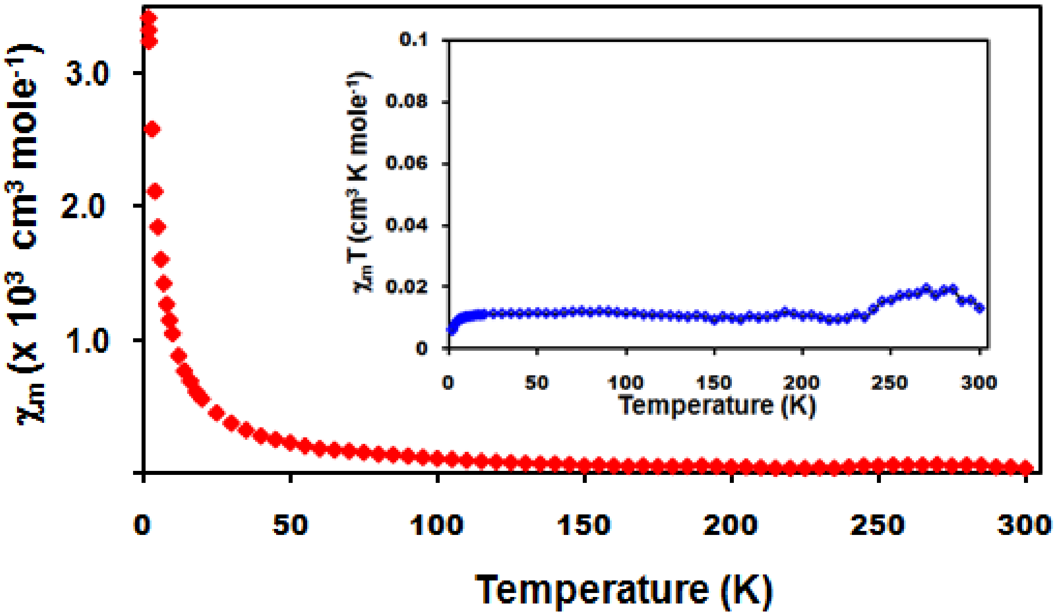


Fig. S7. Magnetic susceptibility **(χ_m)** vs temperature (**T**) plot of **[Pt(1-pdtPyl)(^{t}Bu$_2$bpy)](TFSI)**. Inset shows a χ_m**T** - **T** plot of **[Pt(1-pdtPyl)(^{t}Bu$_2$bpy)](TFSI)**.