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## Electronic Supporting Information

# Highly luminescent imidoylamidinato platinum(II) complexes formed by the coupling of 1*H*-pyrazole-1-carboxamidine with nitriles used as reaction solvents

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## Experimetal section

**Materials**. [$PtCl_2(bpy)_2$] (bpy = 2,2'-bipyridine) was prepared by the literature methods.[1] All other commercially available reagents were used as purchased.

**Physical Measurement and Instrumentation**. The $^1H$ NMR spectra were obtained at 300 MHz with a Varian Gemini 300 spectrometer. UV/Vis spectra were recorded on a Jasco V-560 spectrophotometer at 20°C. Corrected emission spectra were obtained by using a Jasco FP-6500 spectrofluorometer ($\lambda_{ex}$ = 350 nm). Lifetime measurements were conducted by using a streak camera (Hamamatsu C4334) as a detector and the third-harmonic generation of an Nd:YAG Laser (Continuum Minilite) at 355 nm excitation. Emission quantum yields in the solid state were determined by using a Hamamatsu Photonic Absolute PL Quantum Yield Measurement System C9920-02. Powder X-ray diffraction patterns were measured on a Rigaku RINT-2200VL diffractometer using graphite-monochromated Cu K$\alpha$ ($\lambda$ = 1.5418 Å) radiation at 296 K.

**Preparation of Complexes. [Pt(bpy){NH=C(pz)NC(Me)=NH}]$PF_6$ ([1Y]$PF_6$)**. To a suspension of [$PtCl_2$(bpy)] (84 mg, 0.20 mmol) in acetonitrile (10 mL) was added a solution of $AgPF_6$ (125 mg, 0.49 mmol) in acetonitrile (5 mL). The suspension was stirred for 2.5 h at 40 °C under air, and resulted precipitate (AgCl) was filtered off. A solution of 1*H*-pyrazole-1-carboxamidine hydrochloride (NH=C(pz)$NH_2$•HCl) (30 mg, 0.20 mmol) in $CH_3OH$ (5 mL) and $Et_3N$ (80 μl, 0.60 mmol) were added to the filtrate. The solution was refluxed for 24 h and filtered. The filtrate was concentrated, and diethyl ether was added to the solution. The resulted yellow precipitate was collected, washed with diethyl ether, and dried in vacuum. Yield 65 mg (51%). It was recrystallized from $CH_3CN/CH_3OH$. Anal. Calcd for $C_{16}H_{16}F_6N_7PPt$: C, 29.73; H, 2.49; N, 15.17. Found: C, 30.18; H, 2.45; N, 15.22. $^1H$ NMR (300 MHz, DMSO-$d_6$, 25°C, TMS): $\delta$ = 9.26 (d, $J$ = 5.5 Hz, 1H), 8.71 (s, 1H), 8.67 (d, $J$ = 5.5 Hz, 1H), 8.63 (d, $J$ = 8.0 Hz, 2H), 8.44 (d, $J$ = 2.7 Hz, 1H), 8.40 (t, $J$ = 6.1 Hz, 2H), 8.39 (s, 1H), 7.95 (s, 1H), 7.92 (t, $J$ = 6.4 Hz, 1H), 7.82 (t, $J$ = 6.4 Hz, 1H), 6.61 (dd, $J$ = 2.2, 2.0 Hz, 1H), 2.21 ppm (s, 3H). ESIMS: $m/z$ 501.3 $[M - PF_6]^+$. Single crystals suitable for X-ray structural analysis were obtained by recrystallization from benzonitrile.

**[Pt(bpy){NH=C(pz)NC(Et)=NH}]$BF_4$ ([2G]$BF_4$)**. To a suspension of [$PtCl_2$(bpy)] (42 mg, 0.10 mmol) in propionitrile (5 mL) was added a solution of $AgBF_4$ (46 mg, 0.24 mmol) in propionitrile (5 mL). The suspension was stirred for 2 h at 50 °C under air, and resulted precipitate (AgCl) was filtered off. A solution of 1*H*-pyrazole-1-carboxamidine hydrochloride (NH=C(pz)$NH_2$•HCl) (15 mg, 0.10 mmol) in $CH_3OH$ (5 mL) and $Et_3N$ (40 μl, 0.30 mmol) were added to the filtrate. The solution was refluxed for 24 h and filtered. The filtrate was concentrated, and diethyl ether was added to the solution. The resulted yellow precipitate was collected, washed with diethyl ether, and dried in vacuum. Yield 23 mg (37%). It was recrystallized from $CH_3CN/CH_3OH$. Anal. Calcd for $C_{17}H_{18}BF_4N_7PPt$: C, 33.90; H, 3.01; N, 16.28. Found: C, 33.52; H, 3.08; N, 15.96. $^1H$ NMR (300 MHz, DMSO-$d_6$, 25°C, TMS): δ = 9.35 (d, *J* = 5.7 Hz, 1H), 8.82 (d, *J* = 5.9 Hz, 1H), 8.77 (s, 1H), 8.71 (d, *J* = 8.4 Hz, 2H), 8.58 (s, 1H), 8.56 (d, *J* = 2.5 Hz, 1H), 8.46 (t, *J* = 7.9 Hz, 2H), 7.99 (s, 1H), 7.98 (t, *J* = 6.4 Hz, 1H), 7.90 (t, *J* = 6.4 Hz, 1H), 6.63 (dd, *J* = 3.4, 1.7 Hz, 1H), 2.62 (q, *J* = 7.4 Hz, 2H), 1.26 ppm (t, *J* = 7.5 Hz, 3H). ESIMS: *m*/*z* 515.2 $[M - BF_4]^+$. Single crystals suitable for X-ray structural analysis were also obtained by recrystallization from $CH_3CN/CH_3OH$. The recrystallization afforded crystals showing yellow green emission ([**2G**]$BF_4$) as a major component and those showing yellow emission ([**2Y**]$BF_4$) as a minor component.

**[Pt(bpy){NH=C(pz)NC(Ph)=NH}]BF₄ ([3Y]BF₄)**. To a suspension of [$PtCl_2$(bpy)] (168 mg, 0.40 mmol) in benzonitrile (10 mL) was added a solution of $AgBF_4$ (174 mg, 0.89 mmol) in benzonitrile (5 mL). The suspension was stirred for 3 h at 50 °C under air, and resulted precipitate (AgCl) was filtered off. A solution of 1*H*-pyrazole-1-carboxamidine hydrochloride (NH=C(pz)$NH_2$•HCl) (59 mg, 0.40 mmol) in $CH_3OH$ (15 mL) and $Et_3N$ (107 μl, 0.80 mmol) were added to the filtrate. The solution was refluxed for 24 h under air and filtered. The filtrate was concentrated to dryness, and $CH_3OH$ was added to the solution. The resulted precipitate was collected, washed with $CH_3OH$, and dried in vacuum. Yield 120 mg (46%). It was recrystallized from $CH_3CN/CH_3OH$. Anal. Calcd for $C_{21}H_{18}BF_4N_7Pt$: C, 38.79; H, 2.79; N, 15.08. Found: C, 38.69; H, 2.97; N, 15.20. $^1H$ NMR (300 MHz, DMSO-$d_6$, 25°C, TMS): δ = 9.20 (d, *J* = 5.9 Hz, 1H), 9.04 (s, 1H), 8.78 (d, *J* = 5.5 Hz, 1H), 8.69 (s, 1H), 8.65 (d, *J* = 2.7 Hz, 1H), 8.62 (dd, *J* = 8.8, 4.1 Hz, 2H), 8.39 (t, *J* = 7.9 Hz, 2H), 8.14 (d, *J* = 8.3 Hz, 2H), 7.98 (s, 1H), 7.92 (t, *J* = 6.6 Hz, 1H), 7.83 (t, *J* = 6.6 Hz, 1H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 6.65 ppm (dd, *J* = 2.7, 1.5 Hz, 1H). ESIMS: *m*/*z* 563.3 $[M{-}BF_4]^+$. Recrystallization from benzonitrile afforded crystals showing yellow emission ([**3Y**]$BF_4$) as a major component and those showing yellow green emission ([**3G**]$BF_4$•$H_2O$) as a minor component. The crystals of [**3G**]$BF_4$•$H_2O$ quickly lose water molecules in the crystal lattice to exhibit yellow emission.

**X-ray Structural Determinations.** Crystals suitable for X-ray structural analysis were obtained by recrystallization from benzonitrile ([**1Y**]$PF_6$, [**3Y**]$BF_4$ and [**3G**]$BF_4$•$H_2O$) and $CH_3CN$/$CH_3OH$ ([**2G**]$BF_4$), respectively. Intensity data were collected on a Rigaku Saturn724 diffractometer using multi-layer mirror monochromated Mo-Kα (λ = 0.71075 Å) radiation at 94 K. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied.

The crystal structures were solved by direct method (SIR2008).[2] The positional and thermal parameters of non-H atoms were refined anisotropically by the full-matrix least-squares method. The minimized function was $\Sigma w(F_o^2-F_c^2)^2$. Hydrogen atoms were included at calculated positions with fixed displacement parameters. In the final cycle of the refinement, parameter shifts were less than 0.1σ. No correction was made for secondary extinction.

All calculations were performed using the CrystalStructure[3] crystallographic software package except for refinement, which was performed using SHELXL-97.[4] Listings of the selected bond distances and angles are summarized in Tables S1.

**Computational methods**. The geometries of [**1Y**]$^+$, [**2G**]$^+$, [**3Y**]$^+$ and [**3Y**]$^+$ were optimized with the DFT method, where B3LYP functional was employed.[5-7] X-ray structures were used as initial geometries without any geometrical constraints. In these calculations, (541/5511/211) basis sets with ECPs proposed by Christiansen et al were employed for Pt atom.[8-10] For Cl, C, N, and H atoms, usual 6-31G basis sets were used.[11, 12] All calculations were carried out using the Gaussian 03 package.[13] Molecular orbitals with the isovalue of 0.02 were drawn by the Gauss View 4.1.[14]

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Table S1. Selected Bond Lengths [Å] and Angles [°] for [**1Y**]PF$_6$, [**2G**]BF$_4$, [**3Y**]BF$_4$ and [**3G**]BF$_4$•H$_2$O

| | [**1Y**]PF$_6$ | [**2G**]BF$_4$ | [**3Y**]BF$_4$ | [**3G**]BF$_4$•H$_2$O |
|---|---|---|---|---|
| Pt1-N11 | 2.036(5) | 2.031(4) | 2.024(5) | 2.026(4) |
| Pt1-N21 | 2.020(5) | 2.026(4) | 2.021(6) | 2.033(4) |
| Pt1-N1 | 1.976(5) | 1.974(4) | 1.990(6) | 1.983(4) |
| Pt1-N5 | 1.981(5) | 1.994(4) | 1.978(6) | 1.977(4) |
| N1-C2 | 1.285(8) | 1.304(6) | 1.284(9) | 1.294(6) |
| C2-N3 | 1.327(8) | 1.316(6) | 1.325(9) | 1.320(6) |
| N3-C4 | 1.345(7) | 1.345(7) | 1.338(9) | 1.346(6) |
| C4-N5 | 1.306(7) | 1.321(6) | 1.321(9) | 1.309(6) |
| C2-N31 | 1.421(7) | 1.413(7) | 1.398(9) | 1.420(6) |
| C4-C6/C41 | 1.497(8) | 1.496(7) | 1.486(10) | 1.497(7) |
| Pt1•••Pt1’ | 3.509(2)<br>3.558(2) | 4.051(2)<br>4.353(3) | 3.7147(7)<br>4.7935(9) | 4.3970(8)<br>4.8758(9) |
| | | | | |
| N11-Pt1-N21 | 79.89(18) | 80.15(15) | 80.0(3) | 80.35(14) |
| N11-Pt1-N5 | 98.05(18) | 98.38(15) | 97.3(3) | 96.00(15) |
| N21-Pt1-N1 | 95.61(19) | 94.91(16) | 96.8(3) | 96.73(15) |
| N1-Pt1-N5 | 86.45(19) | 86.57(16) | 86.0(3) | 86.89(16) |
| Pt1-N1-C2 | 126.7(4) | 126.9(4) | 128.7(5) | 125.8(4) |
| N1-C2-N3 | 130.8(5) | 115.8(4) | 127.9(6) | 130.9(4) |
| C2-N3-C4 | 120.5(5) | 121.6(4) | 122.1(6) | 121.4(4) |
| N3-C4-N5 | 126.0(6) | 125.7(4) | 126.5(6) | 125.2(4) |
| C4-N5-Pt1 | 129.5(4) | 128.9(4) | 128.6(5) | 129.6(3) |

Table S2. Excitation Energies of $[\mathrm{Pt(bpy)\{NH{=}C(pz)NC(Me){=}NH\}}]^+$ by the TD-B3LYP method

|  | Excitation Energy (eV) | Excitation Energy (nm) | Oscillator Strength | Contribution (%) |
|---|---|---|---|---|
| R=Me | 2.73 | 454 | 0.1214 | HOMO → LUMO 45 % |
|  | 4.07 | 304 | 0.0961 | HOMO-1 → LUMO+2 44 % |
| R=Et | 2.72 | 455 | 0.1255 | HOMO → LUMO 45 % |
|  | 4.08 | 304 | 0.0961 | HOMO-1 → LUMO+2 44 % |
| R=Ph | 2.71 | 458 | 0.1205 | HOMO → LUMO 45 % |
|  | 3.96 | 313 | 0.1217 | HOMO-1 → LUMO+2 43 % |

Table S3. Emission energies (eV) of $[\mathrm{Pt(bpy)\{NH{=}C(pz)NC(R){=}NH\}}]^+$ (R = Me, Et, Ph) by the B3LYP method

|  | B3LYP | exp. |  |
|---|---|---|---|
|  |  | unground | ground |
| R = Me | 2.19 | 2.21 (Type I, [**1Y**]$PF_6$) | 2.08 |
| R = Et | 2.19 | 2.13 (Type I, [**2Y**]$BF_4$) | — |
|  |  | 2.50 (Type II, [**2G**]$BF_4$) | 2.13 |
| R = Ph | 2.19 | 2.25 (Type I, [**3Y**]$BF_4$) | 2.12 |
|  |  | 2.49 (Type II, [**3G**]$BF_4$•$H_2O$) | — |

Table S4. Orbital Composition Percentages of Selected Orbitals in [Pt(bpy){NH=C(pz)NC(R)=NH}]$^+$ (R = Me, Et, Ph) by the B3LYP method

| | HOMO-1 | | | HOMO | | |
|---|---|---|---|---|---|---|
| | Pt | bpy | {NH=C(pz)NC(R)=NH} | Pt | bpy | {NH=C(pz)NC(R)=NH} |
| R = Me | 13 | 2 | 85 | 25 | 7 | 68 |
| R = Et | 13 | 2 | 85 | 25 | 7 | 68 |
| R = Ph | 19 | 3 | 79 | 23 | 7 | 70 |

| | LUMO | | | LUMO+1 | | | LUMO+2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Pt | bpy | {NH=C(pz)NC(R)=NH} | Pt | bpy | {NH=C(pz)NC(R)=NH} | Pt | bpy | {NH=C(pz)NC(R)=NH} |
| R = Me | 4 | 94 | 2 | 1 | 99 | 0 | 1 | 96 | 3 |
| R = Et | 4 | 94 | 2 | 1 | 99 | 0 | 1 | 96 | 3 |
| R = Ph | 4 | 94 | 2 | 1 | 99 | 0 | 0 | 93 | 7 |

Table S5. Selected bond lengths (Å) of $[Pt(bpy)\{NH{=}C(pz)NC(R){=}NH\}]^+$ (R = Me, Et, Ph). The values in parentheses are the bond lengths of X-ray crystal structures

| | R = Me | | R = Et | | R = Ph | |
|---|---|---|---|---|---|---|
| | Singlet | Triplet | Singlet | Triplet | Singlet | Triplet |
| Pt–N1 | 1.991 (1.976) | 1.968 | 1.991 (1.974) | 1.968 | 1.990 (1.983) | 1.965 |
| Pt–N5 | 2.003 (1.982) | 2.026 | 2.003 (1.994) | 2.025 | 2.001 (1.977) | 2.025 |
| Pt–N11 | 2.065 (2.036) | 2.000 | 2.067 (2.031) | 2.000 | 2.065 (2.026) | 2.004 |
| Pt–N21 | 2.066 (2.019) | 2.059 | 2.067 (2.026) | 2.059 | 2.065 (2.033) | 2.058 |
| N1–C2 | 1.320 (1.285) | 1.344 | 1.320 (1.304) | 1.343 | 1.320 (1.294) | 1.344 |
| C2–N3 | 1.331 (1.327) | 1.319 | 1.331 (1.316) | 1.319 | 1.330 (1.320) | 1.316 |
| N3–C4 | 1.335 (1.344) | 1.352 | 1.336 (1.344) | 1.352 | 1.338 (1.346) | 1.356 |
| C4–N5 | 1.329 (1.305) | 1.317 | 1.328 (1.320) | 1.318 | 1.330 (1.309) | 1.322 |
| N11–C12 | 1.366 (1.349) | 1.423 | 1.366 (1.368) | 1.422 | 1.366 (1.365) | 1.422 |
| C12–C22 | 1.472 (1.480) | 1.419 | 1.472 (1.466) | 1.419 | 1.472 (1.471) | 1.418 |
| C22–N21 | 1.365 (1.351) | 1.391 | 1.365 (1.359) | 1.391 | 1.365 (1.359) | 1.391 |
| N11–C16 | 1.348 (1.350) | 1.373 | 1.348 (1.344) | 1.373 | 1.348 (1.341) | 1.372 |
| C16–C15 | 1.390 (1.392) | 1.366 | 1.390 (1.380) | 1.366 | 1.390 (1.381) | 1.366 |
| C15–C14 | 1.396 (1.363) | 1.437 | 1.396 (1.388) | 1.437 | 1.396 (1.393) | 1.436 |
| C14–C13 | 1.392 (1.374) | 1.373 | 1.392 (1.389) | 1.373 | 1.392 (1.368) | 1.373 |
| C13–C12 | 1.399 (1.377) | 1.418 | 1.399 (1.387) | 1.418 | 1.399 (1.380) | 1.418 |
| N21–C26 | 1.348 (1.348) | 1.352 | 1.348 (1.342) | 1.352 | 1.348 (1.346) | 1.353 |
| C26–C25 | 1.391 (1.372) | 1.383 | 1.390 (1.368) | 1.383 | 1.390 (1.377) | 1.383 |
| C25–C24 | 1.395 (1.381) | 1.413 | 1.395 (1.376) | 1.414 | 1.395 (1.374) | 1.414 |
| C24–C23 | 1.393 (1.380) | 1.379 | 1.392 (1.377) | 1.379 | 1.392 (1.383) | 1.379 |
| C23–C22 | 1.399 (1.377) | 1.420 | 1.399 (1.381) | 1.420 | 1.399 (1.388) | 1.420 |

Table S6. Optimized Geometries of [Pt(bpy){NH=C(pz)NC(Me)=NH}]$^+$ by the B3LYP method

| | Singlet | | | | Triplet | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| Pt | 0.285252 | -0.305602 | -0.006770 | Pt | 0.292571 | -0.304394 | 0.072012 |
| N | -1.580402 | 0.387954 | 0.032194 | N | -1.551516 | 0.383215 | 0.067569 |
| N | -2.863301 | -1.639633 | -0.017819 | N | -2.854038 | -1.635570 | 0.059432 |
| N | -0.536735 | -2.131748 | 0.047499 | N | -0.541482 | -2.145661 | 0.201788 |
| N | 2.266404 | -0.886629 | -0.035606 | N | 2.190817 | -0.895120 | -0.145014 |
| N | 1.225897 | 1.533143 | -0.032205 | N | 1.213972 | 1.536389 | 0.088510 |
| N | -3.888597 | 0.429461 | -0.001066 | N | -3.855521 | 0.434288 | -0.122681 |
| N | -3.826322 | 1.789750 | 0.017253 | N | -3.757281 | 1.797194 | -0.187171 |
| C | -2.694213 | -0.319653 | 0.002454 | C | -2.689545 | -0.328125 | 0.003752 |
| C | -1.820669 | -2.472596 | 0.027863 | C | -1.813665 | -2.487497 | 0.197762 |
| C | -2.178312 | -3.937818 | 0.062765 | C | -2.201425 | -3.932465 | 0.353877 |
| C | 3.170077 | 0.135204 | 0.035937 | C | 3.144038 | 0.158707 | -0.078292 |
| C | 4.544854 | -0.121564 | 0.071216 | C | 4.524975 | -0.161910 | -0.111950 |
| C | 5.007465 | -1.433646 | 0.019864 | C | 4.942314 | -1.460780 | -0.266207 |
| C | 4.076741 | -2.469134 | -0.077656 | C | 3.962966 | -2.503484 | -0.405755 |
| C | 2.723723 | -2.152562 | -0.103496 | C | 2.637889 | -2.178046 | -0.341313 |
| C | 2.588482 | 1.487502 | 0.039491 | C | 2.600715 | 1.466048 | 0.010936 |
| C | 3.346701 | 2.661981 | 0.082108 | C | 3.356597 | 2.667846 | 0.025342 |
| C | 2.709274 | 3.899420 | 0.039934 | C | 2.725844 | 3.890624 | 0.122751 |
| C | 1.317559 | 3.934128 | -0.053951 | C | 1.315798 | 3.935527 | 0.210030 |
| C | 0.616082 | 2.733976 | -0.087621 | C | 0.613426 | 2.743944 | 0.188056 |
| C | -5.092222 | 2.182754 | 0.012681 | C | -5.006302 | 2.215638 | -0.296369 |
| C | -5.990587 | 1.078337 | -0.009606 | C | -5.933664 | 1.129375 | -0.304092 |
| C | -5.182939 | -0.034348 | -0.017234 | C | -5.161456 | 0.000028 | -0.190144 |
| H | -1.799155 | 1.387085 | 0.073645 | H | -1.770116 | 1.385297 | -0.008974 |
| H | 0.073435 | -2.941819 | 0.124339 | H | 0.078448 | -2.938519 | 0.363095 |
| H | -2.790039 | -4.141824 | 0.954756 | H | -2.840484 | -4.042540 | 1.243580 |
| H | -1.296322 | -4.593577 | 0.071858 | H | -1.332426 | -4.597911 | 0.445288 |
| H | -2.797887 | -4.178824 | -0.814115 | H | -2.805195 | -4.238260 | -0.514285 |
| H | 5.253439 | 0.702653 | 0.134313 | H | 5.257153 | 0.639598 | -0.017957 |
| H | 6.077761 | -1.643021 | 0.047635 | H | 6.005749 | -1.700737 | -0.292893 |
| H | 4.385903 | -3.512992 | -0.134983 | H | 4.260446 | -3.539268 | -0.564883 |
| H | 1.976317 | -2.938775 | -0.191333 | H | 1.871837 | -2.943133 | -0.463586 |
| H | 4.432508 | 2.611276 | 0.144421 | H | 4.442154 | 2.615843 | -0.048942 |
| H | 3.291786 | 4.821257 | 0.073507 | H | 3.310483 | 4.811582 | 0.131263 |
| H | 0.770166 | 4.875697 | -0.101453 | H | 0.775754 | 4.877344 | 0.298208 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -0.469082 | 2.733034 | -0.168337 | H | -0.473025 | 2.753668 | 0.266920 |
| H | -5.326090 | 3.245909 | 0.025018 | H | -5.213334 | 3.282025 | -0.367333 |
| H | -7.076280 | 1.101828 | -0.018701 | H | -7.015719 | 1.179518 | -0.383274 |
| H | -5.386846 | -1.098930 | -0.032724 | H | -5.397906 | -1.057497 | -0.150472 |

Table S7. Optimized Geometries of [Pt(bpy){NH=C(pz)NC(Et)=NH}]$^+$ by the B3LYP method

| | Singlet | | | | Triplet | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| Pt | 0.362799 | -0.202121 | -0.038548 | Pt | 0.369805 | -0.207795 | 0.009587 |
| N | -1.421508 | 0.680458 | -0.033936 | N | -1.392737 | 0.668231 | 0.023600 |
| N | -2.908614 | -1.198841 | -0.150144 | N | -2.897091 | -1.196687 | -0.144085 |
| N | -0.645734 | -1.929889 | -0.133884 | N | -0.654665 | -1.954376 | 0.000123 |
| N | 2.275922 | -0.982899 | -0.070737 | N | 2.200832 | -0.979868 | -0.216475 |
| N | 1.487167 | 1.527903 | 0.086398 | N | 1.478823 | 1.520252 | 0.165637 |
| N | -3.711089 | 0.967479 | -0.107187 | N | -3.671701 | 0.976216 | -0.220185 |
| N | -3.504699 | 2.312164 | -0.045937 | N | -3.428637 | 2.321785 | -0.187108 |
| C | -2.602915 | 0.095067 | -0.095933 | C | -2.596377 | 0.087197 | -0.112663 |
| C | -1.957735 | -2.136715 | -0.160402 | C | -1.955156 | -2.161551 | -0.043788 |
| C | -2.462531 | -3.565731 | -0.194384 | C | -2.492176 | -3.572376 | 0.031346 |
| C | -3.246258 | -3.940470 | 1.072007 | C | -3.286349 | -3.828113 | 1.322167 |
| C | 3.279925 | -0.058375 | -0.013558 | C | 3.257179 | -0.041847 | -0.054283 |
| C | 4.622550 | -0.450751 | -0.041574 | C | 4.596633 | -0.506237 | -0.079796 |
| C | 4.950006 | -1.800854 | -0.129358 | C | 4.878589 | -1.828653 | -0.319527 |
| C | 3.917316 | -2.737629 | -0.189445 | C | 3.799363 | -2.746951 | -0.558218 |
| C | 2.602842 | -2.287540 | -0.158389 | C | 2.514887 | -2.285953 | -0.498293 |
| C | 2.839686 | 1.342902 | 0.079028 | C | 2.852154 | 1.307716 | 0.112162 |
| C | 3.715659 | 2.430364 | 0.160324 | C | 3.729116 | 2.418811 | 0.220689 |
| C | 3.207726 | 3.723457 | 0.254023 | C | 3.227604 | 3.693426 | 0.383470 |
| C | 1.823898 | 3.900649 | 0.267717 | C | 1.828120 | 3.883033 | 0.442351 |
| C | 1.002381 | 2.782023 | 0.183119 | C | 1.005675 | 2.776728 | 0.328807 |
| C | -4.720191 | 2.839784 | -0.078227 | C | -4.621484 | 2.878709 | -0.306565 |
| C | -5.730141 | 1.839887 | -0.161732 | C | -5.656601 | 1.901458 | -0.419745 |
| C | -5.046261 | 0.647156 | -0.178765 | C | -5.012316 | 0.690545 | -0.360134 |
| H | -1.535111 | 1.697554 | -0.014901 | H | -1.503897 | 1.690668 | 0.010320 |
| H | -0.125014 | -2.803663 | -0.142417 | H | -0.125146 | -2.817935 | 0.117874 |
| H | -1.619455 | -4.259957 | -0.345937 | H | -1.663493 | -4.292147 | -0.063917 |
| H | -3.119883 | -3.654980 | -1.074647 | H | -3.150625 | -3.711284 | -0.841853 |
| H | -3.638334 | -4.965057 | 0.987363 | H | -3.696987 | -4.848405 | 1.313317 |
| H | -4.093209 | -3.254420 | 1.216672 | H | -4.122877 | -3.119668 | 1.411840 |
| H | -2.607000 | -3.891755 | 1.968187 | H | -2.647188 | -3.724586 | 2.213305 |
| H | 5.411891 | 0.297638 | 0.004333 | H | 5.406425 | 0.202955 | 0.089520 |
| H | 5.994360 | -2.115485 | -0.151607 | H | 5.911007 | -2.179267 | -0.339293 |
| H | 4.117610 | -3.806871 | -0.260649 | H | 3.990095 | -3.794503 | -0.788295 |
| H | 1.779934 | -2.997519 | -0.208010 | H | 1.675396 | -2.951772 | -0.694901 |
| H | 4.792260 | 2.268652 | 0.152230 | H | 4.804882 | 2.256471 | 0.165293 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 3.882930 | 4.578014 | 0.317744 | H | 3.905240 | 4.544557 | 0.463615 |
| H | 1.373987 | 4.890740 | 0.343515 | H | 1.387694 | 4.869945 | 0.578309 |
| H | -0.079737 | 2.894346 | 0.196800 | H | -0.075642 | 2.897412 | 0.383279 |
| H | -4.839015 | 3.921266 | -0.040945 | H | -4.712154 | 3.963524 | -0.309588 |
| H | -6.806172 | 1.980523 | -0.203776 | H | -6.723378 | 2.072667 | -0.530691 |
| H | -5.364202 | -0.387538 | -0.235919 | H | -5.361109 | -0.335150 | -0.404384 |

Table S8. Optimized Geometries of [Pt(bpy){NH=C(pz)NC(Ph)=NH}]$^+$ by the B3LYP method

| | Singlet | | | | Triplet | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| Pt | 0.694830 | -0.024280 | -0.001302 | Pt | -0.704042 | -0.047981 | 0.023134 |
| N | -0.457906 | 1.597560 | 0.002213 | N | 0.406437 | 1.572521 | 0.001666 |
| N | -2.658935 | 0.642442 | 0.049757 | N | 2.636521 | 0.682771 | -0.038058 |
| N | -1.009682 | -1.071022 | -0.050280 | N | 1.042154 | -1.071027 | 0.092557 |
| N | 2.005196 | -1.620004 | -0.032861 | N | -1.927917 | -1.632546 | -0.051382 |
| N | 2.506537 | 0.965841 | 0.042851 | N | -2.513572 | 0.933117 | 0.034300 |
| N | -2.343026 | 2.930512 | 0.018896 | N | 2.255046 | 2.958494 | -0.092383 |
| N | -1.525104 | 4.017768 | -0.034008 | N | 1.383446 | 4.011684 | -0.073718 |
| C | -1.777406 | 1.637567 | 0.020610 | C | 1.747560 | 1.653382 | -0.040075 |
| C | -2.268204 | -0.636122 | 0.010873 | C | 2.285377 | -0.625545 | 0.024378 |
| C | 3.327899 | -1.281543 | -0.076002 | C | -3.310062 | -1.307256 | 0.023825 |
| C | 4.321001 | -2.265023 | -0.137988 | C | -4.262980 | -2.357209 | 0.060428 |
| C | 3.965613 | -3.610905 | -0.148428 | C | -3.868413 | -3.669883 | -0.014187 |
| C | 2.612211 | -3.946564 | -0.089324 | C | -2.471025 | -3.977620 | -0.139164 |
| C | 1.670809 | -2.925781 | -0.031845 | C | -1.568259 | -2.952128 | -0.153174 |
| C | 3.608142 | 0.162784 | -0.031068 | C | -3.611073 | 0.078436 | 0.046428 |
| C | 4.896627 | 0.706925 | -0.039592 | C | -4.918999 | 0.631170 | 0.074112 |
| C | 5.066058 | 2.086954 | 0.036393 | C | -5.102266 | 1.997701 | 0.086798 |
| C | 3.933795 | 2.897436 | 0.126752 | C | -3.971215 | 2.845942 | 0.069817 |
| C | 2.678033 | 2.300356 | 0.127645 | C | -2.713698 | 2.270817 | 0.043381 |
| C | -2.347289 | 5.057410 | -0.015429 | C | 2.154312 | 5.084126 | -0.135926 |
| C | -3.710643 | 4.653746 | 0.052549 | C | 3.538511 | 4.741222 | -0.197837 |
| C | -3.671592 | 3.279344 | 0.073979 | C | 3.567598 | 3.368589 | -0.168349 |
| C | -3.359821 | -1.652719 | 0.024157 | C | 3.411816 | -1.593104 | 0.028394 |
| C | -4.598114 | -1.349576 | -0.566466 | C | 4.660621 | -1.205602 | 0.547026 |
| C | -5.621235 | -2.297460 | -0.581038 | C | 5.717843 | -2.113941 | 0.582604 |
| C | -5.430280 | -3.549768 | 0.012377 | C | 5.550250 | -3.408630 | 0.080771 |
| C | -4.209378 | -3.851929 | 0.623032 | C | 4.318650 | -3.795469 | -0.459141 |
| C | -3.178713 | -2.910727 | 0.626861 | C | 3.254521 | -2.895246 | -0.483676 |
| H | -0.078179 | 2.547550 | -0.035506 | H | 0.008002 | 2.520577 | -0.011126 |
| H | -0.964206 | -2.077540 | -0.188308 | H | 1.000059 | -2.076737 | 0.249187 |
| H | 5.371065 | -1.979929 | -0.176171 | H | -5.320465 | -2.109329 | 0.146381 |
| H | 4.733382 | -4.384364 | -0.197483 | H | -4.606507 | -4.472137 | 0.014259 |
| H | 2.279610 | -4.984759 | -0.086757 | H | -2.124733 | -5.006857 | -0.224395 |
| H | 0.609580 | -3.159948 | 0.022624 | H | -0.504228 | -3.156963 | -0.261231 |
| H | 5.766133 | 0.054693 | -0.102406 | H | -5.779576 | -0.036643 | 0.078748 |
| H | 6.066936 | 2.520975 | 0.029767 | H | -6.108969 | 2.417409 | 0.106338 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 4.010580 | 3.982637 | 0.196713 | H | -4.066880 | 3.930914 | 0.078895 |
| H | 1.779751 | 2.909805 | 0.204282 | H | -1.829853 | 2.907527 | 0.033191 |
| H | -1.940376 | 6.066501 | -0.050757 | H | 1.701709 | 6.074135 | -0.135980 |
| H | -4.592925 | 5.286209 | 0.083381 | H | 4.388521 | 5.414578 | -0.258377 |
| H | -4.441665 | 2.518573 | 0.129816 | H | 4.376227 | 2.647090 | -0.200523 |
| H | -4.740059 | -0.369617 | -1.021599 | H | 4.785014 | -0.194784 | 0.933896 |
| H | -6.574905 | -2.057025 | -1.055046 | H | 6.679018 | -1.809583 | 1.000843 |
| H | -6.236050 | -4.286592 | 0.007827 | H | 6.382684 | -4.114800 | 0.100362 |
| H | -4.064269 | -4.818178 | 1.110128 | H | 4.192192 | -4.796805 | -0.874535 |
| H | -2.245820 | -3.143278 | 1.146816 | H | 2.313833 | -3.198660 | -0.949871 |

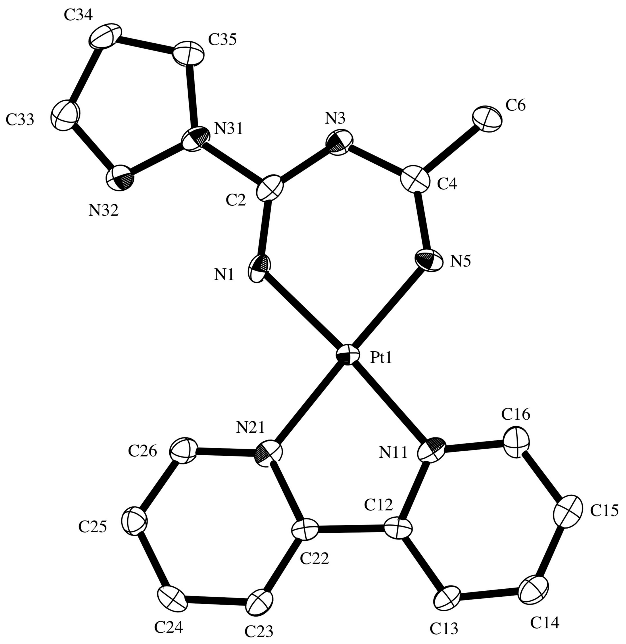


**Fig. S1** ORTEP drawing of the complex cation of [Pt(bpy){NH=C(pz)NC($CH_3$)=NH}]$PF_6$ ([**1Y**]$PF_6$) with the atom numbering scheme (50% probability ellipsoids).

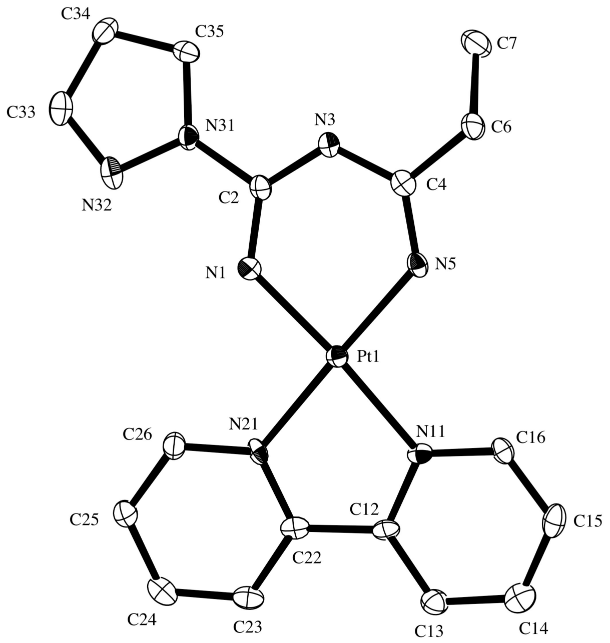


**Fig. S2** ORTEP drawing of the complex cation of [Pt(bpy){NH=C(pz)NC($C_2H_5$)=NH}]$BF_4$ ([**2G**]$BF_4$) with the atom numbering scheme (50% probability ellipsoids).

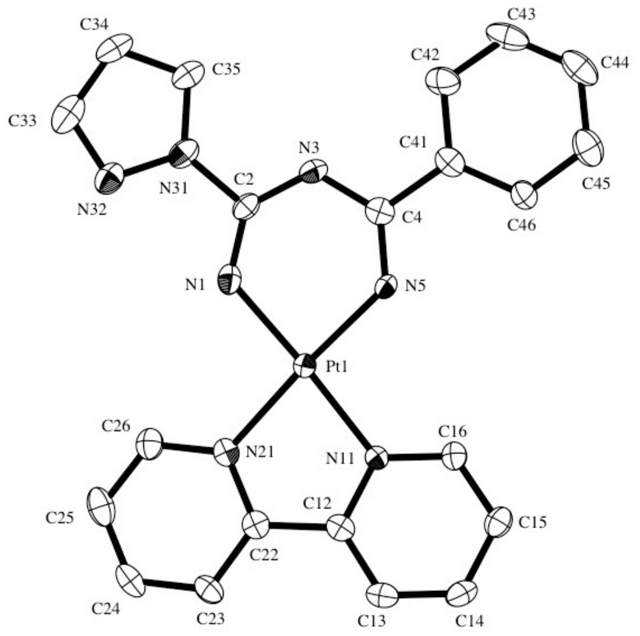


**Fig. S3** ORTEP drawing of the complex cation of [Pt(bpy){NH=C(pz)NC(Ph)=NH}]$BF_4$•$H_2O$ ([**3G**]$BF_4$•$H_2O$) with the atom numbering scheme (50% probability ellipsoids).

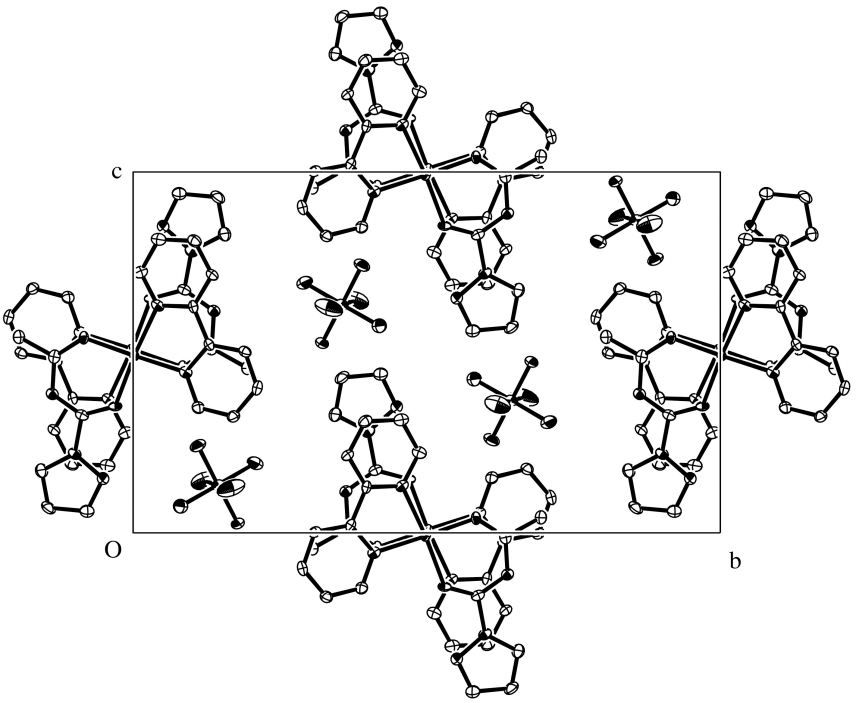


**Fig. S4** Crystal structure of [Pt(bpy){NH=C(pz)NC($CH_3$)=NH}]$PF_6$ ([**1Y**]$PF_6$) viewed along the a-axis.

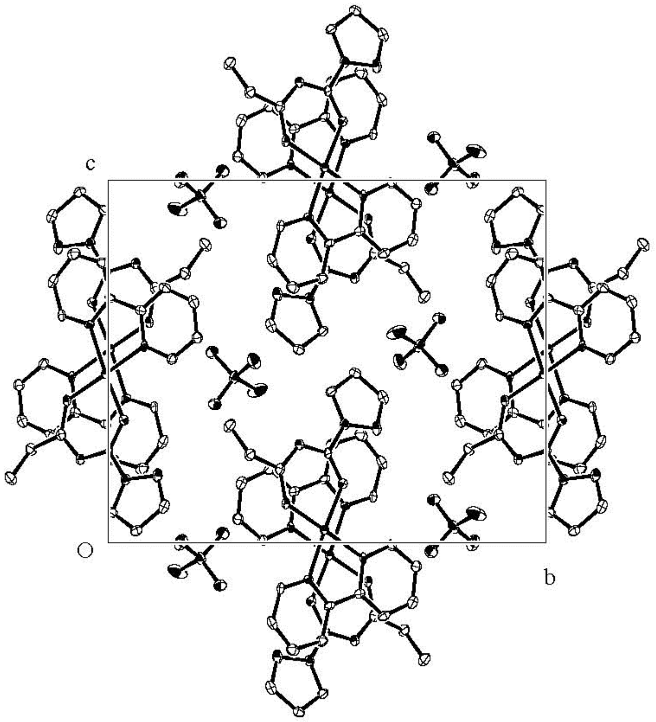


**Fig. S5** Crystal structure of [Pt(bpy){NH=C(pz)NC($C_2H_5$)=NH}]$BF_4$ ([**2G**]$BF_4$) viewed along the a-axis.

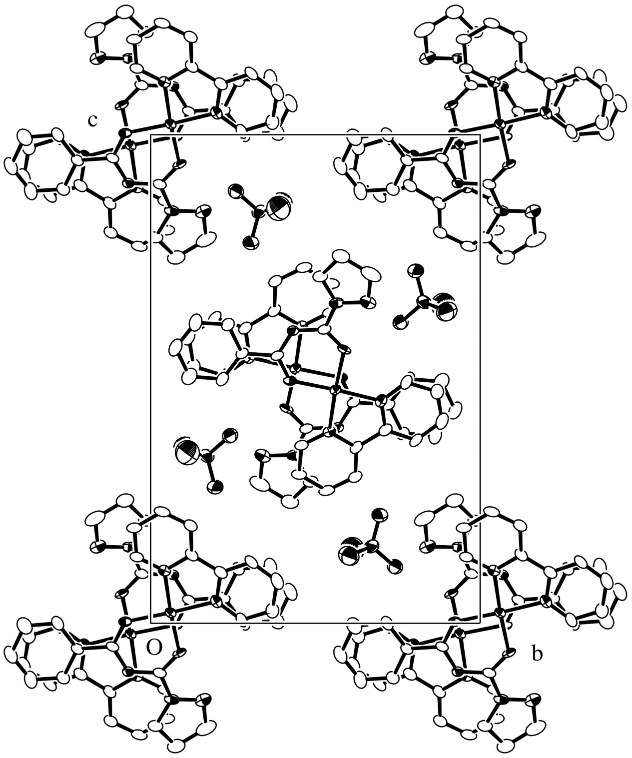


**Fig. S6** Crystal structure of [Pt(bpy){NH=C(pz)NC(Ph)=NH}]$BF_4$ ([**3Y**]$BF_4$) viewed along the a-axis.

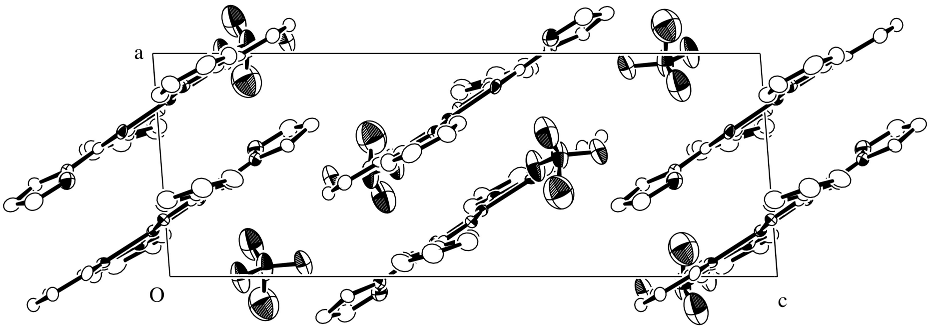


**Fig. S7** Crystal structure of [Pt(bpy){NH=C(pz)NC(Ph)=NH}]$BF_4$ ([**3Y**]$BF_4$) viewed along the b-axis.

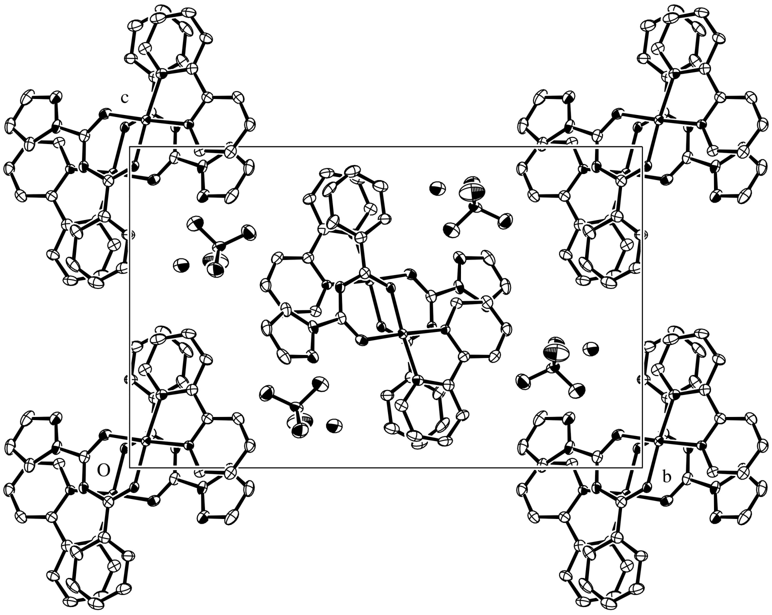


**Fig. S8** Crystal structure of [Pt(bpy){NH=C(pz)NC(Ph)=NH}]$BF_4$•$H_2O$ ([**3G**]$BF_4$•$H_2O$) viewed along the a-axis.

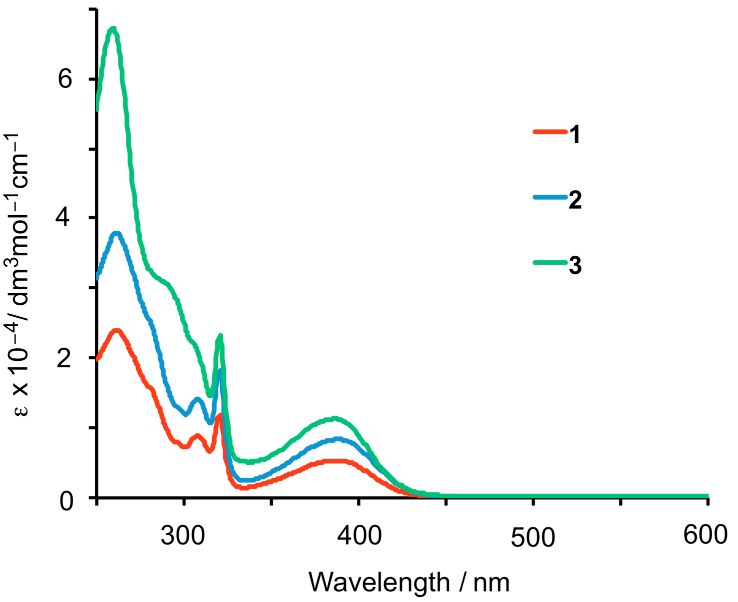


**Fig. S9** Electronic absorption spectra of **1**, **2** and **3** in $CH_3CN$ at 298 K.

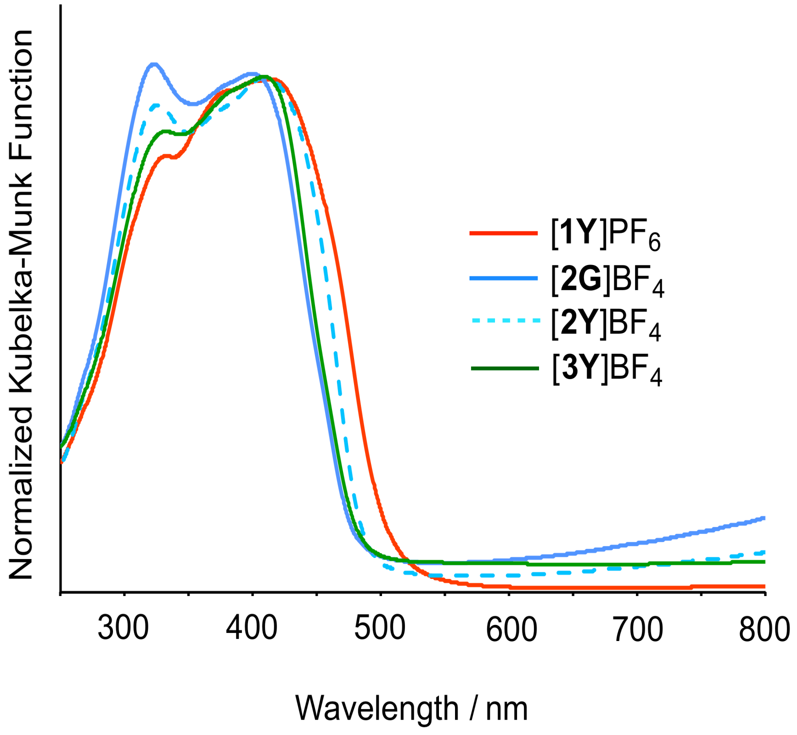


**Fig. S10** UV-Vis diffuse reflectance spectra of [**1Y**]$PF_6$ ( —— ), [**2Y**]$BF_4$ ( – – – ), [**2G**]$BF_4$ ( —— ) and [**3Y**]$BF_4$ ( —— ) in the solid state at 295 K.

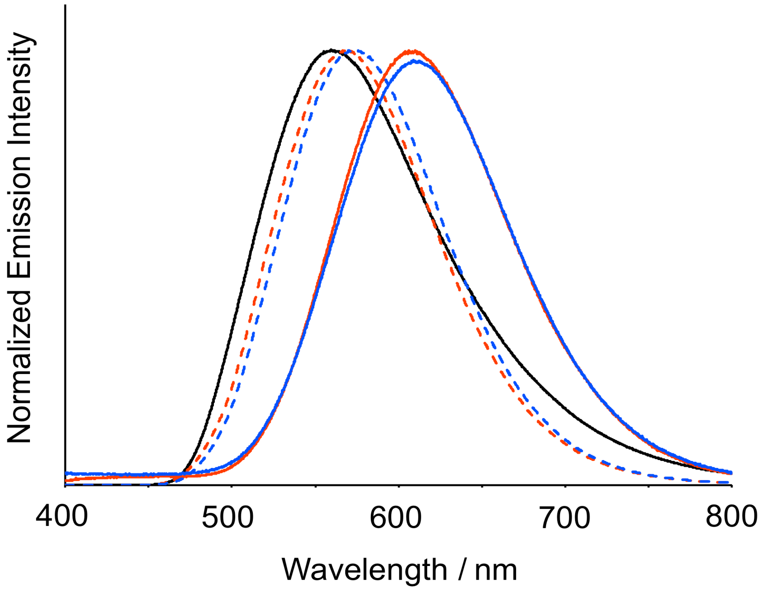


**Fig. S11** Normalized emission spectra of [**1Y**]$PF_6$ in the solid state at 295 K ($\lambda_{ex}$ = 350 nm): unground sample ($\lambda_{max}$ = 560 nm, —— ), completely ground sample (1st time) ($\lambda_{max}$ = 608 nm, —— ), ground sample with a drop of acetonitrile added (1st time) ($\lambda_{max}$ = 568 nm, - - - ), completely ground sample (2nd time) ($\lambda_{max}$ = 610 nm, —— ), ground sample with a drop of acetonitrile added (2nd time) ($\lambda_{max}$ = 574 nm, - - - ).

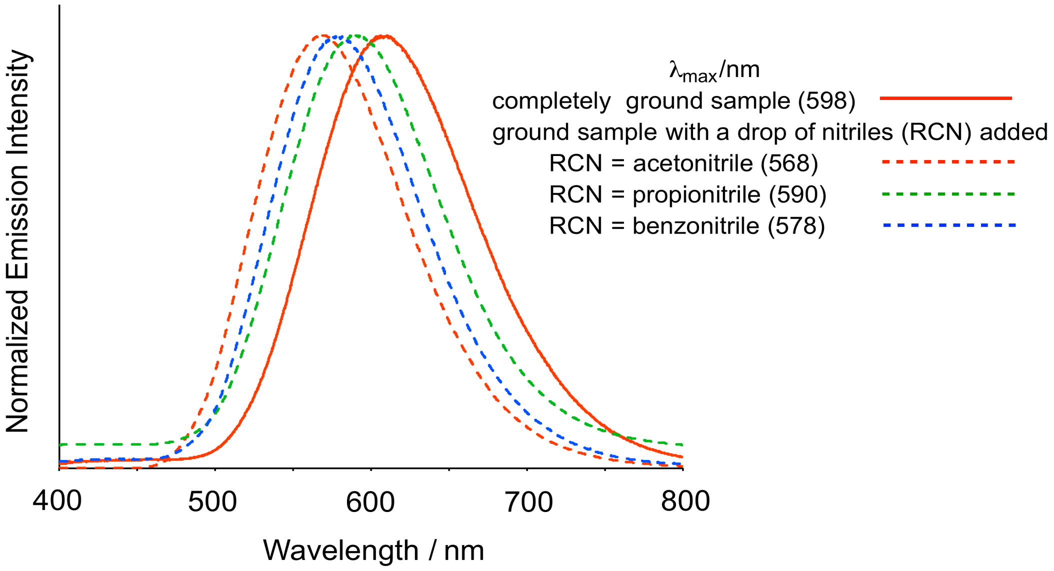


**Fig. S12** Normalized emission spectra of [**1Y**]$PF_6$ in the solid state at 295 K ($\lambda_{ex}$ = 350 nm): completely ground sample and ground samples with a drop of various nitriles added.

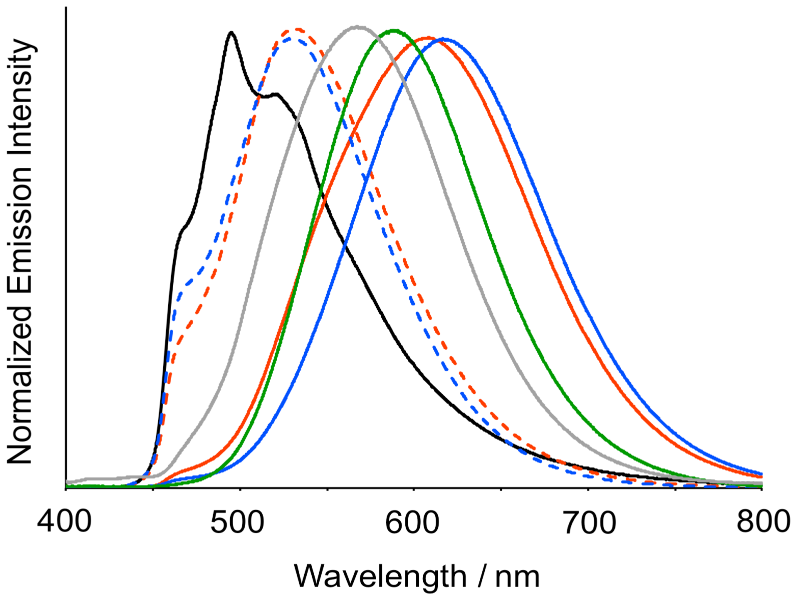


**Fig. S13** Normalized emission spectra of [**2G**]BF$_4$ in the solid state at 295 K ($\lambda_{ex}$ = 350 nm): sample as-prepared ($\lambda_{max}$ = 589 nm, —— ), recrystallized unground sample ($\lambda_{max}$ = 495 nm, —— ), completely ground sample (1st time) ($\lambda_{max}$ = 608 nm, —— ), ground sample with a drop of acetonitrile added (1st time) ($\lambda_{max}$ = 531 nm, - - - ), completely ground sample (2nd time) ($\lambda_{max}$ = 617 nm, —— ), ground sample with a drop of acetonitrile added (2nd time) ($\lambda_{max}$ = 530 nm, - - - ), rapidly precipitated sample obtained from acetonitrile solution of [**2G**]BF$_4$ by addition of diethyl ether ($\lambda_{max}$ = 568 nm, —— ).

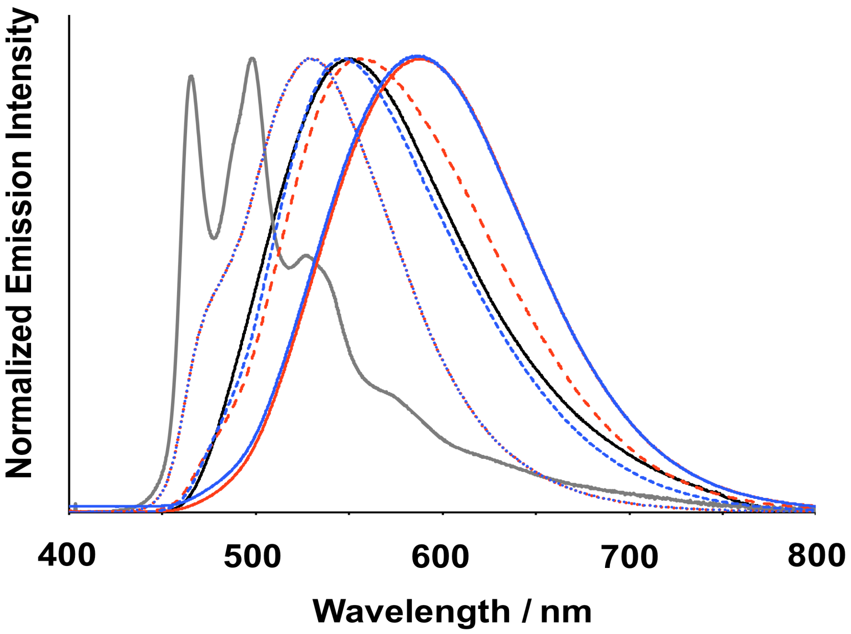


**Fig. S14** Normalized emission spectra of [**3Y**]BF$_4$ in the solid state at 295 K ($\lambda_{ex}$ = 350 nm): unground sample ($\lambda_{max}$ = 550 nm, —— ), completely ground sample (1st time) ($\lambda_{max}$ = 588 nm, —— ), ground sample with a drop of acetonitrile added (1st time, just after addition) ($\lambda_{max}$ = 530 nm, ········ ), ground sample with a drop of acetonitrile added (1st time, 30 sec after addition) ($\lambda_{max}$ = 556 nm, – – – ), completely ground sample (2nd time) ($\lambda_{max}$ = 587 nm, —— ), ground sample with a drop of acetonitrile added (2nd time, just after addition) ($\lambda_{max}$ = 530 nm, ········ ) and ground sample with a drop of acetonitrile added (2nd time, 30 sec after addition) ($\lambda_{max}$ = 556 nm, – – – ). The emission spectrum of [**3G**]BF$_4$•H$_2$O is also depicted for comparison (($\lambda_{max}$ = 497 nm, —— ).

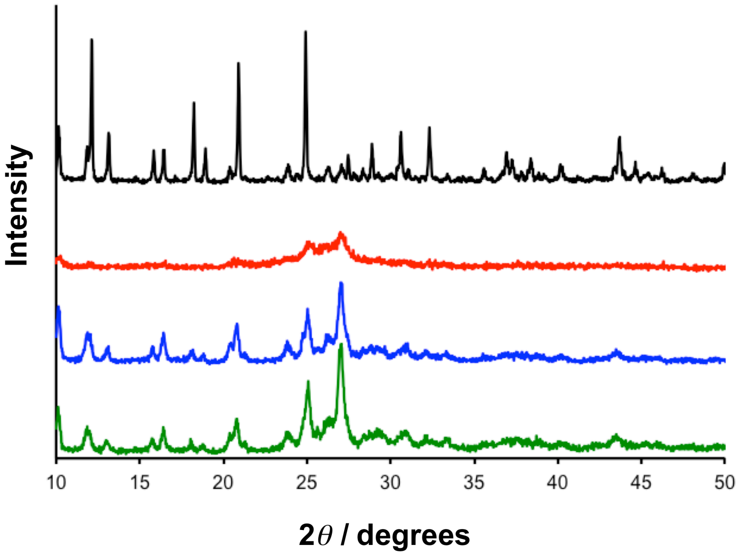


**Fig. S15** Powder X-ray diffraction patterns of [**1Y**]PF$_6$: unground sample ( —— ), completely ground sample ( —— ) and ground sample with a drop of acetonitrile added (1st time, —— , 2nd time —— ).

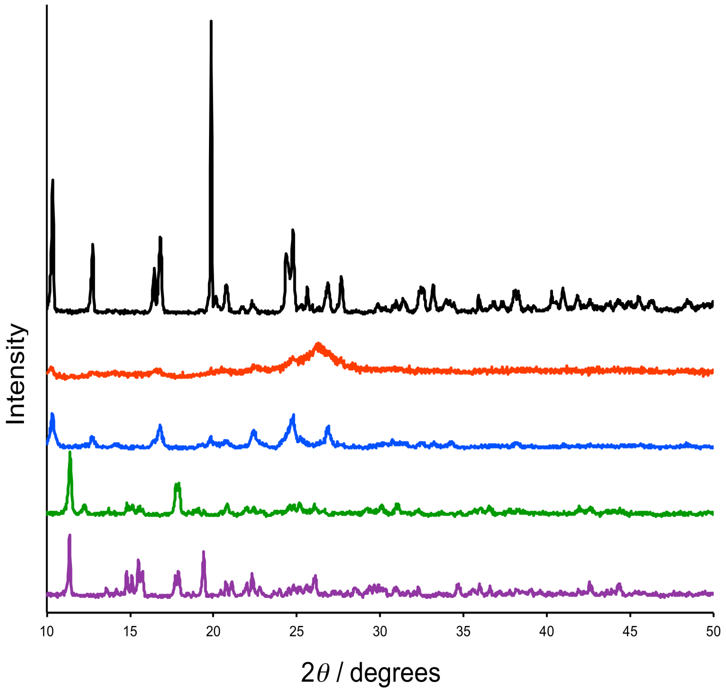


**Fig. S16** Powder X-ray diffraction patterns of [**2G**]BF$_4$ [unground sample (——), completely ground sample (——), ground sample with a drop of acetonitrile added (——), and rapidly precipitated sample obtained from acetonitrile solution (——)] and [**2Y**]BF$_4$ (——).

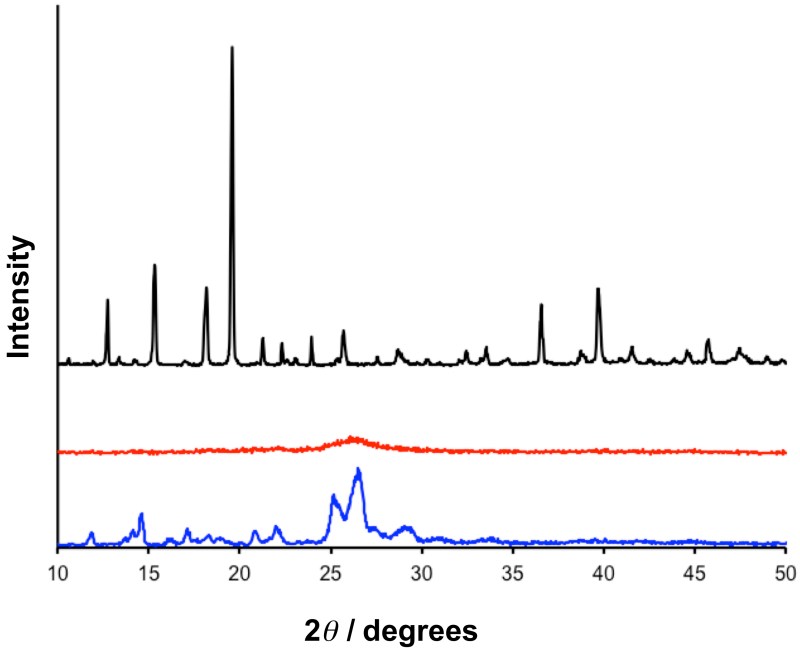


**Fig. S17** Powder X-ray diffraction patterns of [**3Y**]BF$_4$: unground sample (——), completely ground sample (——) and ground sample with a drop of acetonitrile added (——).

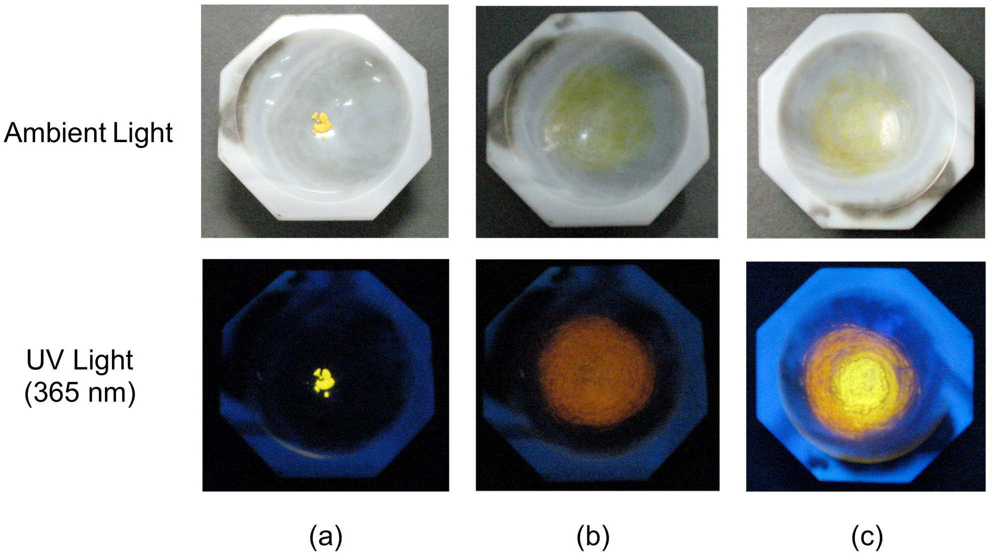


**Fig. S18** Photographic images of [**1Y**]$PF_6$ in response to mechanical grinding under ambient light and UV light irradiation (365 nm): (a) unground sample, (b) completely ground sample, (c) ground sample with a drop of acetonitrile added.

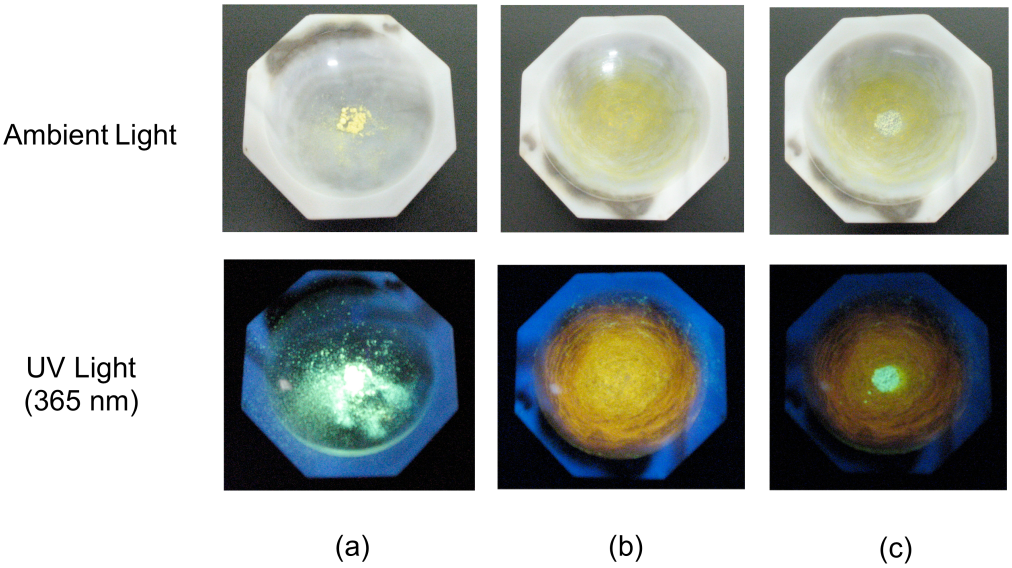


**Fig. S19** Photographic images of [**2G**]$BF_4$ in response to mechanical grinding under ambient light and UV light irradiation (365 nm): (a) unground sample, (b) completely ground sample, (c) ground sample with a drop of acetonitrile added.

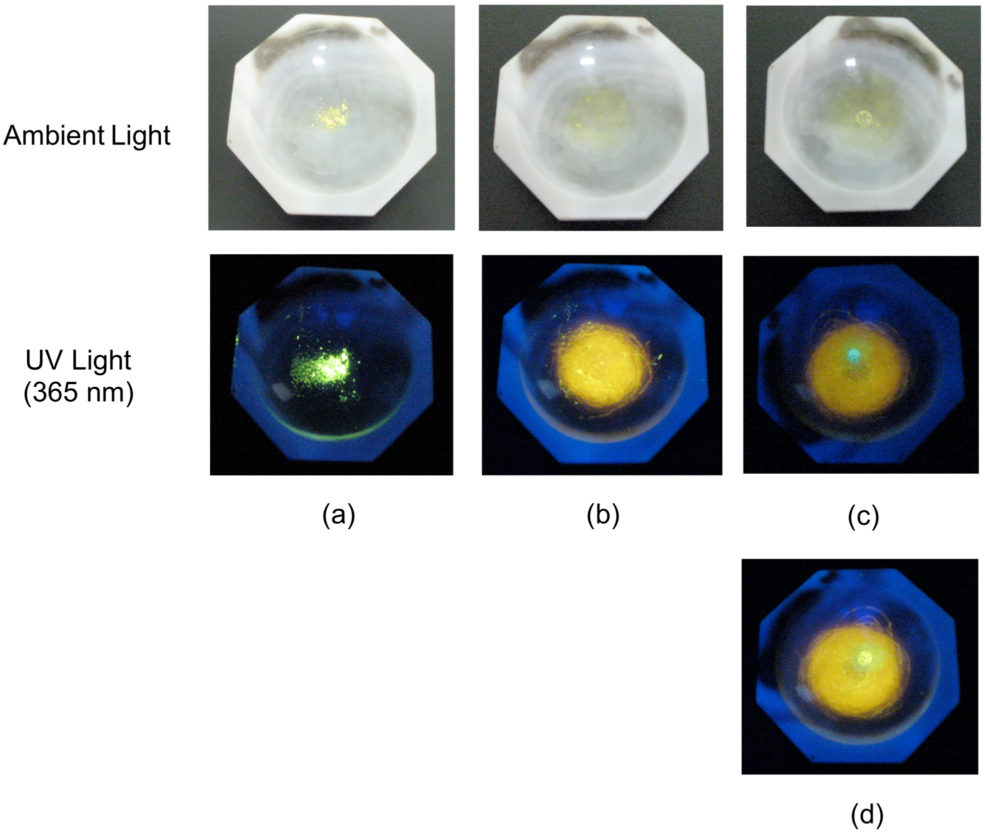
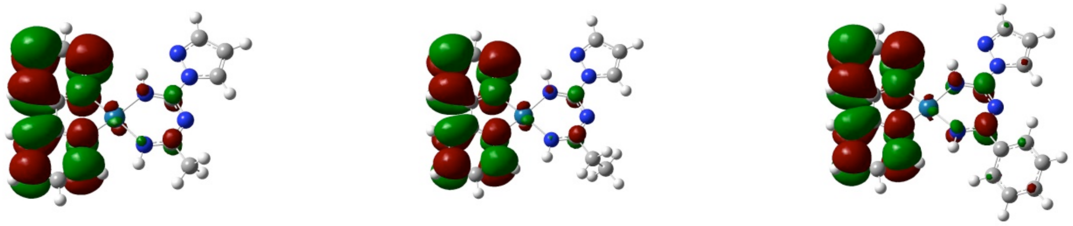
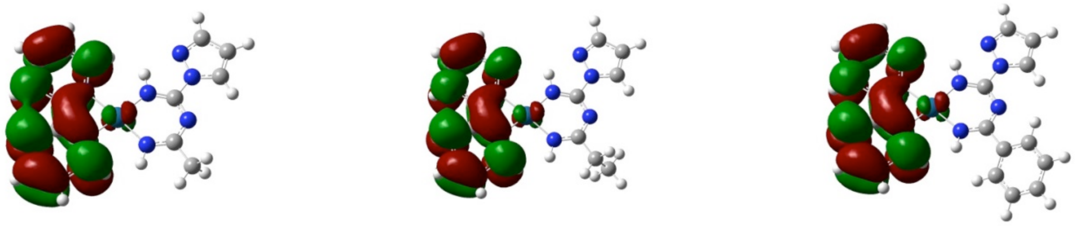


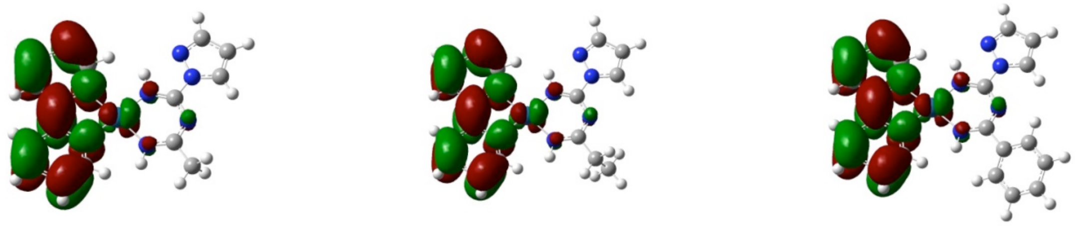
**Fig. S20** Photographic images of [**3Y**]$BF_4$ in response to mechanical grinding under ambient light and UV light irradiation (365 nm): (a) unground sample, (b) completely ground sample, (c) ground sample with a drop of acetonitrile added (just after addition: vapochromic response was observed), (d) ground sample with a drop of acetonitrile added (30 sec after addition: the effect of vapochromism disappeared).



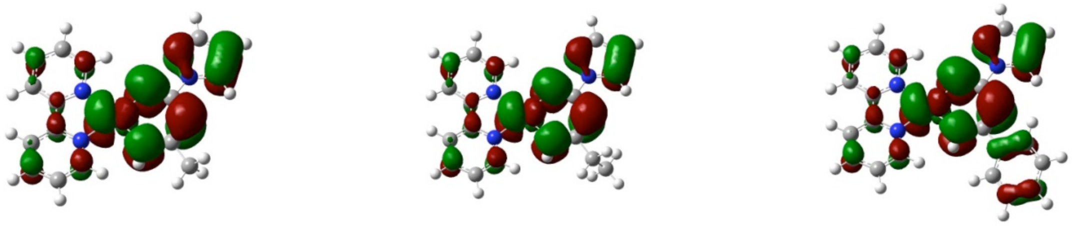
LUMO+2 (−4.74V) LUMO+2 (−4.72V) LUMO+2 (−4.70V)



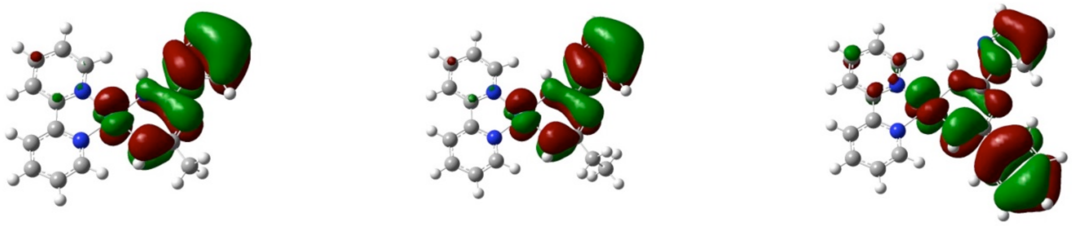
LUMO+1 (−4.90 eV) LUMO+1 (−4.89 eV) LUMO+1 (−4.85 eV)



LUMO (−5.86 eV) LUMO (−5.85 eV) LUMO (−5.81 eV)



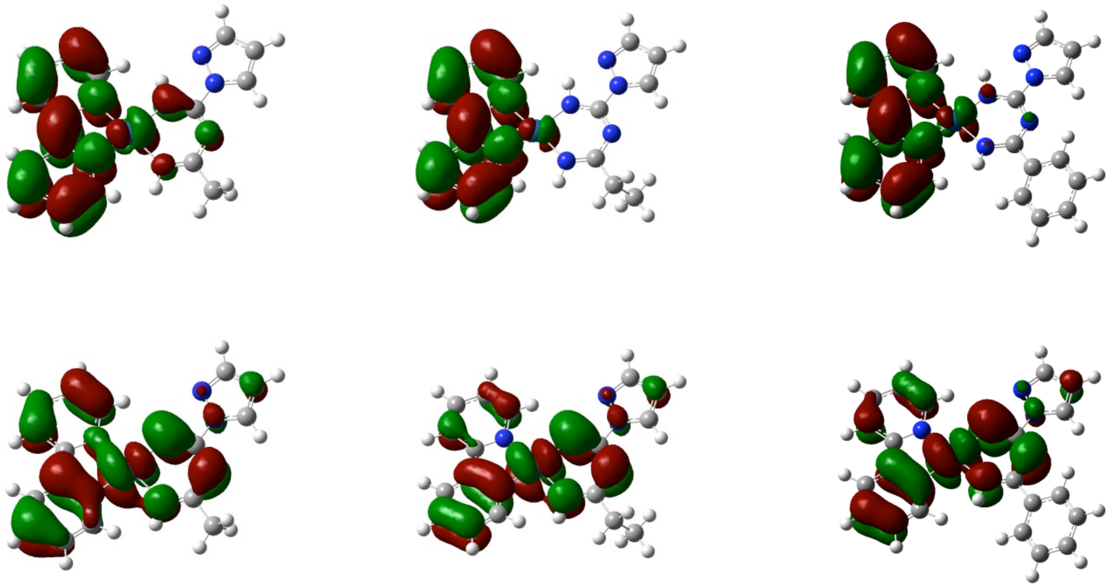
HOMO (−9.09 eV) HOMO (−9.07 eV) HOMO (−9.01 eV)



HOMO−1 (−9.30 eV) HOMO−1 (−9.29 eV) HOMO−1 (−9.16 eV)

**R = Me** **R = Et** **R = Ph**

**Fig. S21** Molecular orbitals of the singlet states for [Pt(bpy){NH=C(pz)NC(R)=NH}]$^+$ (R = Me, Et, Ph) by the B3LYP method.



**R = Me** **R = Et** **R = Ph**

**Fig. S22** Singly occupied molecular orbitals of the triplet states for [Pt(bpy){NH=C(pz)NC(R)=NH}]$^+$ (R = Me, Et, Ph) by the B3LYP method.