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Mechanochemical Changes on Cyclometalated Ir(III) Acyclic Carbene Complexes – Design and Tuning of Luminescent Mechanochromic Transition Metal Complexes.

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Electronic Supplementary Information

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1. Experimental Section

Materials and Reagents. Iridium(III) chloride hydrate was obtained from Precious Metals Online. 2-Phenylpyridine (ppy) and 2-(2,4-difluorophenyl)pyridine (F_2ppy) were obtained from Meryer (Shanghai) Chemical Technology Company. Silver triflate (AgOTf) was obtained from Strem Chemiscals Inc. 2-Aminopyridine (pyNH_2), 2-amino-3-(trifluoromethyl)pyridine (3-CF_3pyNH_2) and 2-amino-5-fluoropyridine (5-FpyNH_2) were obtained from J&K Scientific Company. Solvents such as chloroform (Lab-Scan), dichloromethane (Lab-Scan), acetone (Lab-Scan), ethanol (Sigma-Aldrich), methanol (Lab-Scan) and *n*-hexane (Lab-Scan) were of analytical grade and used as received. Deuterated solvents for NMR spectroscopic measurements were obtained from Cambridge Isotope Laboratories, Inc. ^{13}C-Labelled formic acid were purchased from Aldrich Chemical Co. 4-Chlorophenyl isocyanide (4-ClC_6H_4NC) and 2,4,6-trichlorophenyl isocyanide (2,4,6-$Cl_3C_6H_4NC$) were prepared according to reported literature procedures. [1] $[Ir(ppy)_2Cl]_2$, $[Ir(F_2ppy)_2Cl]_2$ and $[Ir(R_2ppy)_2(CNR')(Cl)]$ (R = H or F; R′ = C_6H_4Cl-4 or $C_6H_2Cl_3$-2,4,6) were prepared according to modified literature procedures.[2,3]

{Ir(ppy)$_2$(N^C-Cl)} (1):

A dichloromethane solution (60 ml) of $[Ir(ppy)_2(CNC_6H_4Cl\text{-}4)(Cl)]$ (300 mg, 428.8 μmol) and AgOTf (132.2 mg, 514.6 μmol) was refluxed for 15 hours. After cooling to room temperature, the precipitated AgCl was filtered. After that, 2-aminopyridine (48.6 mg, 514.6 μmol) was added into the filtrate. The mixture was warmed to 50 °C and stirred at this temperature for additional 15 hours. After cooling to room temperature, the solvent was removed by rotatory evaporation. The target product was isolated by column chromatography on alumina using dichloromethane-acetone (4:1, v/v) as eluent. Further purification can be achieved by recrystallization from slow evaporation of dichloromethane/ethanol or dichloromethane/methanol solution to give the analytically pure complex **1** as yellow solid. Yield: 245.0 mg, 278.3 μmol; 64.9%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (1H, d, J = 5.5 Hz, 6-pyridyl H's of ppy), 7.87 (2H, m, two 3-pyridyl H's of ppy), 7.79 (1H, d, J = 5.7 Hz, 6-pyridyl H's of ppy), 7.70 (2H, d, J = 7.4 Hz, 2-phenyl H's of ppy), 7.66 (2H, m, two 4-pyridyl H's of ppy), 7.56 (2H, d, J = 8.5 Hz, 2-,6- phenyl H's of N^C-Cl), 7.51 (1H, d, J = 5.6 Hz, 6-pyridyl H's of N^C-Cl), 7.48 (1H, t, J = 7.2 Hz, 4-pyridyl H's of N^C-Cl), 7.41 (1H, d, J = 8.1 Hz, 3-pyridyl H's of N^C-Cl), 7.16 (2H, d, J = 8.7 Hz, 3,5-phenyl H's of N^C-Cl), 6.96 (6H, m, two 3-phenyl H's of ppy, two 4-phenyl H's of ppy and two 5-pyridyl H's of ppy), 6.89 (1H, s, NH), 6.60 (1H, d, J = 7.5 Hz, 5-phenyl H's of ppy), 6.51 (2H, d, J = 6.8 Hz, 5-phenyl H's of ppy). ^{13}C NMR (151 MHz, $CDCl_3$) δ 213.01 (carbene C), 175.17, 171.59, 169.82, 167.73, 153.82, 148.77, 147.93, 144.87, 144.61, 143.32, 139.99, 137.98, 136.06, 135.18, 132.35, 130.92, 130.27, 129.87, 128.34, 124.37, 124.11, 122.84, 122.07, 121.44, 121.06, 120.97, 120.43, 118.93, 118.79, 116.57, 115.51, 113.85, 85.48. Positive-ion ESI-MS: *m/z*: 732.6 [M + H]$^+$. IR (KBr disc): υ/cm^{-1}: 3380, 1605 (N–H), 1411, 1298 (C–N). Anal. Calcd for $C_{34}H_{25}ClIrN_5 \cdot CH_3CH_2OH$ (777.33): C, 55.62; H, 4.02; N, 9.01. Found: C, 55.54; H, 3.70; N, 8.70.

{Ir(ppy)$_2$(CF$_3$-N^C-Cl)} (2):

A dichloromethane solution (60 ml) of [Ir(ppy)$_2$(CNC$_6$H$_4$Cl-4)(Cl)] (282 mg, 419.6 µmol) and AgOTf (116.8 mg, 503.5 µmol) was refluxed for 15 hours. After cooling to room temperature, the precipitated AgCl was filtered. After that, 2-amino-3-(trifluoromethyl)pyridine (81.5 mg, 503.5 µmol) was added into the filtrate. The mixture was then warmed to 50 °C and stirred at this temperature for additional 15 hours. After cooling to room temperature, the solvent was removed by rotatory evaporation. The target product was isolated by column chromatography on alumina using dichloromethane-acetone (1:1, v/v) as eluent to give analytically pure complex **2** as yellow solid. Yield: 199.8 mg, 250.0 µmol; 62.1%. ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 8.38 (1H, d, *J* = 6.5 Hz, 6-pyridyl H's of ppy), 8.23 (1H, d, *J* = 8.1 Hz, 3-pyridyl H's of ppy), 8.17 (1H, d, *J* = 8.2 Hz, 3-pyridyl H's of ppy), 7.96 (1H, d, *J* = 7.8 Hz, 6-pyridyl H's of ppy), 7.91 (1H, d, *J* = 8.7 Hz, 4-pyridyl H's of N^C-Cl), 7.88 (3H, m, two 2-phenyl H's of ppy and 3-phenyl H's of ppy), 7.71 (1H, d, *J* = 6.3 Hz, 6-pyridyl H's of N^C-Cl), 7.60 (3H, m, 4-pyridyl H's of ppy and 2-,6- phenyl H's of N^C-Cl), 7.24 (4H, m, 5-pyridyl H's of ppy, 4-pyridyl H's of ppy and 3-,5- phenyl H's of N^C-Cl), 7.03 (1H, s, NH), 7.00 (1H, t, *J* = 7.5 Hz, 5-pyridyl H's of N^C-Cl), 6.93 (3H, m, 3-phenyl H's of ppy and two 4-phenyl H's of ppy), 6.82 (1H, t, *J* = 5.8 Hz, 5-pyridyl H's of ppy), 6.46 (1H, d, *J* = 8.2 Hz, 5-phenyl H's of ppy), 6.31 (1H, d, *J* = 7.1 Hz, 5-phenyl H's of ppy). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 214.51 (carbene C), 171.84, 170.71, 169.19, 167.13, 165.18, 156.44, 153.39, 151.62, 148.86, 148.28, 145.05, 143.75, 140.42, 139.80, 138.00, 137.08, 135.91, 132.04, 130.57, 130.15, 128.74, 126.69, 125.29, 125.02, 124.54, 124.10, 123.80, 123.50, 122.15, 121.38, 121.11, 120.21, 120.05, 115.42, 67.62. ^{19}F NMR (565 MHz, DMSO-d$_6$) δ -62.64 (3F, s, 3-pyridyl CF$_3$'s of N^C-Cl). Positive-ion ESI-MS: *m/z*: 800.0 [M + H]$^+$. IR (KBr disc): υ/cm^{-1}: 3372, 1604 (N–H), 1407, 1293 (C–N). Anal. Calcd for $C_{35}H_{24}ClF_3IrN_5$ (799.27): C, 52.60; H, 3.03; N, 8.76. Found: C, 52.79; H, 3.02; N, 8.16.

{Ir(ppy)$_2$(F-N^C-Cl)} (3):

The complex was synthesized with a similar procedure for **1** except 5-fluoro-2-aminopyridine (53.4 mg, 469.2 μmol) was used instead of 2-aminopyridine and dichloromethane-acetone (9:1, v/v) was used as eluent in the column chromatography. Yield: 91.1 mg, 121.5 μmol; 28.3%. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.55 (1H, d, J = 5.7 Hz, 6-pyridyl H's of ppy), 7.85 (2H, m, two 3-pyridyl H's of ppy), 7.76 (1H, d, J = 5.5 Hz, 6-pyridyl H's of ppy), 7.66 (4H, m, two 4-pyridyl H's of ppy and two 2-phenyl H's of ppy), 7.51 (2H, d, J = 8.6 Hz, 2-,6- phenyl H's of N^C-Cl), 7.33 (2H, m, 4-pyridyl H's of N^C-Cl and 6-pyridyl H's of N^C-Cl), 7.23 (1H, d, J = 7.4 Hz, 3-pyridyl H's of N^C-Cl), 7.13 (2H, d, J = 8.7 Hz, 3-,5- phenyl H's of N^C-Cl), 6.94 (6H, m, two 5-pyridyl H's of ppy, two 3-phenyl H's of ppy and two 4-phenyl H's of ppy), 6.82 (1H, s, NH), 6.55 (1H, d, J = 7.5 Hz, 5-phenyl H's of ppy), 6.46 (1H, d, J = 7.0 Hz, 5-phenyl H's of ppy). ^{13}C NMR (151 MHz, CDCl$_3$) δ 212.34 (carbene C), 172.55, 170.88, 169.84, 167.60, 156.70, 153.79, 148.68, 144.57, 143.16, 139.91, 136.26, 135.34, 134.82, 134.62, 132.31, 130.80, 130.32, 130.10, 129.05, 128.34, 126.85, 126.31, 126.17, 124.40, 124.25, 122.90, 122.15, 121.79, 121.05, 120.57, 119.06, 118.87, 116.72. ^{19}F NMR (565 MHz, CDCl$_3$) δ -138.60 (1F, s, 5-pyridyl F's of N^C-Cl). Positive-ion ESI-MS: *m/z*: 750.2 [M + H]$^+$. IR (KBr disc): υ/cm^{-1}: 3370, 1606 (N–H), 1414, 1375 (C–N). Anal. Calcd for $C_{34}H_{24}ClFIrN_5 \cdot 0.5CH_2Cl_2$ (791.72): C, 52.34; H, 3.18; N, 8.85. Found: C, 52.39; H, 3.23; N, 8.55.

{Ir(ppy)$_2$(CF$_3$-N^C-Cl$_3$)} (4):

The complex was synthesized with a similar procedure for **2** except [Ir(ppy)$_2$(CNC$_6$H$_2$Cl$_3$-2,4,6)(Cl)] (182.7 mg, 237.7 μmol) was used instead of [Ir(ppy)$_2$(CNC$_6$H$_4$Cl-4)(Cl)] and dichloromethane-hexane (1:1, v/v) was used as eluent in column chromatography on alumina. Yield: 80.2 mg, 92.1 μmol; 38.8%. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.89 (1H, d, J = 6.6 Hz, 6-pyridyl H's of ppy), 7.91 (1H, d, J = 8.0 Hz, 3-pyridyl H's of ppy), 7.88 (1H, d, J = 8.0 Hz, 3-pyridyl H's of ppy), 7.71 (5H, m, 6-pyridyl H's of ppy, two 4-pyridyl H's of ppy and two 2-phenyl H's of ppy), 7.66 (1H, d, J = 7.7 Hz, 4-pyridyl H's of N^C-Cl), 7.58 (1H, d, J = 5.6 Hz, 6-pyridyl H's of N^C-Cl), 7.26 (2H, s, two phenyl H's of N^C-Cl), 6.99 (5H, m, two 5-pyridyl H's of ppy, two 3-phenyl H's of ppy and 4-phenyl H's of ppy), 6.87 (1H, t, J = 6.8 Hz, 4-phenyl H's of ppy), 6.60 (2H, m, two 5-phenyl H's of ppy), 6.46 (2H, m, 5-pyridyl H's of N^C-Cl and NH). ^{13}C NMR (151 MHz, CDCl$_3$) δ 214.96 (carbene C), 171.50, 171.46, 169.08, 167.57, 156.01, 154.27, 151.34, 148.84, 145.13, 143.87, 137.86, 136.76, 136.11, 132.38, 132.16, 131.99, 131.10, 131.06, 130.06, 129.82, 129.13, 127.74, 125.02, 124.91, 124.15, 123.10, 122.01, 120.61, 120.18, 119.54, 114.22, 67.88. ^{19}F NMR (565 MHz, CDCl$_3$) δ -63.45 (3F, s, 3-pyridyl CF$_3$'s of N^C-Cl). Positive-ion ESI-MS: *m/z*: 868.5 [M + H]$^+$. IR (KBr disc): υ/cm^{-1}: 3394, 1602 (N–

H), 1473, 1379, 1303 (C–N). Anal. Calcd for $C_{35}H_{22}Cl_3F_3IrN_5$ (867.15): C, 48.42; H, 2.55; N, 8.07. Found: C, 48.72; H, 2.27; N, 7.87.

{Ir(ppy)$_2$(F-N^C-Cl$_3$)} (5):

The complex was synthesized with a similar procedure for **1**, except [Ir(ppy)$_2$(CNC$_6$H$_2$Cl$_3$-2,4,6)(Cl)] (300.0 mg, 390.3 μmol) and 2-amino-5-fluoropyridine (52.93 mg, 468.4 μmol) were used and dichloromethane-acetone (49:1, v/v) was used as eluent in column chromatography. Yield: 188.9 mg, 230 μmol; 58.9%. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.91 (1H, d, J = 6.3 Hz, 6-pyridyl H's of ppy), 7.87 (2H, m, two 3-pyridyl H's of ppy), 7.68 (5H, m, 6-pyridyl H's of ppy, two 4-pyridyl H's of ppy and two 2-phenyl H's of ppy), 7.28 (1H, s, 6-pyridyl H's of N^C-Cl), 7.23 (1H, d, 3-pyridyl H's of N^C-Cl), 7.17 (3H, m, 4-pyridyl H's of N^C-Cl and 3-,5- phenyl H's of N^C-Cl), 6.94 (5H, m, two 5-pyridyl H's of ppy, two 3-phenyl H's of ppy and 4-phenyl H's of ppy), 6.83 (1H, t, J = 7.4 Hz, 4-phenyl H's of ppy), 6.57 (2H, d, J = 7.4 Hz, two 5-phenyl H's of ppy), 6.20 (1H, s, NH). ^{13}C NMR (151 MHz, CDCl3) δ 212.17 (carbene C), 172.11, 171.18, 169.68, 167.94, 156.50, 154.88, 154.64, 153.28, 148.72, 144.66, 143.30, 136.18, 135.32, 135.20, 134.74, 134.55, 132.66, 132.07, 131.23, 130.03, 129.93, 128.54, 127.97, 126.11, 125.97, 124.28, 124.25, 122.72, 121.73, 120.37, 119.04, 118.49, 116.57. ^{19}F NMR (565 MHz, CDCl$_3$) δ –139.10 (1F, s, 5-pyridyl F's of N^C-Cl). Positive-ion ESI-MS: *m/z*: 818.2 $[M + H]^+$. IR (KBr disc): υ/cm^{-1}: 3388, 1607 (N–H), 1475, 1379 (C–N). Anal. Calcd for $C_{34}H_{22}Cl_3FIrN_5\cdot0.5CH_3COCH_3$ (847.19): C, 50.33; H, 2.97; N, 8.27. Found: C, 50.49; H, 2.77; N, 8.09.

{Ir(F$_2$ppy)$_2$(N^C-Cl)} (6):

The complex was synthesized with a similar procedure for **1** except [Ir(F$_2$ppy)$_2$(CNC$_6$H$_2$Cl-4)(Cl)] (171.0 mg, 229.3μmol) was used instead of [Ir(ppy)$_2$(CNC$_6$H$_4$Cl-4)(Cl)] and dichloromethane-acetone (1:1, v/v) was used as eluent in column chromatography. Yield: 150 mg, 186.7 μmol; 81.4%. ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.59 (1H, d, J = 5.5 Hz, 6-pyridyl H's of F$_2$ppy), 8.29 (2H, m, two 3-pyridyl H's of F$_2$ppy), 7.72 (3H, m, two 4-pyridyl H's of F$_2$ppy and 6-pyridyl H's of N^C-Cl), 7.61 (2H, d, J = 8.4 Hz, 2,6-phenyl H's of N^C-Cl), 7.53 (1H, t, J = 7.0 Hz, 4-pyridyl H's of N^C-Cl), 7.47 (1H, d, J = 5.3 Hz, one 6-pyridyl H's of F$_2$ppy), 7.42 (1H, d, J = 8.2 Hz, 3-pyridyl H's of N^C-Cl), 7.20 (2H, d, J = 8.6 Hz, 3,5-phenyl H's of N^C-Cl), 6.99 (2H, m, two 5-pyridyl H's of F$_2$ppy), 6.79 (1H, s, NH), 6.57 (1H, t, J = 6.3 Hz, 5-pyridyl H's of N^C-Cl), 6.52 (1H, t, J = 10.6 Hz, 3-phenyl H's of F$_2$ppy), 6.47 (1H, t, J = 12.1 Hz, 3-phenyl H's of F$_2$ppy), 5.96 (1H, d, J = 7.4 Hz, 5-phenyl H's of F$_2$ppy), 5.86 (1H, d, J = 7.6 Hz, one 5-phenyl H's of F$_2$ppy). ^{13}C NMR (151 MHz, CDCl$_3$) δ 210.21 (carbene C), 176.75, 174.96, 166.24, 164.41, 163.07, 161.63, 161.12, 153.72, 148.68, 147.48, 139.56, 138.59, 137.12, 136.31, 128.44, 127.82, 127.31, 123.22, 123.15, 123.07, 122.93, 122.36, 121.42, 116.97, 115.91, 113.52, 113.43, 112.66, 112.55, 98.01, 96.92, 94.90, 94.17. ^{19}F NMR (565 MHz, $CDCl_3$) δ -107.66 (1F, d, J = 10.2 Hz, 4-phenyl F's of F_2ppy), -108.46 (1F, d, J = 9.4 Hz, 4-phenyl F's of F_2ppy), -109.87 (1F, d, J = 9.1 Hz, 2-phenyl F's of F_2ppy), -110.03 (1F, d, J = 10.3 Hz, 2-phenyl F's of F_2ppy). Positive-ion ESI-MS: *m/z*: 804.4 $[M + H]^+$. IR (KBr disc): υ/cm^{-1}: 3391, 1604 (N–H), 1376 (C–N). Anal. Calcd for $C_{34}H_{21}ClF_4IrN_5{\cdot}CH_3OH$ (835.27): C, 50.33; H, 3.02; N, 8.38. Found: C, 50.28; H, 2.78; N, 8.08.

Physical Measurements and Instrumentation. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AVANCE III HD Ascend 600 MHz FT-NMR spectrometer. Chemical shifts (δ, ppm) were reported relative to tetramethylsilane (Me_4Si). IR spectra were obtained from KBr discs by using a Perkin-Elmer Spectrum 100 FTIR spectrophotometer. Raman spectra were recorded on a Bayspec Agility 785/1064-nm Raman spectrometer. The excitation wavelength used for the experiments was 785 nm, with an excitation power of around 50 mW. All ESI mass spectra were recorded on a PE-SCIEX API 365 EX single quadrupole mass spectrometer. Elemental analyses of all compounds were performed on an Elementar Vario MICRO Cube elemental analyzer. Electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state emission at room temperature and at 77 K were recorded on Edinburgh Instruments FLS980 fluorescence spectrometer. Time-resolved emission and emission lifetime measurements were recorded on LP920 laser flash photolysis system using the third harmonic output (355 nm, 6-8 ns fwhm pulse width) of a Spectra-Physics Quanta-Ray Q-switched LAB-150 pulsed Nd:YAG laser as the excitation source. Solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with no less than four successive freeze pump-thaw cycles. Measurements of the EtOH/MeOH (4:1 v/v) glass samples at 77 K were carried out with a dilute EtOH/MeOH sample solutions contained in a quartz tube inside a liquid nitrogen-filled quartz optical Dewar flask. The neat films were prepared by drop casting 100 μL of a sample solution (5 mM) in dichloromethane-ethyl acetate on quartz plate with 1-cm circular recess and annealed at 80 °C for 16 hours prior to the study. The luminescence quantum yields of the solution emission were determined by using the optical-dilution method using aerated aqueous solution of $[Ru(bpy)_3]Cl_2$ (Φ_{em} = 0.04) as reference standard. [4] Luminescent quantum yields for solid state sample were determined using the integrating sphere assembly accessory (F-M01) of Edinburgh Instruments FLS980. Powder X-ray diffraction pattern were collected on a Bruker D2 PHASER X-ray powder diffractometer using Ni-filtered Cu-Kα radiation (λ = 1.540562 Å, Power = 300 W) with 2θ in the range of 10°–90° and a step-size of 0.036° at a fixed speed of *ca.* 0.2 s per step.

Computational Details. The DFT calculations were performed by GAUSSIAN 09 package, version B.01.[5][1] Ground state structures of the two proposed conformers (*trans*- and *cis*- form) of complex **6** were optimized using B3LYP functional.[6] A combination of 6-31+G(d) [for elements H, C, N, O, F and Cl] and LANL2DZ[7] (for Ir) basis set was employed. Vibrational analysis was done after optimization to ensure that the structures are located at minima of potential energy surfaces. The solvent effects were taken account by the polarized continuum model with integral equation formulism. (IEF-PCM).[8] The molecular surface area of the conformers were calculated by rolling a probe sphere of 1.4 Å over the van der Waals surface of the optimized structures.[9] For the structures of triplet states of the two conformers of **1**, they were optimized using Perdew-Burke-Ernzerhof (PBE) functional.[10]

X-ray Crystal Structure Determination. The crystal structures were determined on a Xcalibur, Sapphire3, Gemini Ultra diffractometer using graphite monochromatized Cu-K$_\alpha$ (λ = 1.54178 Å) or Mo-K$_\alpha$ (λ = 0.7107 Å) radiation. The structures were solved by direct methods employing SHELXL-97 program[11] on PC. Ir and many non-H atoms were located according to direct methods. The positions of other non-H atoms were found after successful refinement by full-matrix least-squares using SHELXL-97 program on PC.[11] All non-H atoms were refined anisotropically in the final stage of least-squares refinement. The positions of hydrogen atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated carbon atoms, and participated in the calculation of final *R*-indices.

2. Data for single-crystal X-ray crystallography

Table S1. Crystal and structure determination data for **1** and **6**.

	1	**6**
Formula	$C_{34}H_{25}ClIrN_5\cdot 0.5(C_4H_8O_2)$	$C_{34}H_{21}ClF_4IrN_5\cdot 0.5(C_4H_{10}O)$
Molecular weight	775.29	840.27
T / K	193	193
a / Å	10.2446 (3)	10.2000 (2)
b / Å	11.5443 (4)	11.7287 (4)
c / Å	14.1376 (4)	14.3157 (5)
α / deg	108.745 (1)	108.612 (3)
β / deg	91.946 (1)	108.612 (2)
γ / deg	105.858 (1)	106.771 (3)
V/ Å^3	1509.39 (8)	1539.94 (8)
Crystal color	Yellow	Yellow
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
$F(000)$	764	822
D_c / gcm^{-3}	1.706	1.812
Crystal dimensions / mm	0.42 × 0.12 × 0.03	0.26 × 0.12 × 0.01
λ / Å	0.71073	1.54178
μ / mm^{-1}	4.55	9.73
Collection range	$2.4 \leq \theta \leq 30.5°$ (h: −14 to 14; k: −16 to 9; l: −20 to 20)	$3.3 \leq \theta \leq 68.2°$ (h: −12 to 12; k: −14 to 13; l: −17 to 17)
Completeness to theta	98.3%	99.3%
No. of data collected	20391	10902
No. of unique data	9085	5608
No. of data used in refinement, m	8428	5361
No. of parameters refined, p	426	453
R^a	0.023	0.023
wR^a	0.052	0.059
Goodness-of-fit, S	1.02	1.04
Maximum shift, $(\Delta/\sigma)_{\max}$	0.004	0.001
Residual extrema in final difference map, eÅ^{-3}	+0.96, −1.86	+2.19, −0.70

$^a w = 1 / [\sigma^2(F_o^2) + (ap)^2 + bP]$, where $P = [2F_c^2 + \mathrm{Max}(F_o^2,0)] / 3$

Table S2. Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for **1**.

Ir(1)–N(5)	2.0404 (18)	Ir(1)–N(4)	2.0474 (18)
Ir(1)–N(3)	2.121 (2)	Ir(1)–C(13)	2.065 (2)
Ir(1)–C(24)	2.004 (2)	Ir(1)–C(7)	2.052 (2)
C(7)–N(1)	1.373 (3)	C(7)–N(2)	1.327 (3)
C(24)–Ir(1)–N(5)	80.27 (8)	N(4)–Ir(1)–C(13)	79.51 (8)
N(3)–Ir(1)–C(7)	75.25 (8)	N(3)–Ir(1)–C(24)	169.60 (8)
C(13)–Ir(1)–C(7)	173.85 (9)	N(5)–Ir(1)–N(4)	170.52 (8)
Ir(1)–C(7)–N(2)	120.41 (16)	Ir(1)–C(7)–N(1)	121.44 (16)
N(1)–C(7)–N(2)	118.1 (2)		

Table S3. Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for **6**.

Ir(1)–N(1)	2.046 (3)	Ir(1)–N(2)	2.053 (3)
Ir(1)–N(3)	2.118 (3)	Ir(1)–C(11)	2.008 (3)
Ir(1)–C(22)	2.075 (3)	Ir(1)–C(28)	2.074 (3)
C(28)–N(5)	1.367 (4)	C(28)–N(4)	1.319 (4)
C(22)–Ir(1)–N(2)	79.80 (12)	N(1)–Ir(1)–C(11)	80.40 (12)
N(3)–Ir(1)–C(28)	75.63 (12)	N(3)–Ir(1)–C(11)	171.04 (11)
C(22)–Ir(1)–C(28)	173.58 (12)	N(1)–Ir(1)–N(2)	171.69 (10)
Ir(1)–C(28)–N(5)	121.0 (2)	Ir(1)–C(28)–N(4)	119.6 (2)
N(5)–C(28)–N(4)	119.5 (3)		

3. NMR spectra of selected compounds

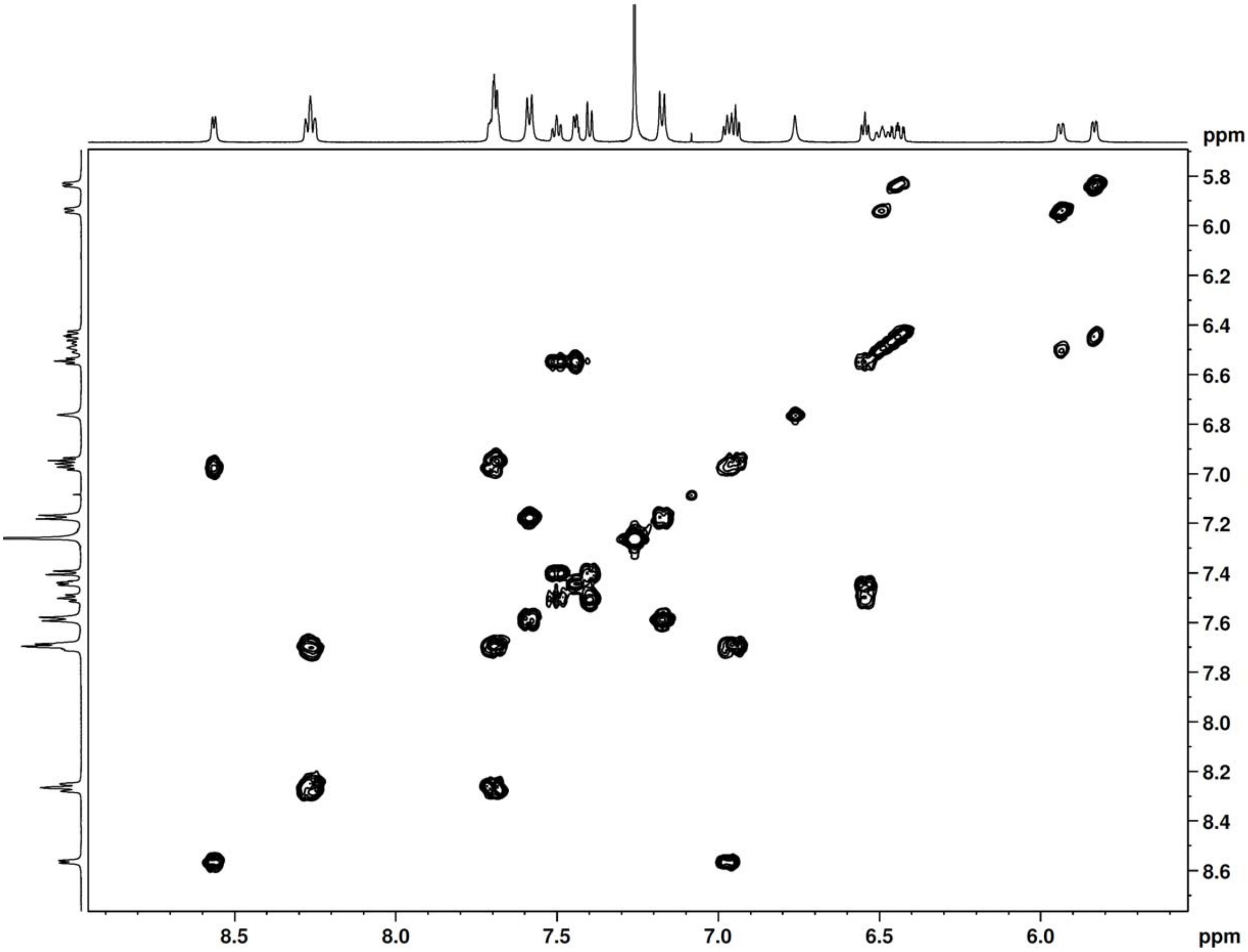


Figure S1 ^{1}H-^{1}H COSY NMR spectrum of **6** in $CDCl_3$.

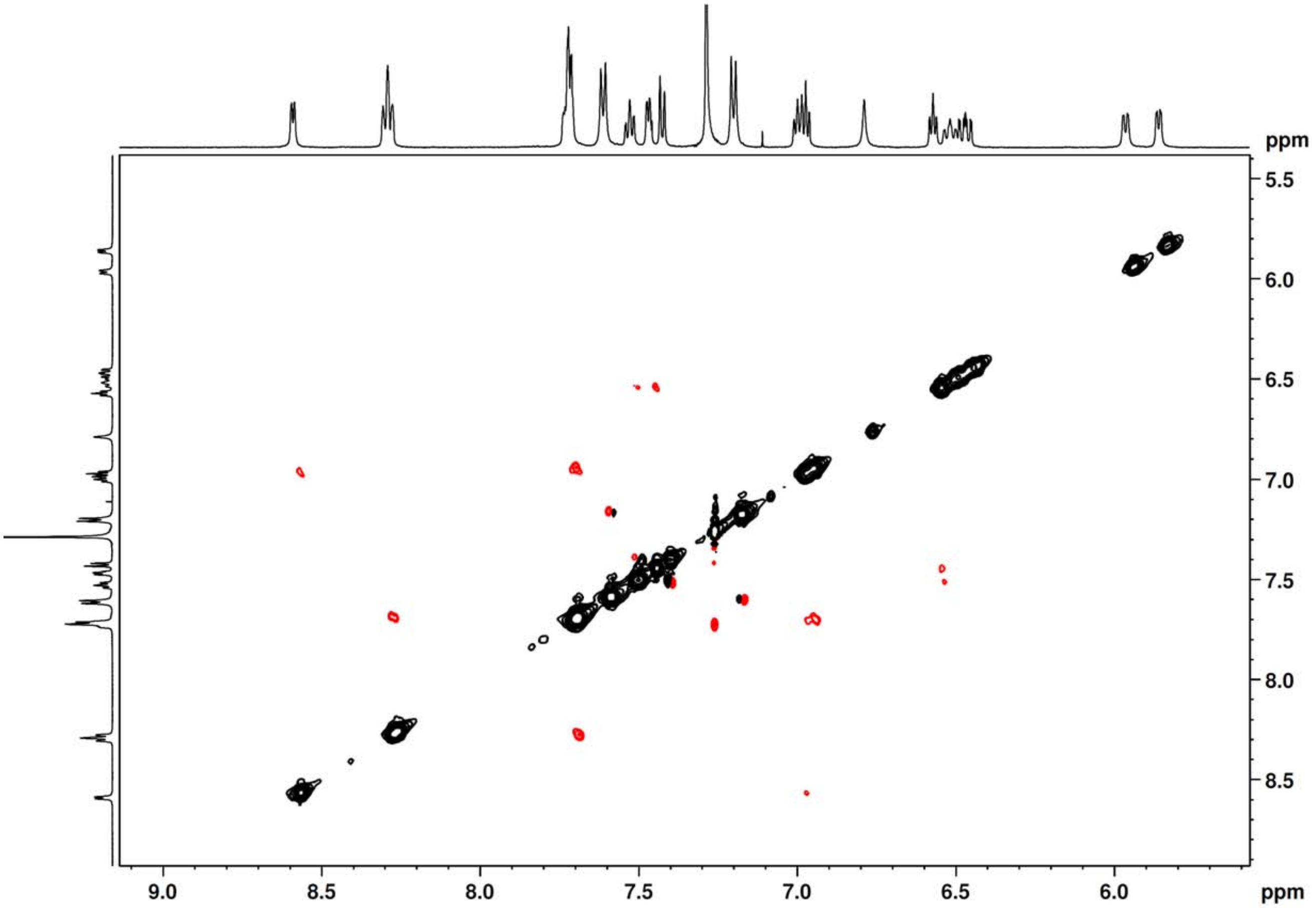


Figure S2. ^{1}H-^{1}H ROESY NMR spectrum of **6** in CDCl$_3$.

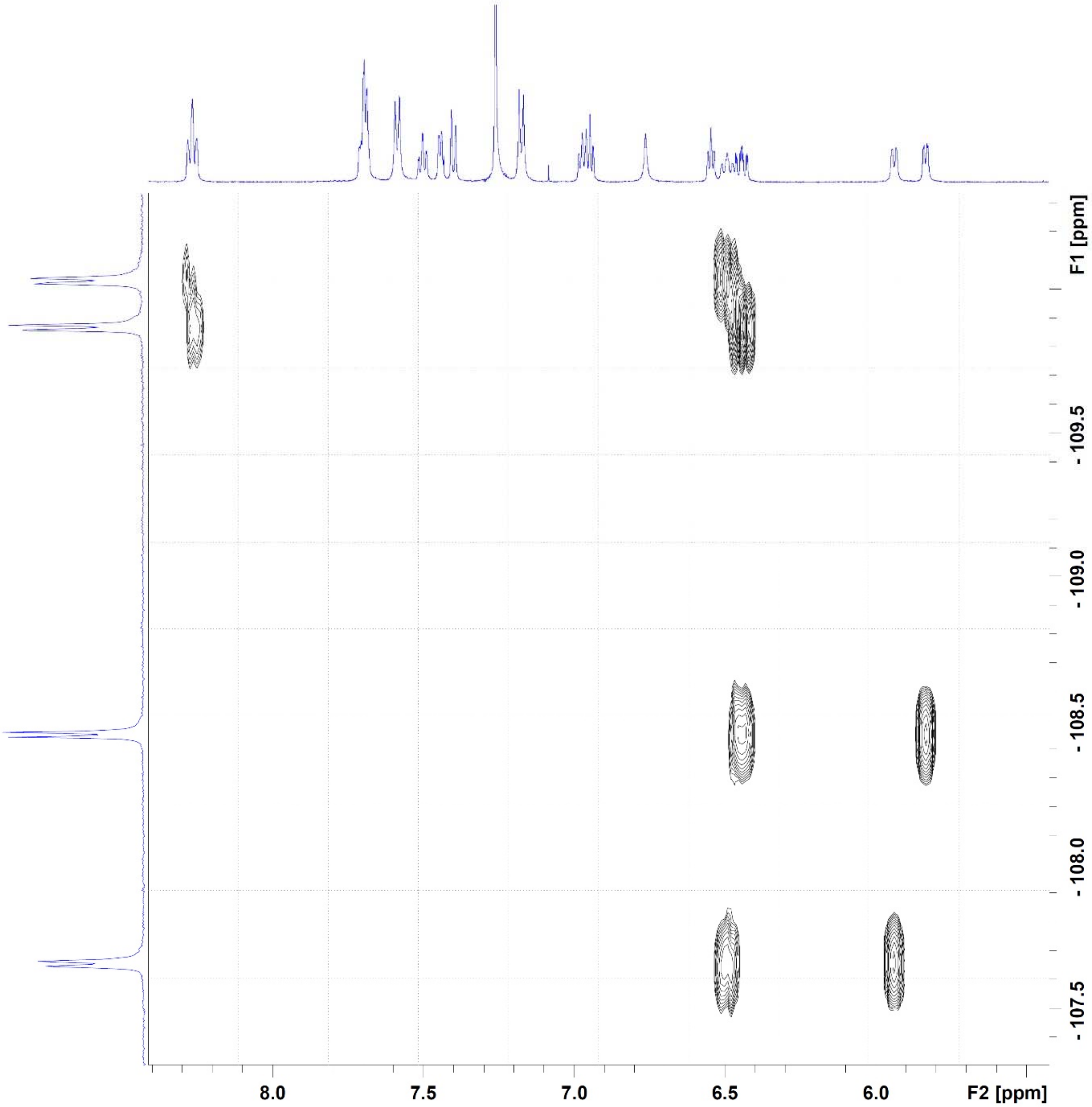


Figure S3. ^{1}H-^{19}F COSY NMR spectrum of **6** in $CDCl_3$.

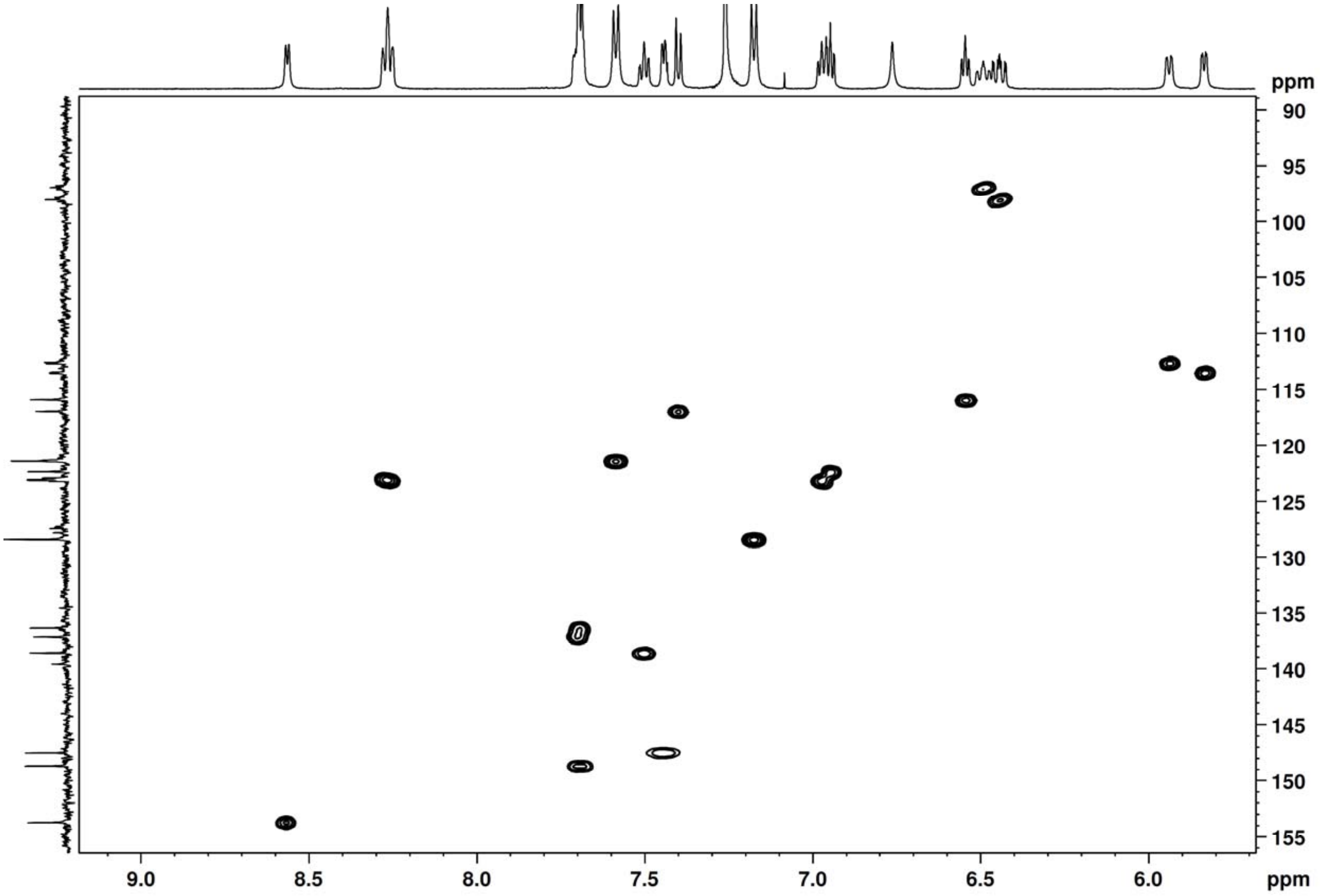


Figure S4. ^{13}C-^{1}H HSQC NMR spectrum of **6** in $CDCl_3$.

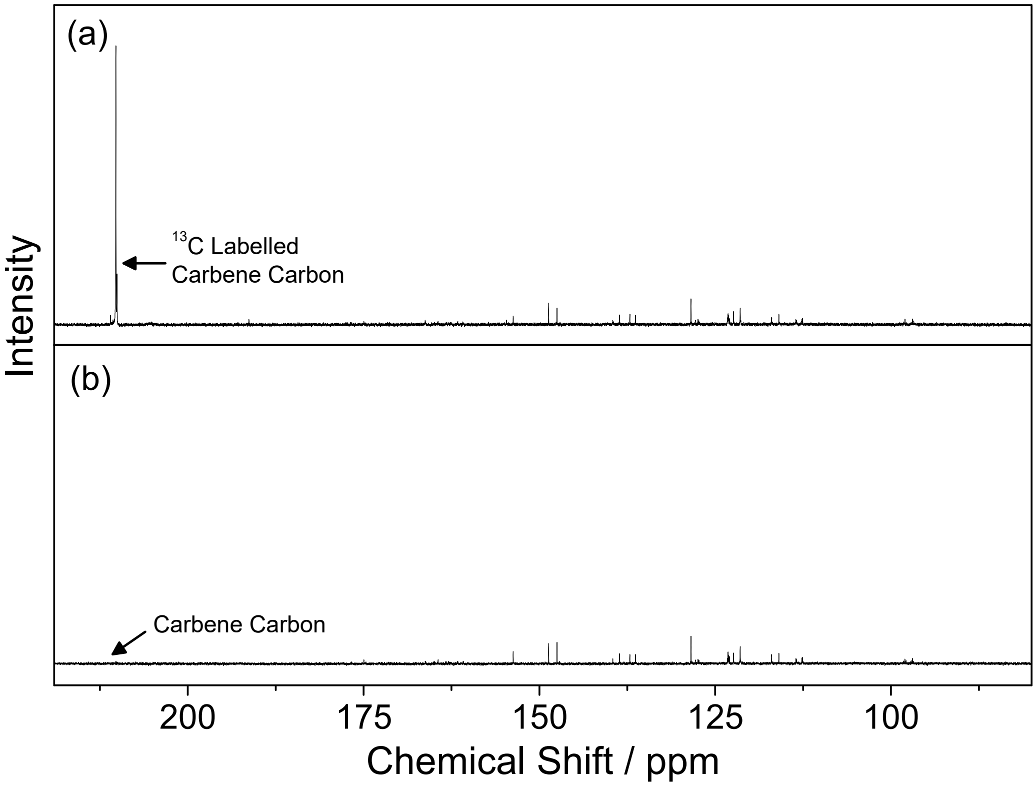


Figure S5. ^{13}C NMR spectra of (a) **6** with ^{13}C-labelled carbene carbon and (b) **6** in $CDCl_3$.

4. UV-Vis absorption spectra of complexes 1 – 6

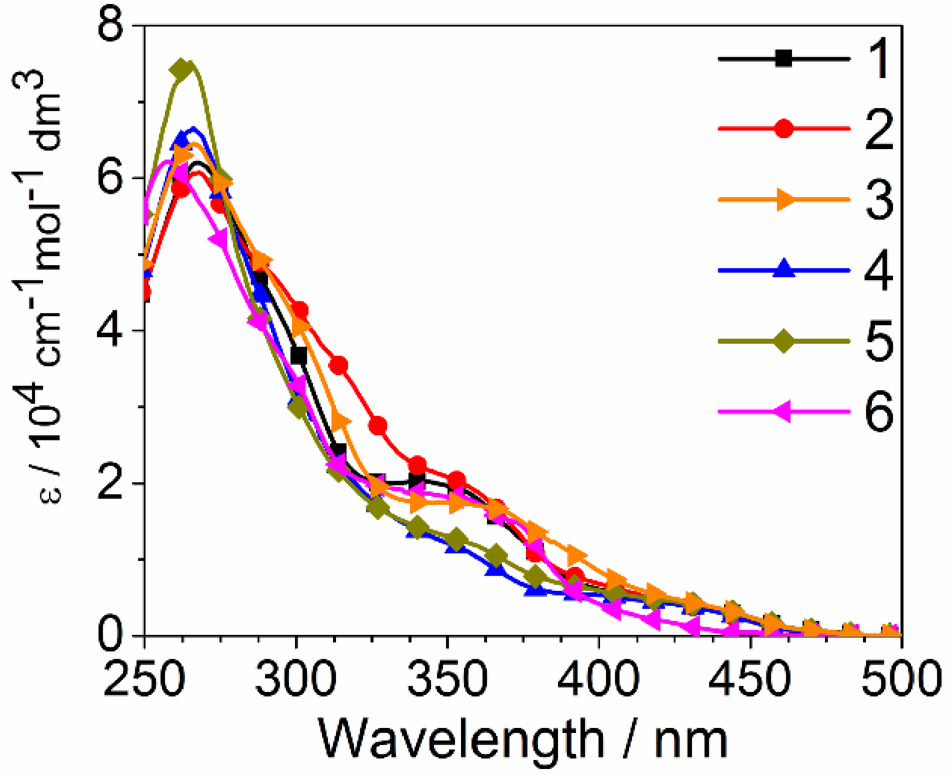


Figure S6. Overlaid UV-Vis absorption spectra of **1–6** in dichloromethane solution at 298 K.

5. DFT calculation on the triplet states of 1

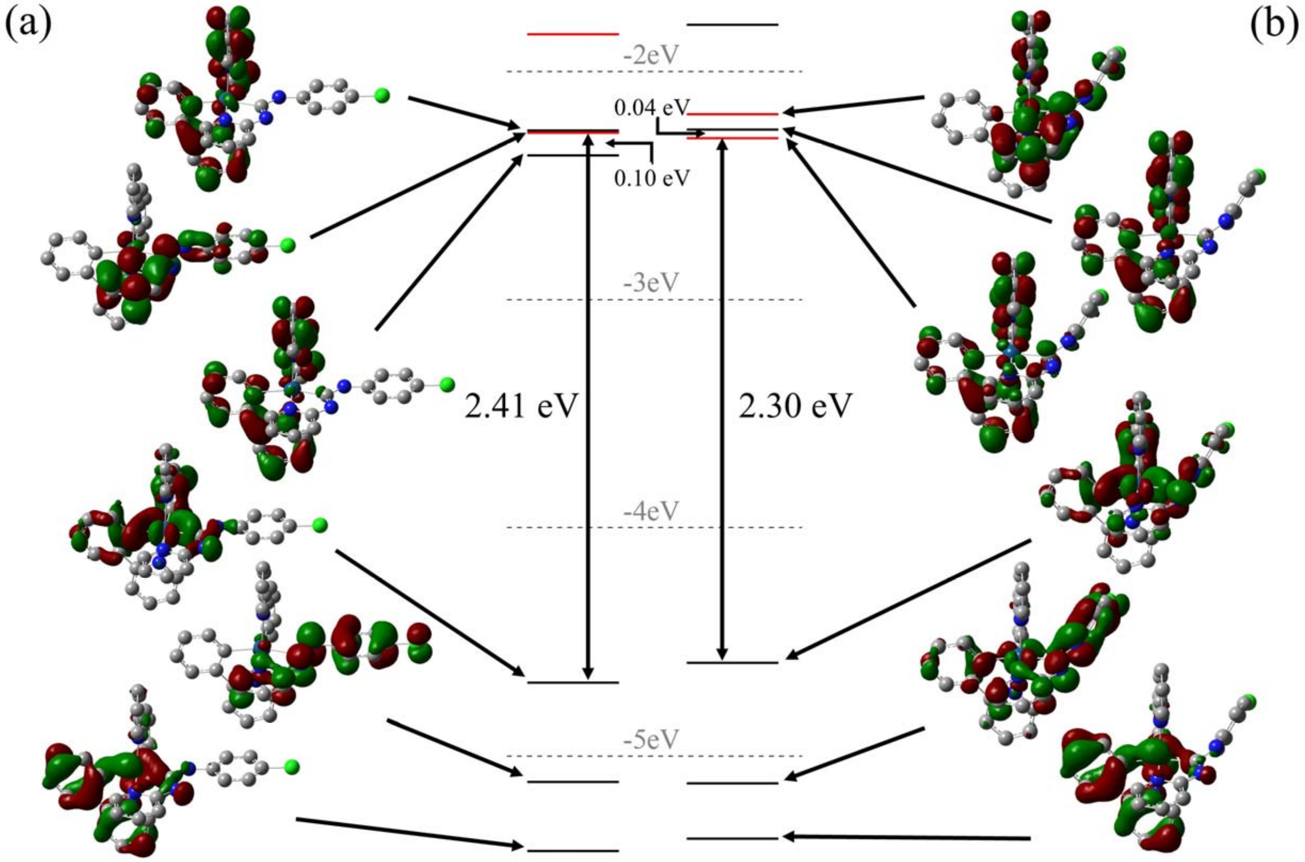


Figure S7. Calculated orbital energy levels and contour maps of the selected molecular orbitals of the triplet state of (a) *trans-* and (b) *cis-* form of **1**. The red lines denote orbitals with significant contribution from π*(N^C$_{\text{carbene}}$) orbital.

6. Selected solid-state emission spectra showing the mechanochromic properties

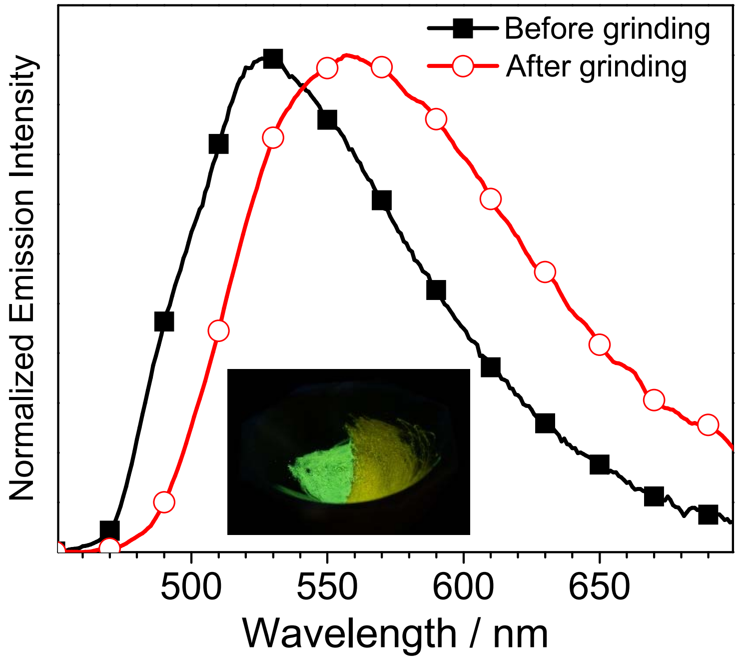


Figure S8. Overlaid solid state emission spectra of **1** before and after grinding. The inset shows the photograph taken under 365-nm illumination showing the emission of unground and ground solids.

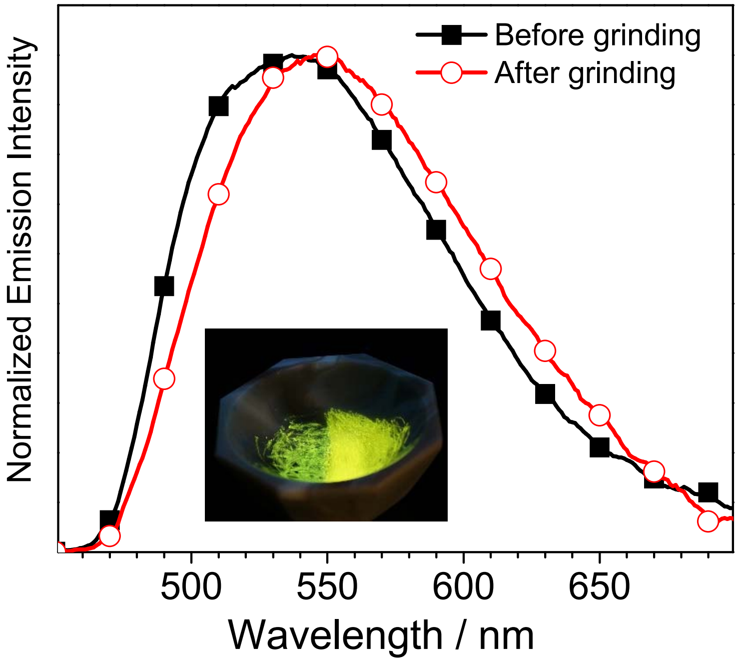


Figure S9. Overlaid solid state emission spectra of **2** before and after grinding. The inset shows the photograph taken under 365-nm illumination showing the emission of unground and ground solids.

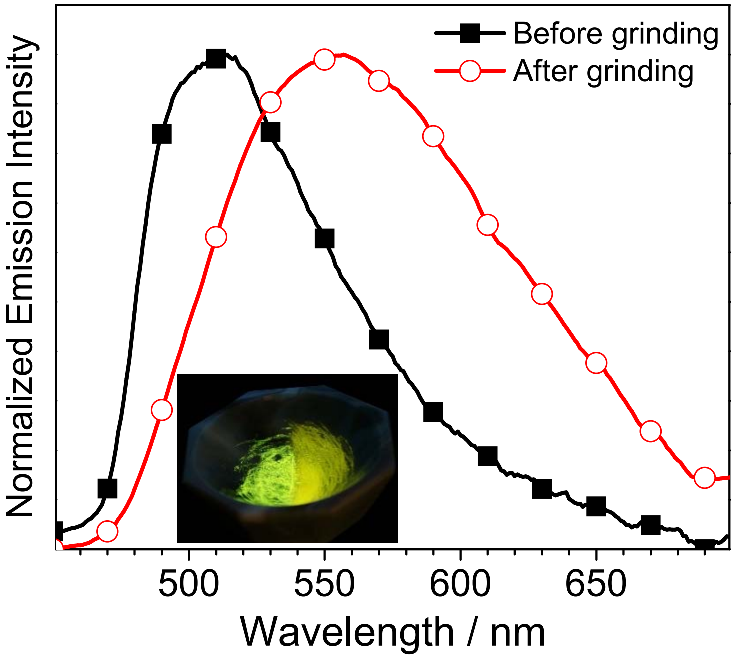


Figure S10. Overlaid solid state emission spectra of **3** before and after grinding. The inset shows the photograph taken under 365-nm illumination showing the emission of unground and ground solids.

7. Raman spectra of 6 and their assignments

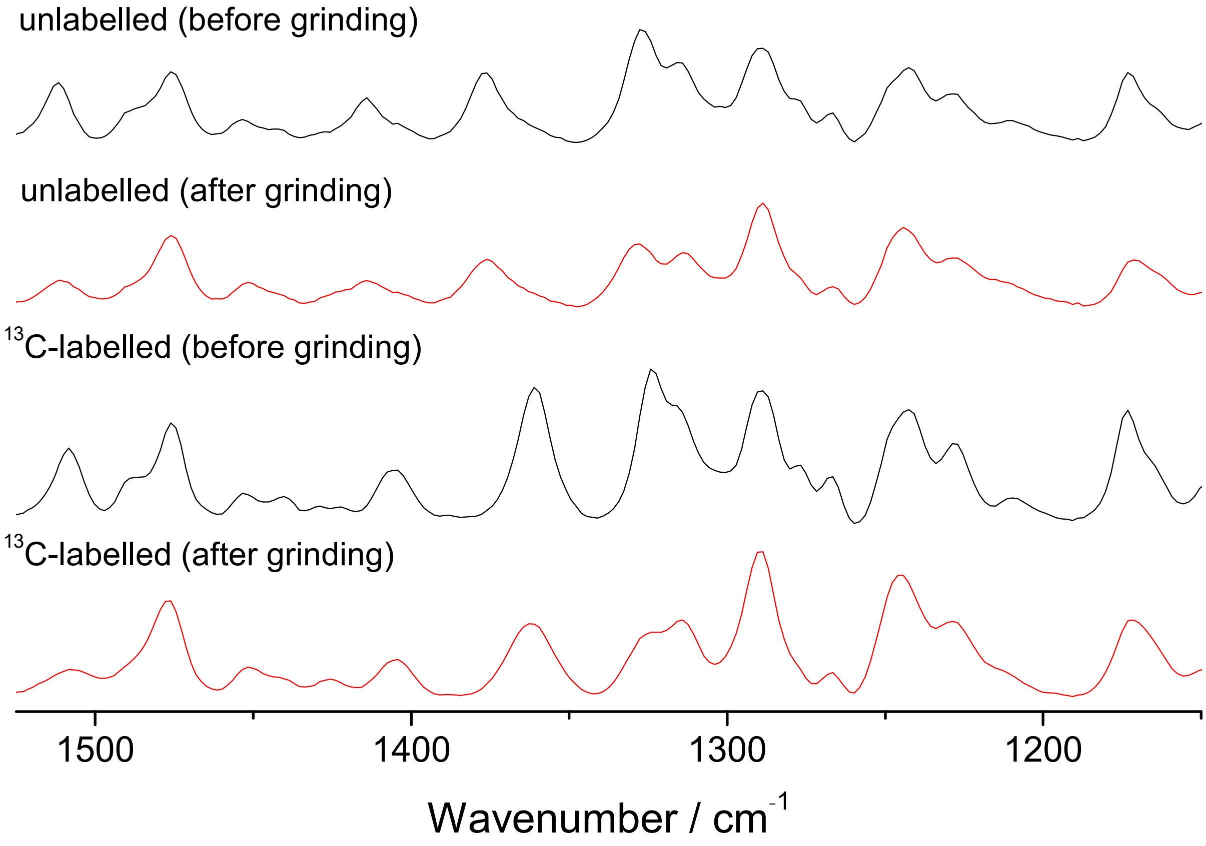
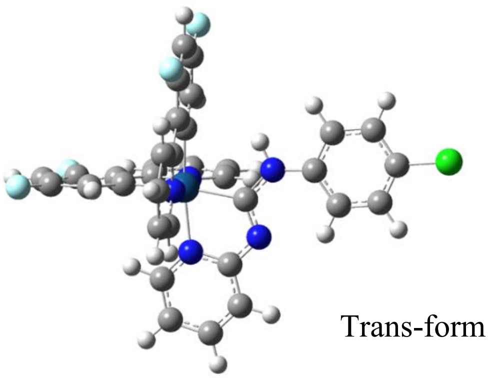
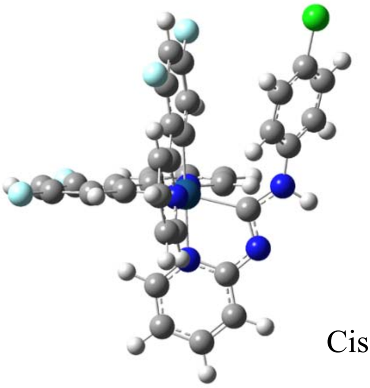


Figure S11. Raman spectra of complex **6** before (black) and after (red) grinding.

Table S4. Major Raman bands identified in the difference Raman spectra (Figure 6, calculated from Raman signals of the ground solid – Raman signals of unground solid) of **6** and their assignments using DFT-optimized geometries of two possible conformers.



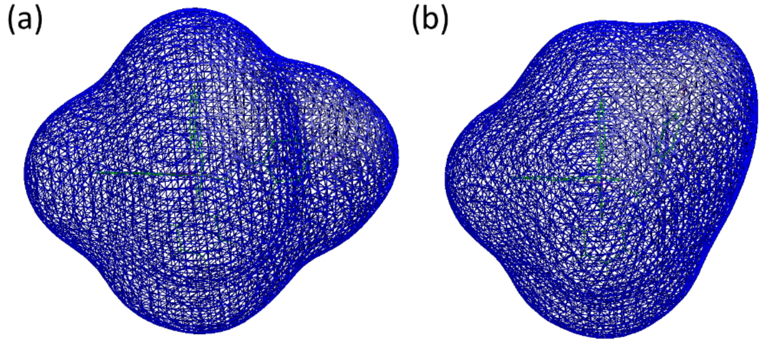
Trans-form



Cis-form

Negative peak (exp.) / Trans-form (calc.)				
6 /cm^{-1}	**6 / cm^{-1} (calc.)**	**^{13}C-labelled 6 /cm^{-1}**	**^{13}C-labelled 6 /cm^{-1} (calc.)**	**Assignment**
1512	1508	1508	1505	N-H bending (carbene)
1414	1397	1407	1391	carbene C=N str. + C-H bending (4-Cl-C$_6$H$_4$-)
1378	1360	1361	1344	carbene C=N str.
1326	1318	1324	1312	C-H bending (4-Cl-C$_6$H$_4$-) + carbene C=N str.
1276	1273	1276	1273	C-H bending (ppy)
1175	1161	1175	1161	C-H bending (4-Cl-C$_6$H$_4$-)
Positive peak (exp.) / Cis-form (calc.)				
6 /cm^{-1}	**6 / cm^{-1} (calc.)**	**^{13}C-labelled 6 /cm^{-1}**	**^{13}C-labelled 6 /cm^{-1} (calc.)**	**Assignment**
1500	1489	1497	1487	N-H bending (carbene) + C-H bending (4-Cl-C$_6$H$_4$-)
1426	1422	1426	1421	N-H bending (carbene) + C-H bending (py)
1389	1363	1373	1356	carbene C=N str.
1289	1275	1289	1275	C-H bending (ppy)
1246	1237/1239	1247	1237/1239	C-H bending (ppy)

8. Calculated van der Waals surface of the *trans*- and *cis*- forms of 6



trans- *cis*-

Surface Area: 824.5 Å^2 800.4 Å^2

Figure S12. Calculated van der Waals surfaces of the *trans*- and *cis*- isomers of **6**.

9. Data of X-ray Crystallography of [6-H]OTf

Table S5. Crystal and structure determination data for [**6-H**]OTf

	[**6-H**]OTf
Empirical formula	$C_{35}H_{23}O_{3.5}SClIrN_5F_7$
*M*r	962.29
T, [K]	173 (2)
a, [Å]	18.7077 (2)
b, [Å]	9.02641 (11)
c, [Å]	21.5017 (3)
α, [deg]	90
β, [deg]	109.0463 (14)
γ, [deg]	90
V, [Å^3]	3232.09 (7)
Crystal color	Yellow
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	4
F(000)	1876
D_c [g/cm^3]	1.862
Crystal dimensions [mm]	0.31 × 0.22 × 0.02
λ [Å]	1.54178
μ [mm^{-1}]	9.579
Collection range	4.252° ≤ θ ≤ 68.243° (*h*: -22 to 22, *k*: -9 to 10, *l*: -25 to 24)
Completeness to theta	99.7%
No. of data collected	14210
No. of unique data	6265
No. of data used in refinement, *m*	482
R^a	0.0267
wR^a	0.0609
Goodness-of-fit, *S*	1.050
Maximum shift, $(\Delta/\sigma)_{max}$	0.003
Residual extrema in final difference map, eÅ^{-3}	+0.942, -0.943

10. Mechanochromism in diluted solid sample

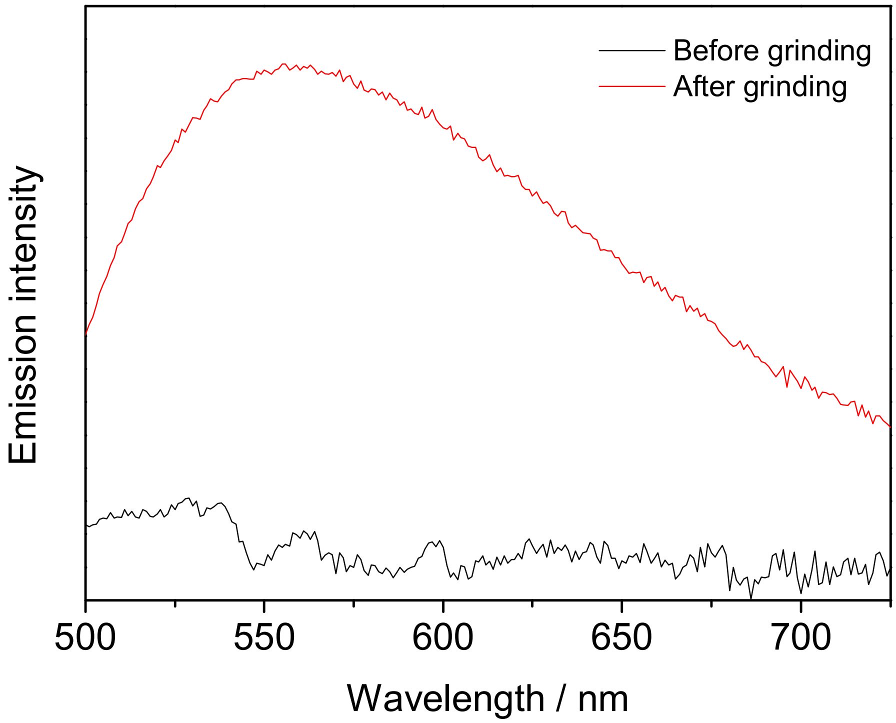


Figure S13. Overlaid emission spectra of unground (black) and ground (red) dilute solid sample of **6** doped in cellulose propionate (w/w, 10%) with 475-nm excitation to selectively excite the *cis*-form of **6**.

11. Reversibility of the mechanochromism

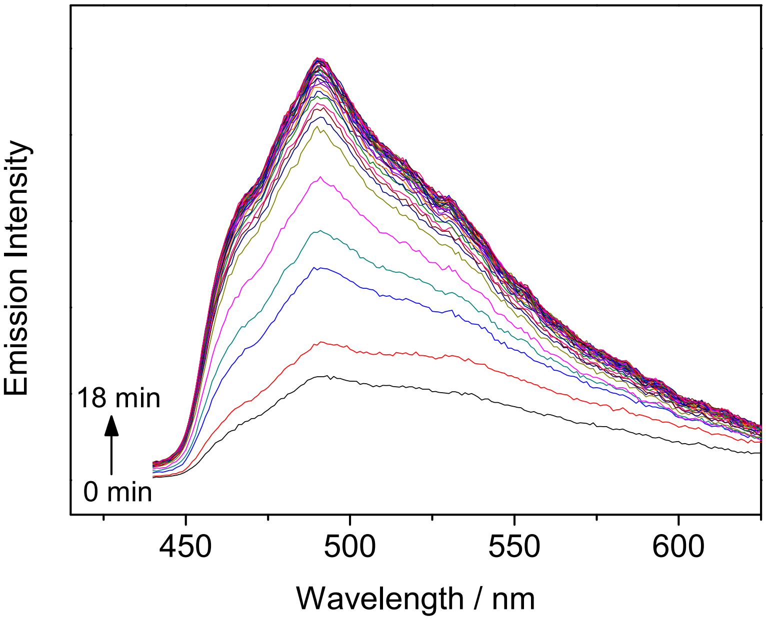


Figure S14. Emission spectral changes of the ground film upon exposure to ethyl acetate vapor.

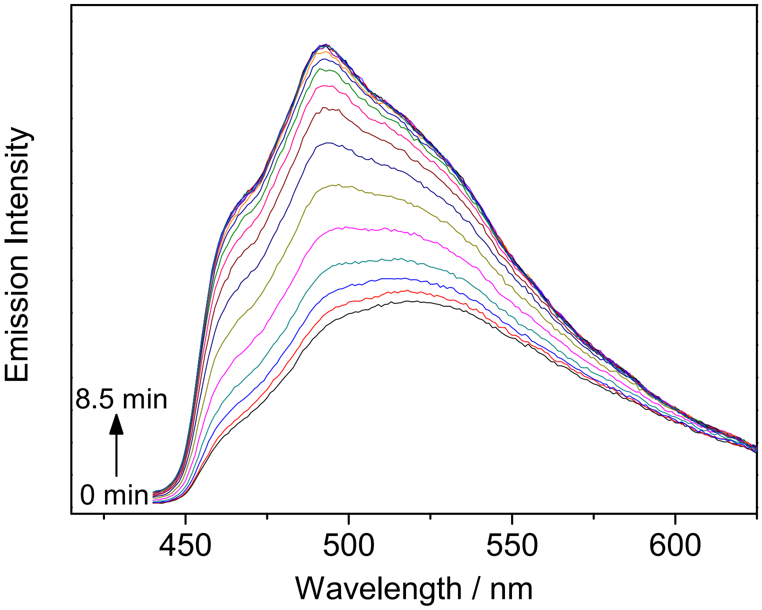


Figure S15. Emission spectral changes of the ground film upon exposure to n-hexane vapor.

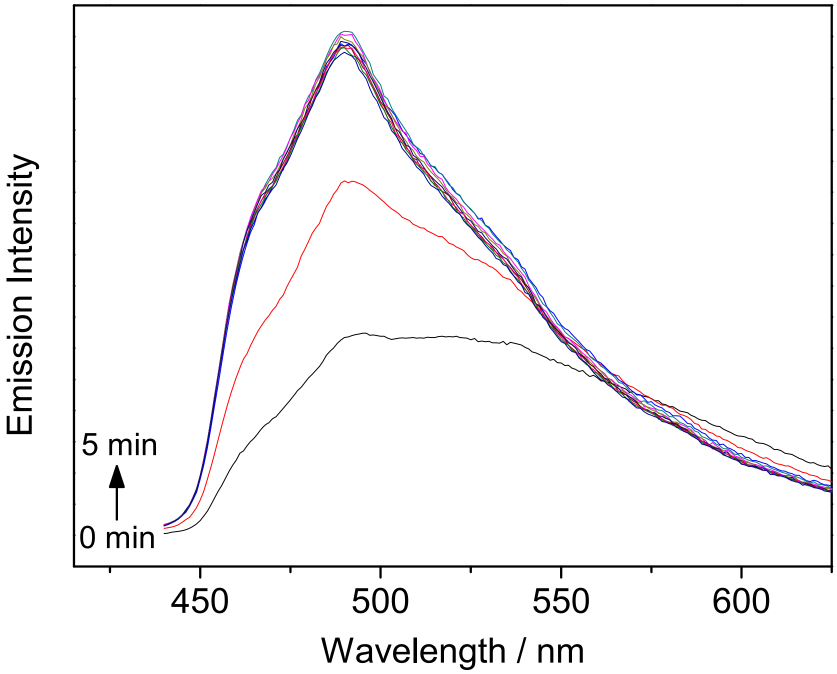


Figure S16. Emission spectral changes of the ground film upon exposure to chloroform vapor.

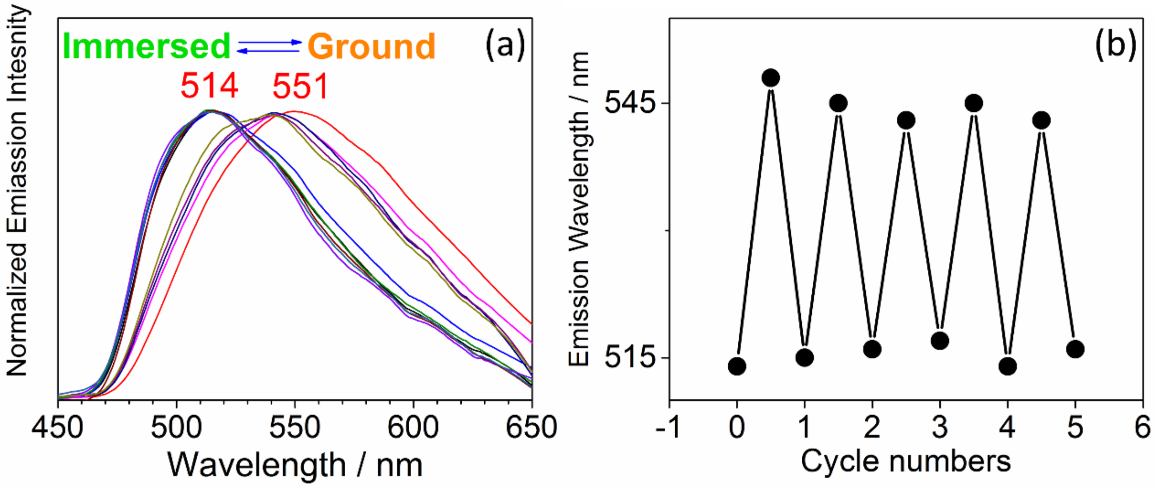


Figure S17. (a) Emission spectra of neat film of **4** on a quartz plate upon grinding and immersion in ethyl acetate for 5 cycles. (b) Switching of the emission maxima in grinding–immersion cycles.

11. References

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