Electronic Supporting Information for:

Solvent-Induced Configuration Mixing and Triplet Excited State Inversion Exemplified in a Pt(II) Complex

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Experimental Procedures

General: All reactions were carried out under an inert and dry argon atmosphere using standard techniques. Anhydrous CH_2Cl_2, diisopropylamine and triethylamine suitable for synthesis were freshly distilled over CaH_2. All other reagents from commercial sources were used as received.

^{1}H NMR and ^{13}C-{^{1}H} NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer. All chemical shifts are referenced to the residual solvent signals previously referenced to TMS and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). ^{31}P NMR spectra were run on a Varian VXR-400 spectrometer and chemical shifts were related to external 85% H_3PO_4. EI mass spectra (70 eV) were measured in-house using a direct insertion probe in a Shimadzu QP5050A spectrometer. FT-IR spectra were measured by a ThermoNicolet IR 200 spectrometer.

Preparations: [1,2-Bis-(dicyclohexylphosphino)ethane platinum dichloride],[1] 1-ethynyl-4-((4-(phenylethynyl)phenyl)ethynyl)benzene,[2] [4,4'-di(*tert*-butyl)-2,2'-bipyridine platinum dichloride],[3] and Pt(dbbpy)(C≡ C-Ph)$_2$ **(2)**[4,5] were synthesized according to the literature procedures and yielded satisfactory mass and ^{1}H NMR spectra.

Complex 1. A Schlenk flask was charged with [4,4'-di(*tert*-butyl)-2,2'-bipyridine platinum dichloride] (50.0 mg, 9.35 x 10^{-2} mmol), 1-ethynyl-4-((4-(phenylethynyl)phenyl)ethynyl)benzene (70.7 mg, 0.23 mmol), CH_2Cl_2 (50 mL) and *i*-Pr_2NH (5mL). The solution was Argon degassed for 30 min. CuI (0.9 mg, 4.67 x 10^{-3} mmol) was added, the solution was stirred at room temperature for 12 h, and then the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel, eluting with CH_2Cl_2-Petroleum Ether (v/v 20/80) to CH_2Cl_2-Petroleum Ether (v/v 80/20) to give 74.9 mg (75%) of **1** as a yellow solid after recrystallization in a mixture of CH_2Cl_2/*n*-Hexanes; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 9.96 (d, ^3J = 6.1 Hz, 2H), 7.96 (d, ^3J = 1.9 Hz, 2H), 7.61 (dd, ^3J = 6.1 Hz, ^4J = 1.9 Hz, 2H), 7.55-7.48 (m, 16H), 7.44-7.40 (m, 4H), 7.37-7.34 (m, 6H), 1.46 (s, 18H); FT-IR (KBr, cm^{-1}): 2963, 2107 ($\nu_{C\equiv C}$), 1619, 1591, 1511, 1415, 1364, 1252, 833, 731; ES-MS *m*/*z* (nature of the peak, relative intensity): 1066.7 ($[M+H]^+$, 100); Anal. Calcd for $C_{62}H_{46}N_2Pt$: C, 74.35; H, 4.73; N, 2.63. Found: C, 74.12; H, 4.51; N, 2.53.

Complex 3. A Schlenk flask was charged with [1,2-Bis-(dicyclohexylphosphino)ethane platinum dichloride] (50.0 mg, 7.26 x 10^{-2} mmol), 1-ethynyl-4-((4-(phenylethynyl)phenyl)ethynyl)benzene (54.9 mg, 0.18 mmol), CH_2Cl_2 (40 mL) and *i*-Pr_2NH (5mL). The solution was Argon degassed for 30 min. CuI (0.7 mg, 3.63 x 10^{-3} mmol) was added, the solution was stirred at room temperature for 12 h, and then the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel, eluting with CH_2Cl_2-Petroleum Ether (v/v 20/80) to CH_2Cl_2-Petroleum Ether (v/v 70/30) to give 79 mg (89%) of **3** as a white solid after recrystallization in a mixture of CH_2Cl_2/*n*-Hexanes; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.55-7.48 (m, 12H), 7.37-7.34 (m, 14H), 2.33-2.22 (m, 8H), 1.82-1.60 (m, 20H), 1.33-1.21 (m, 16H); 31P{^{1}H} (161.9 MHz, $CDCl_3$): δ 62.6 (s), 62.6 (d, ^1J = 2263 Hz); FT-IR (KBr, cm^{-1}): 2923, 2848, 2094 ($\nu_{C\equiv C}$), 1591, 1510, 1442, 1212, 1175, 1003, 831, 750; ES-MS *m*/*z* nature of the peak, relative intensity): 1220.6 ($[M+H]^+$, 100); Anal. Calcd for $C_{62}H_{46}N_2Pt$: C, 72.83; H, 6.11. Found: C, 72.59; H, 5.81.

Photophysical Measurements. UV-VIS absorption spectra were measured with a Varian 50 Bio spectrophotometer, accurate to ± 2 nm. Steady-state photoluminescence spectra were obtained with a single photon counting spectrofluorimeter from PTI. Solutions prepared for all photophysical experiments were optically dilute (OD = 0.09-0.11 for steady-state photoluminescence and OD = 0.01 for emission lifetimes) and in spectroscopic grade solvents. All luminescence samples in 1 cm^2 anaerobic quartz cells (Starna Cells) were deoxygenated with solvent-saturated argon for at least 20 minutes prior to measurement.[6,7] Emission lifetimes were measured using a nitrogen-pumped broadband dye laser (PTI GL-3300 N_2 laser, PTI GL-301 dye laser, C-460 dye) as the excitation source. Pulse energies were typically attenuated to ~ 50 μJ/pulse, measured with a Molectron Joulemeter (J4-05). An average of 64 transients was collected, transferred to a computer, and processed using Origin 7.5. Goodness of fit was established by inspection of residuals. Transient absorption spectra were collected on an Andor iStar iCCD detector equipped with a Micro HR Horiba/JY spectrograph (300 gr/mm, 500 nm blaze grating). Excitation at 450 nm (2mJ/pulse) from a computer-controlled Nd:YAG laser/OPO system from Opotek (Vibrant LD 355 II) operating at 10 Hz was directed to the sample with an optical absorbance of 0.4 at the excitation wavelength. The white-light probe (Perkin Elmer) was a pulsed Xe flash pack oriented 90 degrees to the excitation beam. The camera and Xe flash lamp were synchronized through a DG535 digital delay generator (Stanford Research Systems) which was triggered from the laser (Kr flash lamp) output. All samples was prepared with spectroscopic grade solvents in 1 cm^2 anaerobic quartz cells (Starna Cells), degassed by argon for at least 35 minutes prior to the measurements and maintained under argon atmosphere throughout the experiment. All data were collected from the Andor software and processed in Origin 7.5.

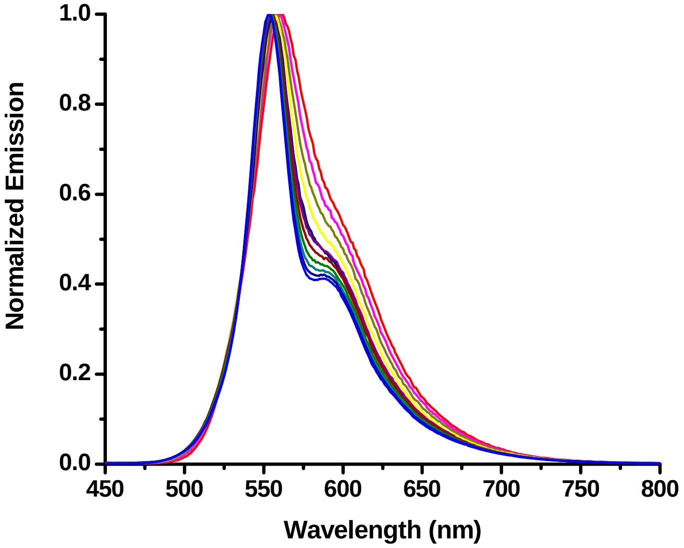


Figure S1. Emission spectra of **1** as a function of percent volume CH_2Cl_2 in benzene from 0% (red line) to 100% (blue line); all solutions are deaerated.

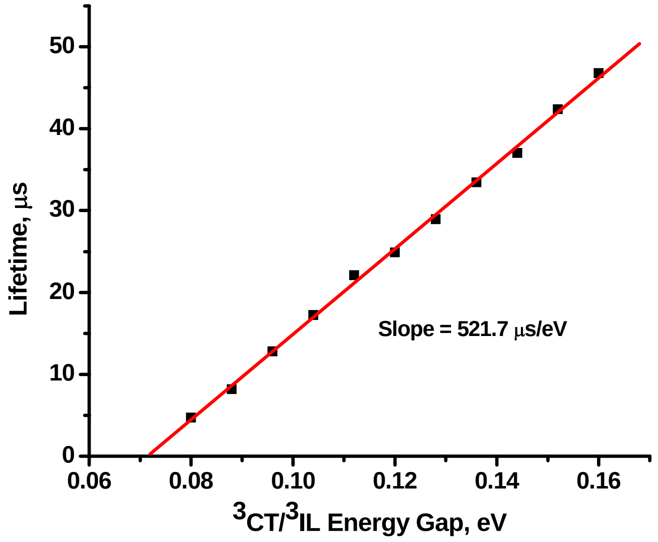


Figure S2. Changes in excited state lifetime of **1** plotted as a function of ^{3}CT/^{3}IL energy gap which changes with benzene/CH_2Cl_2 solvent composition. The energy gaps were estimated by measuring the emission spectra of **2** and **3** in identical solvent mixtures.

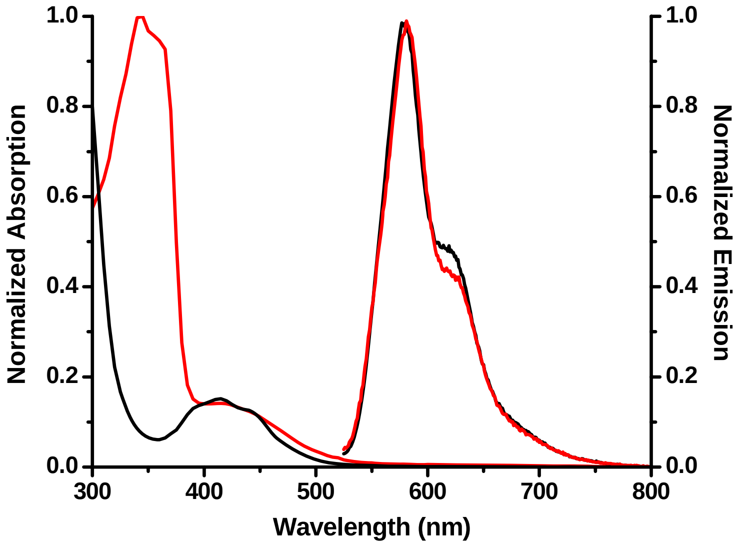


Figure S3. Absorption (left) and emission (right) spectra of **1** (red) and **2** (black) in deaerated *n*-hexanes doped with <1% CH_2Cl_2.

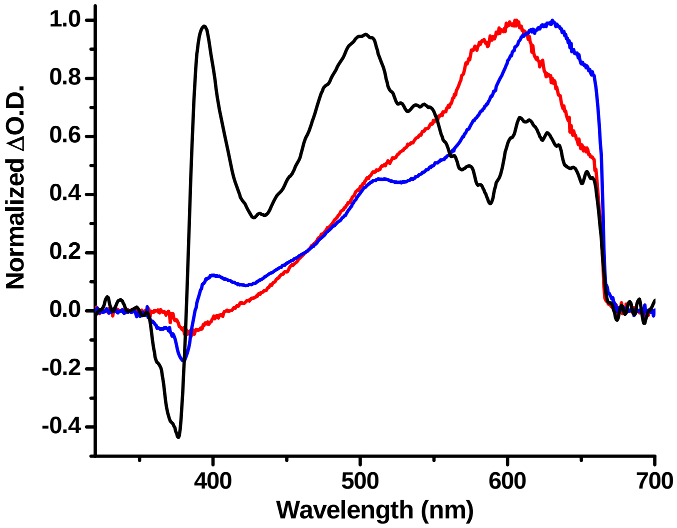
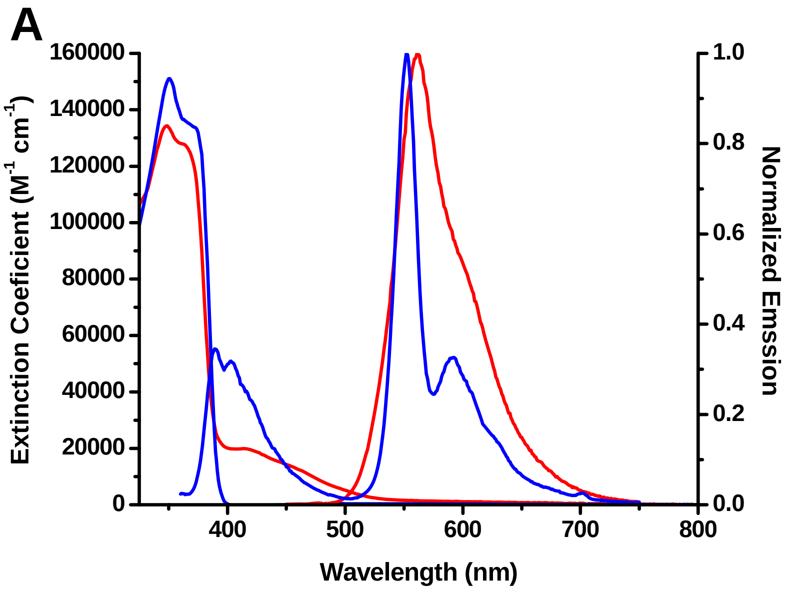


Figure S4. Normalized transient absorption difference spectra of **1** in deaerated *n*-hexanes doped with 5% benzene (black), benzene (blue) and CH_2Cl_2 (red) measured using 450±2 nm excitation promptly after the laser pulse.



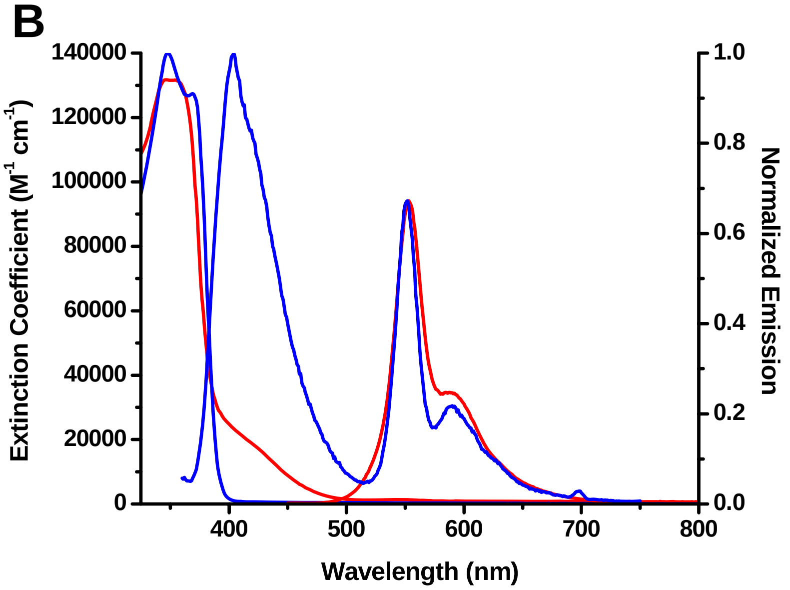


Figure S5. (A) Absorption (left) and emission (right) spectra of **1** (red) and **3** (blue) in deaerated benzene. (B) Absorption (left) and emission (right) spectra of **1** (red) and **3** (blue) in deaerated CH_2Cl_2.

SI References

1 S. M. ALQaisi, K. J. Galat, M. Chai, D. G. Ray, P. L. Rinaldi, C. A. Tessier, W. J. Youngs, *J. Am. Chem. Soc.*, 1998, **120**, 12149.

2 T. Ljungdahl, K. Pettersson, B. Albinsson, J. Martensso, *Eur. J. Org. Chem.*, 2006, **14**, 3087.

3 K. D. Hodges, J. V. Rund, *Inorg. Chem.*, 1975, **14**, 525.

4 M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte, R. Eisenberg, *Inorg. Chem.*, 2000, **39**, 447.

5 S. Chan, W. Chan, Y. Wang, C. Che, K. Cheung, N. Zhu, *Chem. Eur. J.*, 2001**, 7**, 4180.

6 D. S. Tyson, F. N. Castellano, *J. Phys. Chem. A*, 1999**, 103**, 10955.

7 D. S. Tyson, K. B. Henbest, J. Bialecki, F. N. Castellano, *J. Phys. Chem. A*, 2001**, 105,** 8154.