Supplementary Information

Ultrafast Charge Transfer Dynamics in Supramolecular Pt(II) Donor-Bridge-Acceptor Assemblies: the Effect of Vibronic Coupling

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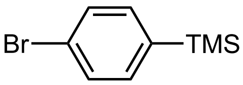
Analytical methods

MALDI mass spectra were obtained from a Bruker Reflex III instrument, utilising (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as a matrix. Electron ionisation (EI) mass spectra were recorded *via* a VG AutoSpec magnetic sector instrument. Elemental microanalysis for carbon, hydrogen and nitrogen was performed using a Perkin Elmer 2400 Series II CHNS/O system. Analysis for sulphur, bromine and iodine was carried out through the 'Schoniger Flask Combustion' technique.

Synthesis.

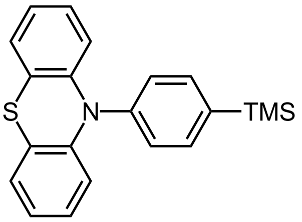
Synthesis of 1-bromo-4-trimethylsilyl-benzene [1-2]



1,4-Dibromobenzene (9.124 g, 38.67 mmol) in dry, deaerated Et_2O (60 ml) was cooled to -78 °C. To the slurry was added *n*-BuLi (15.5 ml, 2.5 M, 38.75 mmol) in small portions over a period of 15 minutes. The reaction mixture was stirred at -78 °C for 1.5 hours before the dropwise addition of chlorotrimethylsilane (5.9 ml, ρ = 0.856 g/ml, 46.48 mmol). The solution was allowed to warm to room temperature and stirred for a further 1.5 hours. H_2O (75 ml) was added and the organic layer removed. The aqueous phase was extracted with a further 1 x 50 ml Et_2O, with the combined organic phases then being washed with 1 x 25 ml saturated aqueous $NaHCO_3$, 1 x 25 ml brine and 1 x 50 ml H_2O. The organic layer was then dried over $MgSO_4$, filtered and the solvent removed to yield a colourless oil which was purified via column chromatography (SiO_2, Hexane). Yield = 7.652 g, 86 %.

^1H NMR ($CDCl_3$, 400 MHz): 0.30 (s, 9H), 7.41 (d, *J* = 8.24 Hz, 2H), 7.52 (d, *J* = 8.24 Hz, 2H). EI-MS: m/z = 230 (M^+, 27%), 215 (M^+-CH_3, 100%).

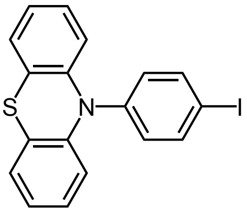
Synthesis of *N*-(4-trimethylsilylphenyl)-phenothiazine [3]



1-Bromo-4-trimethylsilyl-benzene (4.934 g, 21.52 mmol), phenothiazine (3.900 g, 19.57 mmol), ^{t}BuOK (3.286 g, 29.28 mmol) and Pd(dba)$_2$ (0.225 g, 0.39 mmol, 2 mol%) were suspended in dry, deaerated toluene (75 ml). P^{t}Bu$_3$ (0.1 ml, ρ = 0.834 g/ml, 0.41 mmol, 2.1 mol%) was added and the resulting yellow coloured suspension stirred at 60 °C for 66 hours. Evaporation of the solvent gave dark orange coloured crude material which was purified by column chromatography (SiO_2, 1:10 CH_2Cl_2 / Hexane) to afford the pure product as an off-white coloured solid. Yield = 5.549 g, 82 %.

^{1}H NMR (d$_6$-Acetone, 400 MHz): 0.34 (s, 9H), 6.27 (dd, *J* = 1.20, 8.16 Hz, 2H), 6.86 (td, *J* = 1.28, 7.43 Hz, 2H), 6.93 (td, *J* = 1.72, 7.43 Hz, 2H), 7.06 (dd, *J* = 1.64, 7.47 Hz, 2H), 7.39 (d, *J* = 8.16 Hz, 2H), 7.83 (d, *J* = 8.20 Hz, 2H). EI-MS: m/z = 347 (M^+, 100%). Anal. Calc. for $C_{21}H_{21}NSSi$ (%): C 72.57, H 6.09, N 4.03. Found (%): C 72.34, H 5.94, N 3.96.

Synthesis of *N*-(4-iodophenyl)-phenothiazine [3]



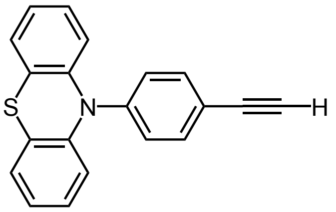
N-(4-Trimethylsilylphenyl)-phenothiazine (2.110 g, 6.07 mmol) was suspended in 3:1 (v/v) dry, deaerated MeCN / CH_2Cl_2 (40 ml) and cooled in ice to approximately 0 °C. A solution of iodine monochloride (3.125 g, 19.24 mmol) in dry, deaerated CH_2Cl_2 (40 ml) was added to the reaction vessel slowly in 4 x 10 ml portions over a period of 20 minutes. The resulting deep red coloured solution was stirred at 0 °C for 10 minutes before being allowed to warm to room temperature and stirred for a further 23 hours. Excess ICl was quenched through the addition of saturated aqueous sodium metabisulphite (200 ml). The bi-phasic reaction mixture was stirred for 15 minutes before the addition of CH_2Cl_2 (200 ml). The organic layer was removed and the aqueous phase extracted with a further 1 x 100 ml CH_2Cl_2. The combined organic layers were washed with 1 x 100 ml saturated aqueous sodium metabisulphite followed by 1 x 100 ml H_2O and then dried over $MgSO_4$. Removal of the solvent afforded the crude product which was subsequently purified via column chromatography (Al_2O_3, gradient elution, Hexane to 1:10 CH_2Cl_2 / Hexane). Yield = 1.598 g, 66 %.

^{1}H NMR (d$_6$-Acetone, 400 MHz): 6.37 (dd, *J* = 1.24, 8.17 Hz, 2H), 6.91 (td, *J* = 1.28, 7.45 Hz, 2H), 6.99 (td, *J* = 1.68, 7.81 Hz, 2H), 7.10 (dd, *J* = 1.60, 7.52 Hz, 2H), 7.22 (d, *J* = 8.60 Hz, 2H), 8.00 (d, *J* = 8.64 Hz, 2H). EI-MS: m/z = 401 (M^+, 100%), 274 (M^+ -I, 29%), 198

(M^+-C_6H_4I, 36%). Anal. Calc. for $C_{18}H_{12}NIS$ (%): C 53.88, H 3.01, N 3.49, I 31.63. Found (%): C 53.84, H 2.96, N 3.42, I 31.58.

(Note: more efficient chromatographic separation may be achieved on SiO_2, however, significant decomposition of the product to afford pink coloured degradation material was observed.)

Synthesis of *N*-(4-ethynylphenyl)-phenothiazine (L2)



N-(4-Iodophenyl)-phenothiazine (1.000 g, 2.49 mmol), $Pd(PPh_3)_2Cl_2$ (100 mg, 0.14 mmol, 5.7 mol%) and CuI (47 mg, 0.24 mmol, 9.8 mol%) were dissolved in deaerated benzene (35 ml). Trimethylsilylacetylene (1.4 ml, $\rho = 0.695$ g/ml, 9.90 mmol) was added and the solution stirred at room temperature for 15 minutes. Deaerated Et_3N (3.5 ml) was added, upon which a rapid colour change from yellow to dark red was observed. After 3.5 days, the solvent was removed and the crude residue purified by column chromatography (SiO_2, 1:5 CH_2Cl_2 / Hexane) to afford the trimethylsilyl protected product. Deprotection was achieved by adding *N*-(4-trimethylsilyl-ethynylphenyl)-phenothiazine (0.598 g, 1.61 mmol) to a suspension of K_2CO_3 (0.660 g, 4.78 mmol) in 1:1 (v/v) deaerated THF / MeOH (40 ml). The resulting mixture was stirred at room temperature for 18 hours before the addition of H_2O (30 ml). Evaporation of the organic solvent gave an aqueous suspension which was subsequently extracted with 3 x 75 ml CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and evaporated to yield a pale yellow oil which was purified via column chromatography (SiO_2, 1:4 CH_2Cl_2 / Hexane), affording the product as a pale yellow-white solid. Yield = 0.430 g, 58 %.

^{1}H NMR (d_6-Acetone, 400 MHz): 3.78 (s, 1H), 6.48 (dd, $J = 1.20, 8.16$ Hz, 2H), 6.95 (td, $J = 1.28, 7.55$ Hz, 2H), 7.03 (td, $J = 1.64, 7.87$ Hz, 2H), 7.15 (dd, $J = 1.64, 7.55$ Hz, 2H), 7.37 (d, $J = 8.64$ Hz, 2H), 7.71 (d, $J = 8.56$ Hz, 2H). EI-MS: (m/z) = 299 (M^+, 100%). Anal. Calc. for $C_{20}H_{13}NS$ (%): C 80.23, H 4.38, N 4.68. Found (%): C 79.66, H 4.08, N 4.70.

Synthesis of 'Cl-Pt-NDI' (1) [4]

N-Octyl-*N*'-(*p*-ethynylphenyl)-1,4,5,8-naphthalene tetracarboxylic diimide (**L1**) (160 mg, 0.334 mmol) and *cis*-$Pt(PBu_3)_2Cl_2$ (300 mg, 0.447 mmol) were dissolved in deaerated 1:2 (v/v) $^iPr_2NH$ / MeCN (40 ml) and heated to 90 °C in the dark for 24 hours. Removal of the solvent afforded a dark red-orange coloured residue which was purified by column chromatography (SiO_2, CH_2Cl_2). The product may be purified further by recrystallisation from the minimum volume of boiling hexane, giving shiny orange plates. Yield 274 mg, 74 %. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.87 (t, $J = 7.00$ Hz, 3H), 0.94 (t, $J = 7.24$ Hz, 18 H), 1.22-1.53 (m, 22H), 1.53-1.65 (m, 12H), 1.71-1.81 (m, 2H), 1.93-2.13 (m, 12H), 4.21 (t, $J = 7.64$

Hz, 2H), 7.14 (d, J = 8.52 Hz, 2H), 7.39 (d, J = 8.48 Hz, 2H), 8.79 (s, 4H). ^{1}H NMR (d_6-Acetone, 400 MHz): 0.88 (t, J = 7.00 Hz, 3H), 0.95 (t, J = 7.32 Hz, 18H), 1.25-1.56 (m, 22H), 1.61-1.79 (m, 14H), 2.06-2.17 (m, 12 H), 4.16 (t, J = 7.52 Hz, 2H), 7.31 (d, J = 8.52 Hz, 2H), 7.40 (d, J = 8.52 Hz, 2H), 8.74-8.80 (m, 4H). ^{31}P NMR ($CDCl_3$, 101 MHz): 7.07 ($J_{Pt\text{-}P}$ = 2367 Hz). ^{31}P NMR (d_6-Acetone, 101 MHz): 7.36 ($J_{Pt\text{-}P}$ = 2380 Hz). Anal. Calc. for $C_{54}H_{79}N_2O_4ClP_2Pt$ (%): C 58.29, H 7.16, N 2.52. Found (%): C 58.24, H 7.07, N 2.42.

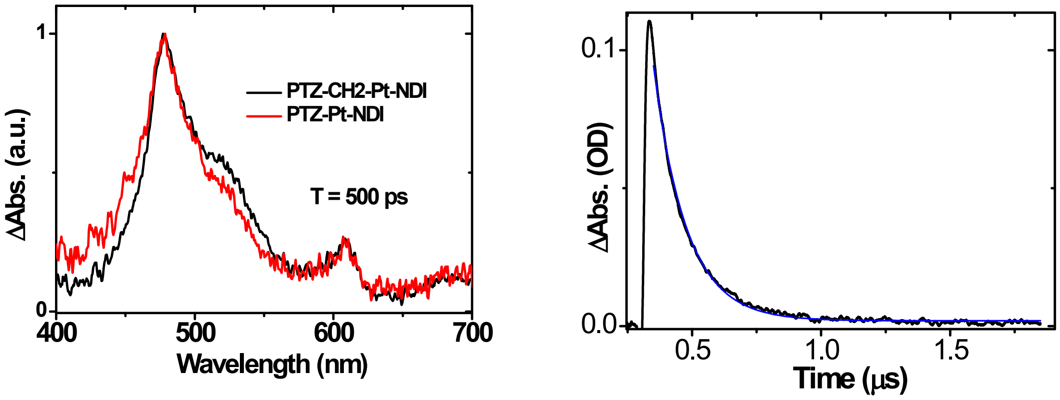


Figure SI.1. Transient absorption at 500 ps time delay for complexes 3 and 4, and their corresponding decay to the ground state using ps Transient Absorption (IRF = 25 ps) and flash photolysis for longer-lived compounds (IRF = 25 ns) with 355 nm excitation. The transient absorption profiles correspond very well to those previously reported for NDI anions. This has an extremely strong extinction coefficient and thus does not allow monitoring the weaker PTZ cation species, although the shoulder at 525 nm may be an indication of its presence. For PTZ-Pt-NDI, the 5 ± 2 ns is not as well as constrained as the 3 ± 1 ns from TRIR, so the latter value is used; however they are consistent within instrumental error.

TRIR and IR-pump measurements on ULTRA were performed with the following parameters:

UV pump beam: beam diameter at the sample 150 μm, energy 0.8 μJ at 400 nm, 1μJ at 380 nm. IR pump beam: beam diameter at the sample 100 μm, energy 0.5-0.6 μJ at 1900 cm^{-1}, IR probe: beam diameter at the sample 80 μm, energy 0.1 μJ.

Transient absorption measurements performed on the picosecond set-up at Sheffield.

Picosecond transient absorption experiments were performed on a home-built pump-probe setup. The fundamental output (~ 3 mJ, 20 ps, 10 Hz, 1064 nm) of a ps mode-locked Nd:YAG laser PL2251 (EKSPLA) was passed through the computer-controlled optical delay line (made of IMS600 linear stage from NEWPORT; 60 cm travel range), and focused with a

0.5 m lens into 10 cm cell with D_2O to generate a picosecond supercontinuum, which served as a probe beam. The broadband supercontinuum beam was split with a beam splitter into signal and reference beams of equal intensity. Both signal and reference beams were passed through the sample one above each other, each focused into a ~ 0.5mm spot on the sample. Afterwards the signal and reference beams were focused with an achromatic condenser onto the entrance slit of the spectrograph (former Hilger & Watts 30 cm monochromator home-converted into spectrograph by replacing the grating, exit flat mirror, removing exit slit, and fitting CCD mounting adaptor). Both signal and reference beams were detected with a CCD camera (ANDOR iDus, DV420A) operated in the dual-track mode.

The sample was excited with a 355nm pump beam generated from the 3rd harmonic output (~ 6 mJ, 10 Hz, 355 nm) of the PL2251 ps laser. The excitation beam was focused into 1 mm spot on the sample, with the pulse energy of 460 μJ at the sample.

The pump and signal probe beams were overlapped at the sample at small angle.

Probe (White Light Continuum): 0.5 mm, energy per pulse approximately 80 μJ integrated.

The instrumental response function duration of the setup is estimated to be ca. 25 ps. The operation of the setup and data acquisition process is computer-controlled with a custom-developed software.

All the measurements were performed in flow-through quartz cells with 2 mm path length and solutions were purged with N_2.

Nanosecond Flash Photolysis studies.

Nanosecond Flash Photolysis studies were conducted at the University of Sheffield on a home-built setup. The 355 nm third harmonic of a Q-switched Nd:YAG laser LS-2137U (LOTIS TII) was used to excited the samples. The energy of excitation pulses delivered to the sample was about 1.5 mJ per pulse in 3 mm spots, at 10 Hz repetition rate and 7 ns pulse width.

150 W Xe arc lamp (Hamamatsu) was used as the probe light source. The probe beam was detected by a monochromator equipped with a home-built detector unit, based on FEU-118 PMT. Detector current output was coupled into a Tektronix TDS 3032B digital oscilloscope and subsequently transferred to a computer.

References

1. B.-H. Ye and Y. Naruta, *Tetrahedron*, 2003, **59**, 3593-3601

2. J. J. S. Lamba and J. M. Tour, *J. Am. Chem. Soc.,* 1994, **116**, 11723-11736

3. D. Hanss and O. S. Wenger, Eur. *J. Inorg. Chem*., 2009, 3778-3790

4. J. M. Keller and K. S. Schanze, *Organometallics*, 2009, **28**, 4210-4216