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Photophysics and Electrochemistry of a Platinum-Acetylide Disubstituted Perylene-diimide

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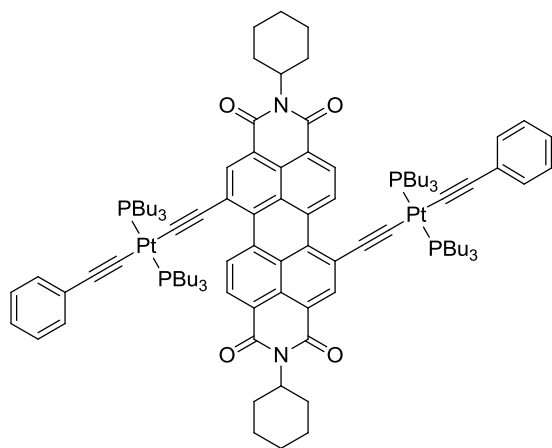
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The synthesis and photophysical study of a perylene diimide (PDI) functionalised with platinum acetylide units of the type, *trans*{-C≡C-Pt(PBu₃)₂-C≡C-Ph} and comparison with a phenylacetylide substituted model compound are reported. The model compound demonstrates typical perylene absorption and photoluminescence spectra characteristic of singlet excited state formation and decay. The Pt-substitution, however, appears to induce spin-orbit coupling into the chromophore and giving rise to a triplet excited state which was confirmed by transient absorption measurements. This excited state is quenched by oxygen, leading to the formation of singlet oxygen in dichloromethane, recorded by time-resolved near-infrared luminescence measurements.

Introduction

The use of 3,4:9,10-perylenetetracarboxylic diimide (PDI) chromophores as photofunctional materials continues to rapidly develop.¹ Their intense fluorescence and efficient visible light harvesting properties have lead to PDIs establishing applications in light emitting diodes,² chemical sensing,³ organic field-effect transistors⁴ and photovoltaics.⁵ We have developed PDI derivatives as useful building-blocks in surface-based self-assembly processes, exploiting their molecular architecture and supramolecular properties.⁶⁻⁹ In the context of this work we have also developed PDI systems, including rotaxanes, functionalised with redox active centres in order to control the electronic and optical properties of the PDI species.¹⁰⁻¹⁴



Scheme 1 Structures of the Pt-bearing PDI complex 1.

Of particular interest are attempts to access the PDI triplet excited state and the possible enhancement of polymeric photovoltaic performance attainable by utilizing this relatively

long-lived excited state, a desirable goal for efficient solar energy conversion.¹⁵⁻²⁰ Over a number of years platinum acetylides and related species have been effectively employed to stabilize the triplet state of organic molecules by intersystem crossing.²¹ Promising research into hexa-*peri*-hexabenzocoronenes (HBCs), exploiting the covalent attachment of Pt-acetylide substituents to the organic chromophore to induce strong spin-orbit coupling and facilitate singlet → triplet intersystem crossing, has demonstrated the potential of heavy-atom substituents for this purpose.¹⁵ However, the direct σ-attachment of palladium to the bay area of a PDI unexpectedly did not result in any significant intersystem crossing and the complex retained the highly fluorescent singlet emission of the unsubstituted PDI chromophore.¹⁶ This was rationalised and supported by TD-DFT calculations in terms of weak interactions between the PDI π-system and the metal centres. A more successful attempt to access the triplet excited state in perylenediimides utilized Pt substituents attached via an acetylide linker,^{17,18} in a similar manner to the hexa-*peri*-hexabenzocoronene example. Fluorescent emission was quantitatively quenched and the presence of the triplet excited state identified both by transient absorption measurements and by bimolecular sensitisation of singlet oxygen phosphorescence at 1270 nm, but in contrast to the Pt-HBCs no low-energy phosphorescence was observed. More recently Espinet *et al.* reported a series of Pt-substituted perylenyl compounds in which the substituent is σ-bonded directly to the bay area that demonstrate short-lived emission (~4 ns) assigned to solely singlet-state fluorescence.¹⁹ Castellano *et al.* described²⁰ the synthesis and photophysics of a Pt(II) terpyridyl perylenediimide which displayed short-lived singlet emission (600 nm, τ = 109 ps, φ = 0.014) with a small Stokes shift (611 cm⁻¹), significantly quenched relative to the non-Pt-containing model complex. Transient absorption experiments identified the presence of a triplet ³PDI-acetylide excited state with a lifetime of 372 ns which was non-emissive and capable of singlet-oxygen

production.

We describe in this paper the synthesis, (spectro)electrochemical and photophysical studies of bis-(-C≡C-Pt(PBu₃)₂-C≡C-Ph) substituted PDI compounds (**1**, **2**) and compare these results with those from a phenylacetylide substituted model compound to investigate the effect of the acetylide substituents on the PDI photophysics.

Experimental Section

General Methods

All starting materials were used as received unless otherwise stated. Perylene-3,4:9,10-tetracarboxylic acid (Aldrich) was brominated according to a literature procedure²² and converted to N,N'-bis(cyclohexyl)-1,7-dibromo-PDI²³ or N,N'-bis(*n*-butyl)-dibromo-PDI²³ through reaction with cyclohexylamine or *n*-butylamine respectively. N,N'-bis(*n*-butyl)-dibromo-3,4:9,10-perylenetetracarboxylic diimide was isolated as an intractable mixture of 1,7- and 1,6-isomers.²⁴ N,N'-Di-(cyclohexyl)-1,7-di(tri-isopropyl-silylethynyl)-PDI and N,N'-Di-(cyclohexyl)-1,7-di-ethynyl-PDI were prepared in an analogous manner to their *n*-butyl functionalised analogues, N,N'-Di-(*n*-butyl)-di(trimethylsilylethynyl)-PDI and N,N'-Di-(*n*-butyl)-di-ethynyl-PDI, as previously described.¹² Experimental details for the two new cyclohexyl functionalised species are given below. N,N'-Di-(*n*-butyl)-di(phenylethynyl)-PDI **3** has been reported previously¹² but details of the synthesis are given in supporting information. *trans*-Phenylethynylchlorobis(tri-*n*-butylphosphine)platinum(II) was prepared according to a literature procedure.²⁵ All reactions were carried out under an atmosphere of dinitrogen. Column chromatography was performed on silica gel (Merck silica gel 60, 0.2-0.5 mm, 50-130 mesh). Dichloromethane (Fisher) was freshly distilled under an atmosphere of dinitrogen from calcium hydride. Ferrocene (Aldrich) was used as received. [NBu₄][BF₄] was prepared by literature methods.²⁶

The ¹H, ¹³C-{¹H} and ³¹P-{¹H} NMR spectra were obtained on a Bruker 400 MHz spectrometer. Microanalyses were performed by Stephen Boyer, London Metropolitan University. MS spectra (MALDI-TOF-MS) were determined on a Voyager-DE-STR mass spectrometer.

Synthesis

N,N'-Di-(cyclohexyl)-1,7-di(tri-isopropyl-silylethynyl)-PDI.

Synthesis was adapted from a literature procedure.¹² N,N'-bis(cyclohexyl)-1,7-dibromo-PDI (200 mg, 0.281 mmol) was dissolved in a mixture of dry tetrahydrofuran (12 ml) and dry triethylamine (5 ml). PdCl₂(PPh₃)₂ (8.4 mg, 0.011 mmol), CuI (3 mg, 0.140 mmol) and tri-isopropyl-silylethynyl (0.25 ml, 1.12 mmol) were added and the mixture was heated at reflux for 3h under N₂. The reaction mixture was cooled to room temperature, poured onto HCl (2 M, 100 ml), the product was extracted with CH₂Cl₂ and the organic layer was washed with water until neutral. The crude product was purified by column chromatography (SiO₂, CH₂Cl₂) to give the pure product as a red powder (251 mg, 0.274 mmol, 97%). ¹H NMR (CDCl₃, 400 MHz) δ_H: 10.38 (d, 2H, ³J = 8 Hz), 8.82 (s, 2H); 8.62 (d, 2H, ³J =

8 Hz); 2.63 – 2.55 (dq, 4H, ³J = 32 Hz 4 Hz); 1.97 – 1.93 (d, 4H, ³J = 16Hz); 1.79 (t, 6H, 12); 1.55 – 1.23 (m, 44H). MS (MALDI-TOF) m/z: 913.8 (M⁺). CHN analysis calculated for C₃₆H₂₈Br₂N₂O₄, C 76.10 % H 7.71 % N 3.06 %. Found C 76.28 % H 7.86 % N 3.17 %.

N,N'-Di-(cyclohexyl)-1,7-diethynylperylene-PDI.

Synthesis was adapted from a literature procedure.¹² N,N'-Di-(cyclohexyl)-1,7-di(tri-isopropyl-methylsilylethynyl)-PDI (220 mg, 0.295 mmol) was dissolved in a mixture of CHCl₃ (15 ml) and MeOH (5 ml). NaOH (13 mg) was added and the mixture was stirred for 1.5 h. The crude product was suspended in MeOH, sonicated and the solvent was filtered off giving the pure product as a purple solid (159 mg, 0.264 mmol, 90%). The poor solubility of the product precluded the acquisition of NMR data. MS (MALDI-TOF) m/z: 602.1 (M⁺).

N,N'-Di-(cyclohexyl)-1,7-di(trans-di(tri-*n*-butylphosphine)-phenylethynyl-platinum(II)-ethynyl)-PDI **1**.

N,N'-Di-(cyclohexyl)-1,7-diethynylperylene-PDI (80 mg, 0.13 mmol) and *trans*-phenylethynylchlorobis(tri-*n*-butylphosphine)platinum(II) (194 mg, 0.27 mmol) were dissolved in a mixture of CH₂Cl₂ (20 ml) and diethylamine (10 ml). CuI (27 mg) was added and the solution was degassed with N₂ for 15 mins and stirred for 18 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO₂, CH₂Cl₂:petroleum ether 50:50) to give the pure product, **1**, as a blue-black powder (48 mg, 0.0240 mmol, 18%). ¹H NMR (CDCl₃, 400 MHz) δ_H: 11.55 (d, 2H, ³J = 8 Hz); 9.31 (s, 2H); 9.10 (d, 2H, ³J = 8Hz); 7.28 (m, 10H); 2.28 – 2.26 (m, 24H); 1.86 – 1.84 (m, 26H); 1.57 – 1.48 (m, 24H); 1.06 (t, 36H, J = 8 Hz). ³¹P-{¹H} NMR (CDCl₃, 162 MHz) δ_P: 4.06 (J_{Pt-P} = 2888 Hz). MS (MALDI-TOF) m/z⁺: 1998.6 (M⁺) CHN analysis calculated for C₁₀₄H₁₄₆N₂O₄P₄Pt₂, C 62.38 % H 7.35 % N 1.04 %. Found C 62.24 % H 7.24 % N 1.12 %.

N,N'-Di-(*n*-butyl)-di(trans-bis(tri-*n*-butylphosphine)-phenylethynyl-platinum(II)ethynyl)-PDI **2**.

A stirred solution of N,N'-Di-(*n*-butyl)-di-ethynyl-PDI (55 mg, 0.1 mmol), *trans*-phenylethynylchlorobis(tri-*n*-butylphosphine)platinum(II) (146 mg, 0.2 mmol) and CuI (20 mg) in diethylamine/CH₂Cl₂ (5 ml/10 ml) was degassed for 15 min and stirred under Ar atmosphere for 16 h. Silica gel was added to the reaction solution and the solvent evaporated. The residue was purified by column chromatography (SiO₂/CH₂Cl₂) to afford **2** as a green solid (89 mg, 46%). ¹H NMR (CDCl₃, 400 MHz): δ = 11.03 (d, 2H, ³J = 8.34 Hz); 8.74 (s, 2H); 8.54 (d, 2H, ³J = 8.34 Hz); 7.33 - 7.16 (m, 10H); 4.23 (t, 4H); 2.15 (m, 24H); 1.75 (m, 4H); 1.64 (m, 24H); 1.50 (m, 4H); 1.42 (t, 24H); 1.01 (t, 6H); 0.88 (t, 36H). ¹³C-{¹H} NMR (CDCl₃ 126 MHz): δ = 163.61, 163.56, 152.14, 135.47, 130.75, 128.36, 124.41, 123.77, 123.64, 122.03, 121.58, 121.03, 66.60, 51.81, 40.54, 40.38, 30.30, 20.45, 13.09. ³¹P-{¹H} NMR (CDCl₃, 162 MHz) δ = 1.8 ppm (J_{Pt-P} = 1764 Hz); Calcd. for C₁₀₀H₁₄₂N₂O₄P₄Pt₂: C: 61.59; H: 7.34; N: 1.44. Found: C: 61.66; H: 7.39; N: 1.32. MS (MALDI-TOF): m/z 1950 (M⁺).

Photophysical Measurements

UV/visible absorption spectra were recorded on a Perkin-

Elmer Lambda 25 spectrometer. Emission measurements were performed on a combined fluorescence lifetime and steady state spectrometer (Edinburgh Instruments FLS920). Steady state emission and excitation spectra were obtained with a xenon arc lamp as the excitation source and were corrected for detector sensitivity. Emission lifetime measurements were performed using the time-correlated single-photon counting technique, with an EPL400 pulsed diode laser (405 nm, pulse width 95 ps) as the excitation source (time resolution *ca.* 1 ns). Solutions were thoroughly freeze-pump-thaw degassed in specially modified 1 x 1 cm quartz cuvettes. Sample concentrations were adjusted to be optically dilute ($Abs_{max} < 0.1$, $c < 1 \times 10^{-6}$ M).

Singlet oxygen experiments were performed in dichloromethane, initially air-equilibrated, subsequently oxygenated by bubbling with a steady stream of oxygen for 5 minutes, then deoxygenated by bubbling with N₂ gas for 5 minutes and finally reoxygenated by bubbling with O₂ gas for 5 minutes. Excitation was with a 532 nm Nd:YAG laser (GCR150-10, 10 Hz, 8 ns FWHM, ~45 μ J per pulse at sample). Time-dependent emission traces at 1200, 1275 and 1300 nm (500 μ s, 0.5 μ s/bin, ~1000 shots per spectrum) were collected at 90° via a monochromator (TRIAx-320), onto a NIR-PMT (Hamamatsu H10330A-45, -750 V, -60°C) connected to a USB multichannel scalar controlled by LabVIEW. The absorbance for **1** or **2** was initially 0.072 at 532 nm, corresponding to a concentration of *ca.* 3×10^{-6} M. To test concentration effects, the experiments were repeated with a diluted sample ($Abs = 0.032$ at 532 nm, corresponding to a concentration of *ca.* 6×10^{-7} M). In all cases in the presence of oxygen, emission was observed at 1275 nm, weakly at 1300 nm and no emission was observed at 1200 nm. Finally, the solvent emission (without **1** or **2**) was recorded under the same conditions at 1275 nm and no emission was observed.

Transient Absorption Spectroscopy

Fast Transient Absorption Spectroscopies measurements were performed using a pump-probe method and has been described in detail elsewhere.²⁷ In brief, the probe beam of white light continuum is generated by focusing a small amount of 800nm (~400nJ) laser beam into a 4mm thick Sapphire disk. The picosecond 400 nm pump beam is obtained from a commercial Ti:sapphire oscillator / regenerative amplifier system (*Spectra Physics, USA*) and a TP-1 harmonic generator (*TimePlate Tripler, Minioptic Technology, Inc*) and the time difference (up to 3 ns) between the pump and probe pulses is controlled by an optical delay line. The nanosecond 355 nm pump beam is produced with a Q-switched Nd:YVO laser (*ACE-25QSPXHP/MOPA, Advanced Optical Technology, UK*) which is electronically synchronised to the Spitfire Pro amplifier. The delay between pump and probe pulses can be controlled with a pulse generator (*DG535, Stanford Research System, USA*) from 0.5 ns to 100 μ s. The white light beam is split into two parts. One part passes through the sample spatially overlapped with the pump beam. Another part serves as a reference to the probe beam fluctuations. The polarization

of the pump pulse is set at the magic angle (54.7 degree) relative to the probe pulse to recover the isotropic absorption spectrum. Both parts of the probe beam are monitored by a dual array detector (512 pixels) (*Cronin Camera, Spectronic device Ltd, UK*). The detector is mounted in the focal plane of a 303 mm Acton spectrograph (*Acton, USA*) with a 150 g/mm grating. The pump beam size (~400 μ m diameter) is larger than the probe spot (~200 μ m diameter). A Harrick solution cell with 2-mm-thick CaF₂ windows is mounted on a motorized cell mount, which moves the cell in x and y dimensions rapidly and continuously.

Electrochemical and Spectroelectrochemical measurements

Cyclic voltammetric and coulometric studies were carried out using an Autolab PGSTAT20 potentiostat. Standard cyclic voltammetry was carried out under an atmosphere of argon using a three-electrode arrangement in a single compartment cell. A glassy carbon working electrode, a Pt wire secondary electrode and a saturated calomel reference electrode, chemically isolated from the test solution *via* a bridge tube containing electrolyte solution and fitted with a porous vycor frit, were used in the cell. The solutions were 10^{-3} M in test compound and 0.4 M in [NBu₄][BF₄] as supporting electrolyte. Redox potentials are quoted *versus* the ferrocenium-ferrocene couple used as an internal reference. Compensation for internal resistance was not applied.

Bulk electrolysis experiments, at a controlled potential, were carried out using a two-compartment cell. The Pt/Rh gauze basket working electrode was separated from the wound Pt/Rh gauze secondary electrode by a glass frit. A saturated calomel reference electrode was bridged to the test solution through a vycor frit orientated at the centre of the working electrode. The working electrode compartment was fitted with a magnetic stirrer bar and the test solution was stirred rapidly during electrolysis.

The solutions used were 0.4 M in [NBu₄][BF₄] as supporting electrolyte and 10^{-3} M in test compound and were prepared using Schlenk line techniques. Electrolysed solutions were transferred to quartz tubes, via teflon canula, for analysis by EPR spectroscopy. EPR spectra were recorded on a Bruker EMX spectrometer and simulated using WINEPR SimFonia, Shareware version 1.25, Brüker Analytische Messtechnik GmbH.

The UV/vis spectroelectrochemical experiments were carried out with an optically transparent electrochemical (OTE) cell (modified quartz cuvette, optical pathlength: 0.5 mm). A three-electrode configuration, consisting a Pt/Rh gauze working electrode, a Pt wire secondary electrode (in a fritted PTFE sleeve) and a saturated calomel electrode, chemically isolated from the test solution *via* a bridge tube containing electrolyte solution and terminated in a porous frit, was used in the cell. The potential at the working electrode was controlled by a Sycopel Scientific Ltd. DD10M potentiostat. The UV/vis spectra were recorded on a Perkin Elmer Lambda 16 spectrophotometer. The cavity was purged with dinitrogen and temperature control at the sample was achieved by flowing cooled dinitrogen across the surface of

the cell.

X-ray crystallography

Single-crystal X-ray diffraction experiments were performed on either a Rigaku FR-E+ Ultra High Flux Diffractometer, 5 1, or a Rigaku FR-E+ Very High Flux Diffractometer, N,N'-bis(cyclohexyl)-1,7-dibromo-PDI and N,N'-Di-(cyclohexyl)-1,7-di(tri-isopropyl-silylethynyl)-PDI. All three structures were collected at 100 K, with the aid of an Oxford Cryosystems Cobra, using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$).²⁸ 10 The structures were solved by direct methods using SHELXS97 and refined by full-matrix least squares on F^2 using SHELXL97.²⁹ Due to weak data arising from poor crystallinity of the crystals of N,N'-Di-(cyclohexyl)-1,7-di(tri-isopropyl-silylethynyl)-PDI rigid bond and similarity 15 restraints were applied to the anisotropic displacement parameters of all atoms in the structure and the displacement parameters of the isopropyl groups have been restrained to be more isotropic. Disorder was observed in the conformation of cyclohexyl ring and the occupancies of the two components 20 were refined and constrained to sum to unity (major component occupancy 0.55(1)). Geometric similarity restraints were applied to the 1,2 and 1,3 bond lengths of the disordered and ordered cyclohexyl groups reflecting their 2-fold symmetry. The atoms of the two disordered cyclohexyl 25 rings were refined with isotropic displacement parameters. Similarly disorder was observed in the orientation of isopropyl group C88-C90 and the occupancies of the two components were refined and constrained to sum to unity (major component occupancy 0.55(2)). The two components 30 share the position of the methine carbon (C88A/C88B) and one methyl carbon (C89A/C89B). In both cases, cyclohexyl and isopropyl groups, the atoms of the two disordered components were refined with isotropic displacement parameters. Additional geometric similarity restraints were 35 applied to various bond lengths, see CIF for further details. A residual electron density peak of 1.11 e \AA^{-3} is observed 1.56 \AA from C86 and is likely to be a result of further unresolved disorder in the triisopropylsilyl group.

Similarly single crystals of **1** gave weak data arising from 40 poor crystallinity and rigid bond and similarity restraints were applied to the anisotropic displacement parameters of all atoms in the structure. The C-C 1,2 and 1,3 distances in the butyl chains were all constrained to have values of 1.50 \AA and 2.50 \AA respectively. The P-C distances, C-O carbonyl 45 distances, C-N imide distances and C-C imide-perylene distances were all restrained to have similar values to their chemically identical equivalents and the terminal phenyl ring has been constrained to have regular hexagonal geometry. A residual electron density peak of 3.46 e \AA^{-3} is observed 0.83 \AA 50 from Pt1 which is likely to be an artefact caused by deficiencies in the adsorption correction for the heavy-metal-containing platey crystal. A further electron density peak of 2.33 e \AA^{-3} is observed 1.54 \AA from C6, which, although this is within the range of a chemical bond to the perylene core, the 55 peak is in a chemically nonsensical position above the aromatic plane and likely to be a result of unresolved disorder or other experimental artefact.

Crystal data for N,N'-bis(cyclohexyl)-1,7-dibromo-PDI:

C₃₆H₂₈Br₂N₂O₄, $M = 712.42$, monoclinic, $P2_1/c$, $a = 15.2582(4)$, $b = 11.8210(3)$, $c = 16.0098(11) \text{ \AA}$, $\beta = 103.389(7)^\circ$, $U = 2809.2(2) \text{ \AA}^3$, $Z = 4$, $T = 100(2) \text{ K}$, $D_{\text{calc}} = 1.684 \text{ g cm}^{-3}$, $\mu = 2.933 \text{ mm}^{-1}$, $F(000) = 1440$. A total of 33301 reflections were collected, of which 6431 were unique, with $R_{\text{int}} = 0.031$. Final $R_1 (wR_2) = 0.0223 (0.0555)$ with GOF 65 = 1.05.

Crystal data for N,N'-Di-(cyclohexyl)-1,7-di(tri-isopropyl-silylethynyl)-PDI: C₅₈H₆₈N₂O₄Si₂, $M = 913.32$, monoclinic, $P2_1/n$, $a = 17.734(8)$, $b = 12.986(5)$, $c = 23.8022(10) \text{ \AA}$, $\beta = 111.456(7)^\circ$, $U = 5102(3) \text{ \AA}^3$, $Z = 4$, $T = 100(2) \text{ K}$, $D_{\text{calc}} = 1.189 \text{ g cm}^{-3}$, $\mu = 0.118 \text{ mm}^{-1}$, $F(000) = 1960$. A total of 28020 reflections were collected, of which 8667 were unique, with $R_{\text{int}} = 0.036$. Final $R_1 (wR_2) = 0.1845 (0.5150)$ with GOF = 1.91.

Crystal data for **1** N,N'-Di-(cyclohexyl)-1,7-di(trans-di(tri-n-butylphosphine)-phenylethynyl-platinum(II)-ethynyl)-PDI: 75 C₁₀₄H₁₄₆N₂O₄P₄Pt₂, $M = 2002.29$, orthorhombic, $Pbcn$ (No. 60), $a = 33.88(3)$, $b = 14.178(13)$, $c = 20.595(18) \text{ \AA}$, $U = 9893(15) \text{ \AA}^3$, $Z = 4$, $T = 100(2) \text{ K}$, $D_{\text{calc}} = 1.344 \text{ g cm}^{-3}$, $\mu = 2.939 \text{ mm}^{-1}$, $F(000) = 4128$. A total of 36399 reflections were 80 collected, of which 8315 were unique, with $R_{\text{int}} = 0.096$. Final $R_1 (wR_2) = 0.1490 (0.3850)$ with GOF = 1.16.

Results and Discussion

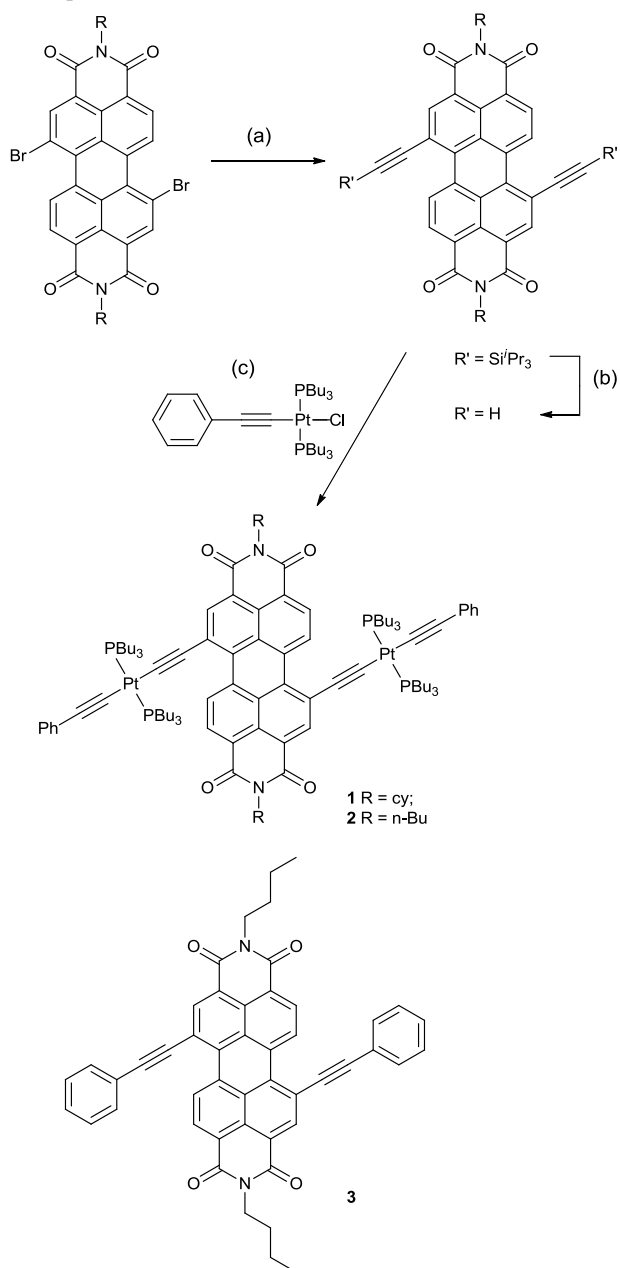
Synthesis

The synthesis of **1** and **2** is outlined in Scheme 2. The 1,7-di- 85 tri-isopropyl-silylacetylene perylene bisimide derivative, N,N'-di-(cyclohexyl)-1,7-di(tri-isopropyl-silylethynyl)-PDI, was synthesised from N,N'-bis(cyclohexyl)-1,7-dibromo-PDI²⁴ and ethynyl-tri-isopropyl-silane under standard Sonogashira conditions, and deprotected using sodium 90 hydroxide in a solvent mixture of methanol and dichloromethane. Hagihara coupling with *trans*-phenylethynylchlorobis(tri-*n*-butylphosphine)platinum(II) afforded the Pt-perylene bisimide derivative **1**. **2**, N,N'-di(*n*-butyl)-di(*trans*-bis(tri-*n*-butylphosphine)-phenylethynyl- 95 platinum(II)ethynyl)-PDI, was prepared in an analogous fashion. It is known that bromination of perylene bisanhydride affords a mixture of 1,7 and 1,6 isomers in an approximate ratio of 4:1. In the case of N,N'-bis(cyclohexyl)-1,7-dibromo-PDI these isomers can be separated by recrystallisation²⁴ but 100 in the case of N,N'-bis(butyl)-1,7-dibromo-PDI this is not possible. Thus, whereas **2** exists as mixture of 1,7 and 1,6 isomers a pure sample of N,N'-bis(cyclohexyl)-1,7-dibromo-PDI was used to prepare an isomerically pure complex, **1**. The purity of the 1,7-isomers used in this synthetic pathway was 105 confirmed by both NMR spectroscopy and single crystal X-ray diffraction for **1**, N,N'-bis(cyclohexyl)-1,7-dibromo-PDI and N,N'-di-(cyclohexyl)-1,7-di(tri-isopropyl-silylethynyl)-PDI.

Single Crystal Structures

110 Crystals of N,N'-bis(cyclohexyl)-1,7-dibromo-PDI, N,N'-Di-(cyclohexyl)-1,7-di(tri-isopropyl-silylethynyl)-PDI and **1** of suitable quality for analysis by single crystal X-ray diffraction were grown by slow diffusion of methanol into a solution of

the compound in chloroform.



Scheme 2 Synthesis of **1**, R = cy; **2**, R = *n*-Bu. (a) THF, NEt₃, Ethynyltrimethylsilane, PdCl₂(PPH₃)₂, CuI, 70°C, 89%; (b) MeOH/CHCl₃, NaOH, 95%; (c) HNEt₂, CH₂Cl₂, CuI, 46%.

A single crystal structure of N,N'-bis(cyclohexyl)-1,7-dibromo-PDI has been reported previously²⁴ as a dichloromethane solvate, and the structure obtained was very similar in most respects to the structure obtained here. However in our study the compound crystallises in an alternative space group, *P2₁/c*, as opposed to *P-1*,²⁴ and is not a solvate. As a result an alternative packing arrangement of pairs of N,N'-bis(cyclohexyl)-1,7-dibromo-PDI molecules is observed but in all other respects the bond lengths, angles and twisting of the perylene core (inter-naphthyl twisting angle of 24°) are similar in the two structures.

The single crystal structure of N,N'-di-(cyclohexyl)-1,7-di-

isopropyl-silylethynyl)-PDI confirms the formation of the 1,7-isomer of this species as desired (Figure 1a). The structure reveals a twisting of the perylene core as expected for disubstituted PDIs with an inter-naphthyl angle of 14.2°. The twisting of the perylene core is accompanied by a lengthening of the central carbon-carbon bond lengths to 1.474(10)Å (C17-C18) and 1.452(9)Å (C13-C14) in comparison to the other average C=C bond lengths of 1.405Å for the naphthyl moieties of the molecule. Disubstituted PDI derivatives can exhibit inherent chirality due to the twisting of the aromatic perylene core leading to both *M* and *P* atropo-enantiomers.³⁰ Interconversion of the isomers would be expected to be facile for the compounds in this study at room temperature³⁰ and therefore it is not surprising that N,N'-di-(cyclohexyl)-1,7-di-(tri-isopropyl-silylethynyl)-PDI crystallises in the centrosymmetric space group *P2₁/n* and does not exhibit overall chirality. The structure contains pairs of *M* and *P* isomers³¹ (Figure 1b) that are π - π stacked (centroid...centroid separation of 3.77Å). Such pairs of stacked molecules are not unusual for the 1,7 isomers of disubstituted PDIs.^{12,14}

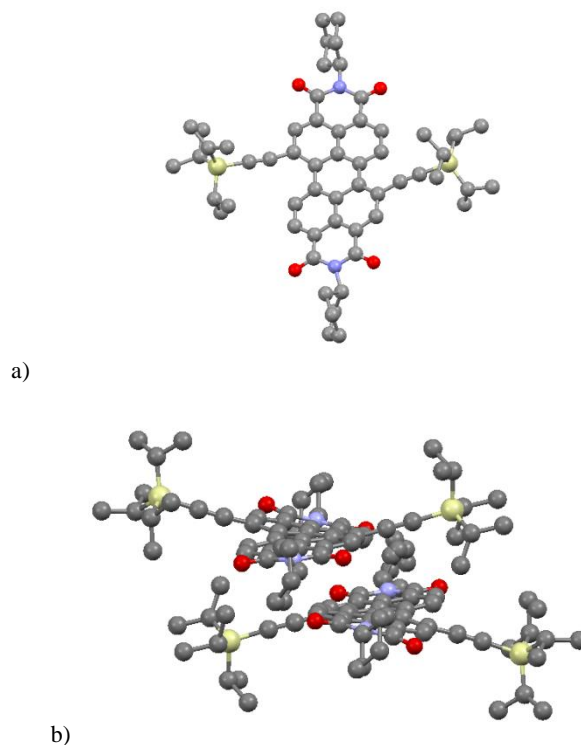


Figure 1 Views of a) the single crystal structure of N,N'-di-(cyclohexyl)-1,7-di-(tri-isopropyl-silylethynyl)-PDI, note the 1,7-isomeric arrangement; b) pairs of π - π stacked *M* and *P* isomers of N,N'-di-(cyclohexyl)-1,7-di-(tri-isopropyl-silylethynyl)-PDI. Carbon - grey, nitrogen - blue, oxygen - red, silicon - yellow. Hydrogen atoms are omitted for clarity.

The single crystal structure of **1** also confirms the desired formation of the 1,7-isomer of the compound (Figure 2). Again the perylene core of the molecule is twisted with a slightly smaller inter-naphthyl angle of 12.4°. Although it is possible to prepare disubstituted PDIs that have a non-twisted, planar, perylene core by careful design of the substituents,³² the inter-naphthyl twisting angle can be as low as 4° for the difluoro-substituted derivative³² but typically takes values of

20-25° for bulkier substituents. The small angle observed for **1** and N,N'-di-(cyclohexyl)-1,7-di(tri-isopropyl-silylethynyl)-PDI is presumably a result of the small steric bulk of the acetylene groups. The bond lengths and angles associated with the platinum centre are within normal ranges [Pt-C = 2.01(2), 2.04(2) Å; Pt-P = 2.324(6), 2.323(6) Å] although the Pt-P bond lengths are the longer end of the range of previous examples (see SI for histograms of previous reports of bond lengths in related complexes).

Lengthening of the inter-naphthyl bond lengths of C13-C14/C17-C18 to 1.470 Å is also seen in **1**, in comparison to the average C=C bond length of 1.41 Å within the naphthyl moieties. The structure of **1** contains both *M* and *P* atropo-enantiomers but unlike N,N'-di-(cyclohexyl)-1,7-di(tri-isopropyl-silylethynyl)-PDI the bulk of the Bu₃P ligands attached to the platinum centres block aggregation of the PDI moieties precluding the formation of any π - π stacking interactions.

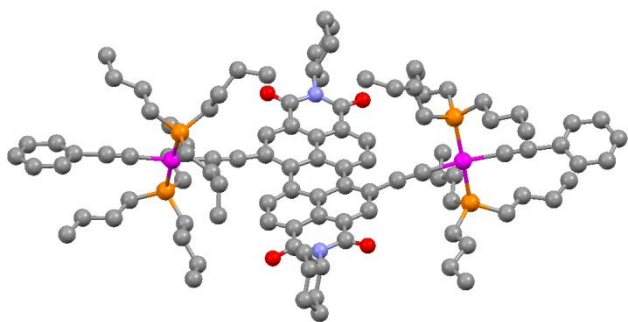


Figure 2. View of the single crystal structure of **1**, note the 1,7-isomeric arrangement. Carbon - grey, nitrogen - blue, oxygen - red, phosphorus - brown, platinum - purple. Hydrogen atoms are omitted for clarity.

Electrochemistry

Reductions of **1** follow trends reported for other PDI compounds. Hence, **1** undergoes two one-electron reduction processes, based on the PDI core, that are reversible (Figure 3). It is noted that reduction potentials for **1** (-1.22 and -1.46 V vs. Fc⁺/Fc) are significantly more negative than other X-acetylene-perylene compounds (X = Ph: -0.96 and -1.13 V;¹² X = Fc: -0.94 and -1.13 V¹²) and other such 'bay' substituted PDIs (including Fc¹², Br¹¹, morpholine¹¹ and thioethers¹⁴) suggesting that {-C≡C-Pt(PBu₃)₂-C≡C-Ph} is donating more electron density into the perylene framework. An oxidation processes, at +0.71 V, was resolved by square wave voltammetry (Figure 3, lower trace).

The electrochemical one-electron reduction of **1** gave a species that was green in colour and paramagnetic. As a fluid solution, at ambient temperature, EPR spectroscopy gave a signal consistent with the generation of a radical anion (g_{iso} 2.0044) (see ESI). A complex hyperfine splitting pattern was observed for [1]⁻ but this was not simulated satisfactorily. No obvious metal hyperfine coupling was observed in the fluid solution spectrum at ambient temperature suggesting that the unpaired electron density resides mainly around the PDI core (see below). For **2**, the frozen solution spectrum at 77 K appeared isotropic, with g_{iso} 2.0035.

The one- and two-electron reductions of **1** were followed by *in situ* UV/vis spectroelectrochemistry at an optically transparent electrode (Figure 4). The one-electron reduced radical anion [1]⁻ show major bands red shifted relative to their parent molecule with a series of transitions extending into the nIR region. The second reduction blue shifts the spectrum with respect to that of the radical monoanion, with the most intense visible transitions occurring as a series of bands centred around 600 nm. This behaviour is highly characteristic of reductions occurring at the PDI core. Oxidation of **1** to [1]⁺ was also investigated and new bands that extended into the nIR were noted however this oxidation was not chemically reversible under the experimental conditions (see SI).

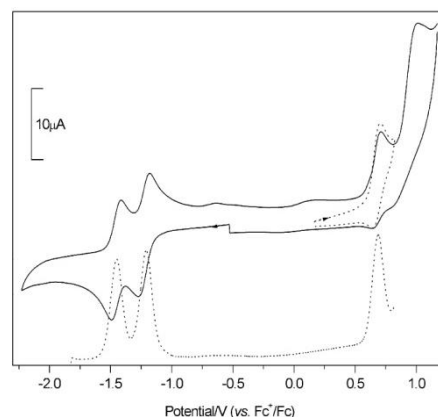


Figure 3. View of cyclic and square wave (lower trace) voltammograms recorded for **1** in CH₂Cl₂ containing [Bu₄N][BF₄] (0.4 M).

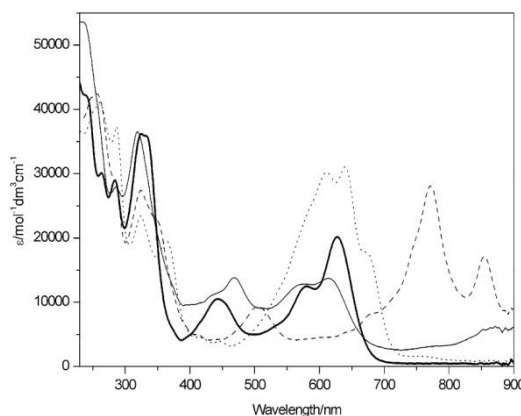


Figure 4. View of UV-visible spectra recorded in CH₂Cl₂ containing [Bu₄N][BF₄] (0.4 M) using spectroelectrochemical methods for **1** at 273 K. The spectrum of **1** is represented by the bold line, [1]⁻ (dashed line), [1]²⁻ (dotted line) and [1]⁺ (solid line, at 243 K).

Absorption and Photoluminescence Spectroscopy

The absorption and emission spectra of **1-3** were examined in CH₂Cl₂ at concentrations in the order of $\sim 5 \times 10^{-7}$ M to minimise the probability of aggregation occurring. The absorption spectra of **1-3** are dominated by characteristic structured π - π^* transitions of the PDI moiety. An example of

the absorption and emission spectra of **1** recorded in CH₂Cl₂ are shown in Figure 5. Whilst the absorption profile to **1** has maxima at 577 and 625 nm, the emission spectrum, in degassed CH₂Cl₂, shows a featureless emission peak at 685 nm corresponding to an approximate Stokes shift of ~1400 cm⁻¹ from the absorption peak at 625 nm. The absorption spectrum of **2** is comparable to that of **1**, with maxima at 580 and 629 nm, but is significantly red-shifted with respect to the spectrum of the phenylacetylene-substituted PDI model compound, N,N'-di-(*n*-butyl)-di(phenylacetylene)-PDI, **3**, which has maxima at 527 and 568 nm.

As with **1**, compound **2** exhibits a large Stokes shift of ~1600 cm⁻¹, from the absorption peak maximum at 627 nm, in the emission spectrum with a peak maximum at 696 nm. In contrast to **1** and **2**, which both show relatively featureless emission spectra, the normalised emission spectrum of **3** is structured and intense ($\Phi = 0.70$), with a maximum at 599 nm. The fluorescence of **3** is typical of singlet excited-state emission from the PDI core. The Stokes shift (~855 cm⁻¹) is a little larger than that of many perylene derivatives¹, possibly due to the presence of the two acetylide groups extending the π -conjugation of the PDI core.

The lifetime of the emission of **1** is only 7 ns (*c.f.* 6.9 ns for **3**). Additionally, oxygenation of the solution by bubbling with O₂ for ~20s results in a decrease in integrated emission intensity of ca. 10%. A recent Pt-substituted perylenyl complex gave only singlet-state fluorescence in fluid solution, with emissive lifetimes in the order of 4-5 ns.¹⁹ However, earlier studies by Castellano^{17,18} and Schanze¹⁵ on related Pt-substituted complexes have shown that the 'heavy-atom' effect can indeed induce formation of a triplet excited state. Pt-acetylide linked perylene complexes described by Castellano *et al.*^{17,18,20} have triplet-state lifetimes of hundreds of nanoseconds (~250-1000 ns).

The lifetime of emission for **2** of 17 ns ($\lambda_{em} = 696$ nm, room temperature) lies between the values observed for **1** and reported literature examples of singlet and triplet emission from PDIs, despite the use of acetylide linkages. Furthermore, recently reported complexes from the Castellano group²⁰ were not emissive. The quantum yield ($\Phi = 0.02$) for **1** is ca. 35 times lower than that of **3**, indicating that the attachment of the platinum groups has significantly quenched the fluorescence of the PDI unit. The short emissive lifetime observed for **3** ($\tau = 6.9$ ns) is consistent with the assignment of this emission to singlet excited state fluorescence.

In order to investigate the nature of the excited-states formed in **1** and **2** further we have undertaken singlet-oxygen sensitisation experiments.

Singlet Oxygen Generation

In air-equilibrated CH₂Cl₂ solution, excitation of **1** or **2** at 532 nm leads to formation of ¹O₂, detected by its characteristic luminescence at 1275 nm, see Figure 6 for emission spectrum of **1**. Oxygenating the solution affords ¹O₂ emission with significantly higher signal. Confirmation that the emission detected was from ¹O₂ was obtained purging the solution of **1** for 5 minutes with N₂ gas, after which no emission was

detected at 1200, 1275 or 1300 nm. The emission at 1275 nm returned on bubbling the solution for 5 minutes with O₂ gas. The same results (with lower signal intensity) were observed on repeating the experiment at a reduced concentration of **1** or **2** (see experimental), further indicating that the complex is acting as a sensitizer for singlet oxygen formation. The lifetime of singlet oxygen emission was determined to be 88 μ s (**1**) or 87 μ s (**2**), in CH₂Cl₂, consistent with literature values for this solvent.³⁴ When the experiment was repeated in toluene for **1** a lifetime of 37 μ s was recorded, again consistent with literature values.

The short lifetimes for emission observed for compounds **1** and **2** (7 and 17 ns respectively) and low quantum yields of emission suggest the presence of a singlet excited-state, but these experiments demonstrate the production of singlet oxygen from the excitation of each of these compounds, indicative of the presence of a triplet-excited state. The report of Castellano *et al.*,²⁰ in which a related mono-Pt-substituted PDI compound demonstrates both a short-lived (100 ps) singlet state and a longer-lived triplet state (372 ns in methylthf), monitored by ultrafast transient absorption spectroscopy. This suggests the presence of both singlet and triplet states in our experiments, the latter being responsible for the production of singlet oxygen emission.

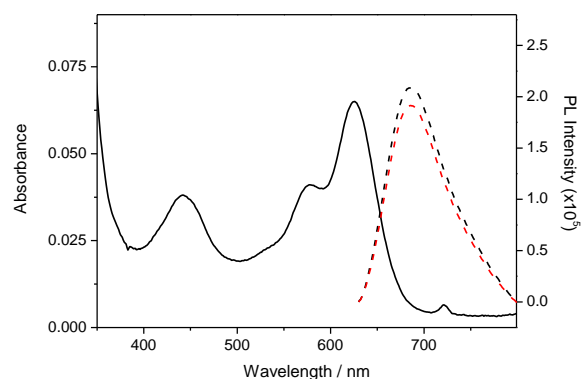


Figure 5 Absorption (solid) and emission (dashed) spectra of **1** recorded in degassed (black) and oxygenated (red) CH₂Cl₂ solution. Emission spectra were recorded with $\lambda_{ex} = 625$ nm.

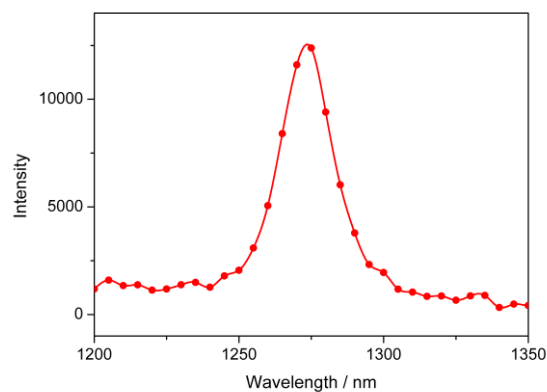


Figure 6 Singlet oxygen emission spectrum of **1** recorded in oxygenated CH₂Cl₂ with $\lambda_{ex} = 337$ nm.

We have investigated further the formation of the triplet state

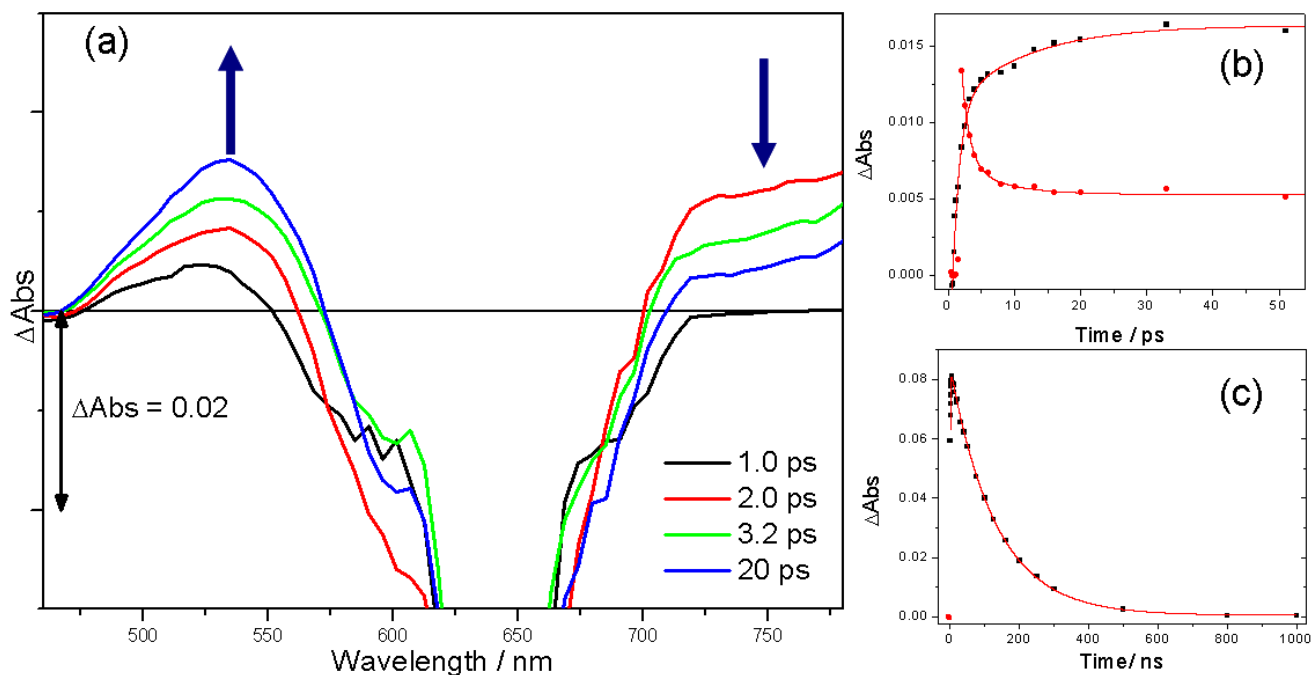


Figure 7 (a) Picosecond transient absorption spectra of **1** in CH_2Cl_2 at selected time delays after 400 nm excitation; (b) ps kinetic traces at 532 nm (black squares) and 760 nm (red circles), and (c) the ns kinetic trace at 505 nm of the same sample after 355 nm excitation. Red lines denote kinetic fits (see text).

in **1** by carrying out analogous transient absorption measurements to those reported by Castellano *et al.*^{17,18} In those experiments excitation of a monosubstituted Pt-complex resulted in the Franck-Condon state initially undergoing intersystem crossing with a time constant of 2-4 ps. The transient absorption difference spectra at select delay times of **1** following excitation by 400 nm laser pulses are shown in Figure 7. It is clear from the spectrum obtained after 2 ps that the parent band is bleached and there are positive transient absorption signals at 532 and a broad band above 700 nm. The lower energy band then decays at the same rate ($\tau = 1.2$ ps) as the 532 nm absorption increases, which is assigned to intersystem crossing and is consistent with the earlier work of Castellano.¹⁸ The triplet absorption at 532 nm increases in intensity on two other timescales. The faster of these ($\tau = 10$ -15 ps) is attributed to vibrational cooling of the triplet state by comparison with the earlier transient absorption measurements.¹⁸ The slower growth over ca. 1 ns is less clear. The triplet state band of **1** at 532 nm formation and decay was monitored following 355 nm excitation. We again observe a fast (sub-nanosecond, ~75%) and slow (ca. 1 ns; ~25%) formation and the decay ($\tau = 132$ ns) is significantly longer than the emission described above. The transient absorption shows that the emission is not due to triplet and it is possible that the weak emission from **1** is due to some form of aggregation and that this decays to form the triplet state. Further work is in progress to fully elucidate the photophysics of these systems.

Conclusions

We have successfully synthesised compounds **1** and **2**, interesting examples of PDI-based molecule functionalised with metal bearing moieties. Studies of the photophysical properties of **1** and **2** reveal the formation of triplet states. The

presence of a triplet excited state has been confirmed by experiments demonstrating the formation of $^1\text{O}_2$. In contrast, a simple, purely organic, model compound **3** displays simple singlet fluorescence confirming the important role played by the Pt-based moiety in modifying the photophysical properties of the PDI molecule. Our studies of modified PDI species are continuing as we further advance our understanding of the photophysical, electrochemical and supramolecular properties of these highly important molecules.

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Notes and references

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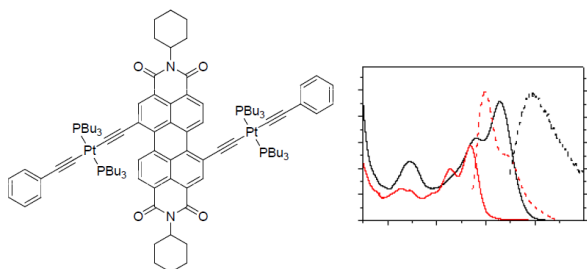
†Electronic Supplementary Information (ESI) available: Additional figures showing a square-wave voltammogram, EPR and spectroelectrochemical measurements recorded for **1**, **2**. Synthetic details for **3** and cifs for the X-ray structures. CCDC 931600 - 931602. See DOI: 10.1039/b000000x/

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Graphical Abstract

Photophysical studies of a perylene diimide (PDI) functionalised with platinum acetylide units reveal the formation of a triplet state upon excitation demonstrating the important role played by the Pt-based moiety in modifying the photophysical properties of the PDI molecule.



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