Pushing Pentacene-Based Fluorescence to the Near-Infrared Region by Platination

Minh-Hai Nguyen and John H. K. Yip*

Department of Chemistry, National University of Singapore, 3 Science 3 Drive, Singapore, 117543

S Supporting Information

ABSTRACT: A series of binuclear platinum complexes of pentacenyl-6,13-diacetylide with different auxiliary ligands were synthesized to probe the effect of metal coordination on electronic spectroscopy and photophysics, to determine the solid-state packing of the complexes, and to tune emission energy. The complexes with anionic, π -donating ligands showed absorption (687–696 nm) and fluorescence (710–726 nm) lower in energy than those with neutral, π -accepting ligands (662–666, 675–686 nm). Our work showed that coordination of Pt ions with π -donating anionic ligands to pentacenyl-6,13-diacetylide could move the fluorescence of the organic chromophore to the near-



infrared region (λ_{em} 710–726 nm). The combined perturbations of alkynation and platination lowered the HOMO \rightarrow LUMO transition up to 0.34 eV.

INTRODUCTION

There is a quest for molecules that display near-infrared (near-IR) luminescence because of their wide applications in fields such as bioimaging, organic photovoltaics, optoelectronics, and photodynamic therapy.1 Various organic and organometallic chromophores (e.g. porphyrin,² squararine,³ and aza-dipyrro-methene⁴), lanthanide complexes,⁵ and nanoparticles^{6a} have been invoked in the development of near-IR emitters.⁶ Incentive to search for new near-IR chromophores arises from the possibility that new chromophores would have different photophysical properties and subcellular localization. For π -conjugated chromophores, their emissions can be shifted to the near-IR region by ring substitution of or extension of π -conjugation of the molecules, which lowers the HOMO-LUMO gap.^{1b,7} In our ongoing study of the photochemistry and photophysics of metalated polycylic aromatic hydrocarbons (PAHs), our attention was drawn to pentacene, which displays fluorescence at the low-energy visible region.⁸ It is envisioned that the chromophore can be converted into a near-IR emitter by lowering its HOMO-LUMO gap. An obvious advantage of pentacene is its intense low-energy visible absorption with an extinction coefficient of $10^4 \text{ M}^{-1}\text{cm}^{-1.9}$ However, the compound is known to be unstable¹⁰ and it is synthetically difficult to modify or add substituents to the ring.¹¹ Nonetheless, Anthony et al. demonstrated that 6,13-bis-(triisopropylsilylethynyl)pentacene (TIPS-pentacene) has higher stability,¹² and lower energy fluorescence,^{8,13a} and lower first ionization energy in the gas phase.^{13b} Recent DFT calculations showed that the red shift of the emission was due to the inductive effect of the ethynyl groups, which reduced the

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LUMO–HOMO gap by stabilizing the LUMO more than the HOMO. $^{\rm 14}$

Metalation of PAHs is an attractive alternative to tune the photophysics of the organic molecules.¹⁵ The d orbitals of transition metals would introduce additional manifolds of orbital interactions and excited states (e.g., MLCT and LMCT). In addition, heavy transition metals, with their high-energy d orbitals and large spin-orbit coupling, can alter the photophysics of PAHs. For instance, attaching a gold(I) or platinum(II) ion to tetracene and tetracenyldiacetylide could lower the fluorescence energy up to 0.53 ${\rm eV}^{16}$ and switch on the phosphorescence of pyrene.¹⁷ Our study of platinated and aurated pyrenes showed that the Pt^{II} ion has stronger perturbation on the electronic structures of the PAHs than the more electrophilic Au^I ion.^{17b} This suggests to us the importance of metal-ligand π interactions in red-shifting the fluorescence of PAHs and the possibility of shifting the fluorescence of pentacene to lower energy by platination. Herein we report a synthetic and spectroscopic study of a series of binuclear [L(Et₃P)₂Pt^{II}]₂pentacenyl-6,13-diacetylide complexes with different auxiliary ligands L (Scheme 1). Our results showed that the collective effect of the ethynyl substitutents and the Pt ions can move the fluorescence of pentacene to the near-IR region and the extent of the red shift is sensitive to the electronic properties of L.

EXPERIMENTAL SECTION

General Methods. All syntheses were carried out under a $\rm N_2$ atmosphere. All the solvents used for synthesis and spectroscopic

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measurements were purified according to the literature procedures. trans-Pt(PEt₃)₂I₂,¹⁸ trans-Pt(PBu₃)₂I₂,¹⁹ and 6,13-bis-(triisopropylsilylethynyl)pentacene²⁰ were prepared according to reported procedures.

Physical Methods. The UV/vis absorption and emission spectra of the complexes were recorded on a Hewlett-Packard HP8452A diode array spectrophotometer and a Perkin-Elmer LS-50D fluorescence spectrophotometer, respectively. Emission lifetimes were recorded on a Horiba Jobin-Yvon Fluorolog FL-1057 fluorescence spectrometer. Cresyl violet was used as a standard in measuring the emission quantum yields.²¹ ¹H and ³¹P{¹H} NMR spectra were recorded on a Bruker ACF 500 spectrometer. All chemical shifts are quoted relative to SiMe₄ (¹H) or H₃PO₄ (³¹P). Elemental analyses of the complexes were carried out in the microanalysis laboratory in the Department of Chemistry at the National University of Singapore.

Synthesis. $[l(Et_3P)_2Pt'']_2$ -pentacenyl-6,13-diacetylide (1a). In a 250 mL Schlenk flask was charged *trans*-Pt(PEt₃)₂I₂ (600 mg, 0.911 mmol), ¹Pr₂NH (5 mL), Bu₄NF (250 mg, 0.800 mmol), CuI (10 mg), and CH₂Cl₂ (30 mL). To the mixture was added a CH₂Cl₂ solution (100 mL) of 6,13-bis(triisopropylsilylethynyl)pentacene (100 mg, 0.156 mmol) over 5 h by using an equalizing funnel. The resulting solution was stirred overnight, and all the solvents were reduced to dryness. The dark green product was collected from column chromatography (silica gel, 20 cm × 4 cm column, hexane/CH₂Cl₂ 2/1 then 1/1, v/v). Yield: 160 mg, 71%. Anal. Calcd for **1a** (C₅₀H₇₂I₂P₄Pt₂): C, 41.68; H, 5.04. Found: C, 41.26; H, 4.72. ¹H NMR (500 MHz, CDCl₃): δ 9.34 (*s*, 4H, H_{5,712,14}), 7.92 (dd, *J* = 3.1, 6.9 Hz, 4H, H_{1,4,8,11}), 7.33 (dd, *J* = 3.1, 6.9 Hz, 4H, H_{2,3,9,10}), 2.30–2.26 (m, 24H, PCH₂CH₃), 1.30–1.23 (m, 36H, PCH₂CH₃).

³¹P{¹H} NMR (202.4 MHz, CDCl₃): δ 9.63 (s, ¹J_{Pt-P} = 2319 Hz). ESI-MS: m/z 1440.0, [M]⁺.

[*I*(*Bu*₃*P*)₂*Pt^{II}*]₂-pentacenyl-6,13-diacetylide (**1b**). The compound was synthesized by following the procedure described for **1a**, except that *trans*-Pt(PBu₃)₂I₂ was used instead of *trans*-Pt(PEt₃)₂I₂. The dark green product was collected from column chromatography (silica gel, 20 cm × 4 cm column, hexane/dichloromethane 4/1, v/v). Yield: 48%. X-ray-quality crystals of **1b** were obtained from CH₂Cl₂/MeOH at room temperature. Anal. Calcd for **1b** ($C_{74}H_{120}I_2P_4Pt_2$): C, 50.00; H, 6.80. Found: C, 50.21; H, 7.01. ¹H NMR (500 MHz, CDCl₃): δ 9.31 (s, 4H, H_{5,712,14}), 7.90 (dd, *J* = 3.1, 6.9 Hz, 4H, H_{1,4,8,11}), 7.31 (dd, *J* = 3.1, 6.9 Hz, 4H, H_{2,39,10}), 2.23–2.20 (m, 24H, PCH₂CH₂CH₂CH₂), 1.68–1.67 (m, 24H, PCH₂CH₂CH₂CH₃), 1.41–1.34 (m, 24H, PCH₂CH₂CH₂CH₃), 0.86–0.83 (t, 36H, PCH₂CH₂CH₂CH₂), 3¹P{¹H} NMR (202.4 MHz, CDCl₃): δ 1.26 (s, ¹*J*_{Pt-P} = 2300 Hz). ESI-MS: *m/z* 1777.3, [M]⁺.

[(C₆H₅S)(Et₃P)₂Pt^l]₂-pentacenyl-6,13-diacetylide (2). To a suspension of **1a** (40 mg, 0.028 mmol) in CH₂Cl₂ (15 mL) was added thiophenol (0.1 mL, 1 mmol) and NEt₃ (0.2 mL, 1.3 mmol). The resulting mixture was stirred for 2 h, and the solvent was then reduced by rotavaporation. The addition of excess MeOH afforded a dark green solid. The product was filtered and thoroughly washed with MeOH and then dried in vacuo. Yield: 28 mg, 72%. X-ray-quality crystals of **2** were obtained from CH₂Cl₂/MeOH at -20 °C. Anal. Calcd for **2** (C₆₂H₈₂P₄Pt₂S₂): C, 52.98; H, 5.88; S, 4.56. Found: C, 52.79; H, 5.83; S, 4.46. ¹H NMR (500 MHz, CDCl₃): δ 9.39 (s, 4H, H_{5,7,12,14}), 7.95 (dd, J = 3.1, 6.3 Hz, 4H, H_{1,4,8,11}), 7.64 (d, J = 7.6 Hz, 4H, *o*-C₆H₅), 7.34 (dd, 4H, H_{2,3,9,10}), 7.11 (t, J = 7.6 Hz, 4H, *m*-C₆H₅), 6.95 (t, J = 7.6 Hz, 2H, *p*-C₆H₅), 2.13-2.08 (m, 24H, PCH₂CH₃),

1.29–1.23 (m, 36H, PCH₂CH₃). ³¹P{¹H} NMR (202.4 MHz, CDCl₃): δ 13.37 (s, ¹J_{Pt-P} = 2409 Hz). ESI-MS: *m*/*z* 1404.2, [M]⁺.

 $[(C_6H_5C_2)(Et_3P)_2Pt^{\parallel}]_2$ -pentacenyl-6,13-diacetylide (3). To a suspension of 1a (50 mg, 0.035 mmol) in CH₂Cl₂ (15 mL) was added CuI (3 mg), triethylamine (5 mL), and phenylacetylene (0.1 mL, 0.892 mmol). Upon stirring for 0.5 h, the suspension turned to a clear green solution. The resulting mixture was further stirred overnight, and all the solvents were removed in vacuo. The dark green product was isolated from column chromatography (basic alumina, $10 \text{ cm} \times$ 2 cm column, hexane/dichloromethane 1/1, v/v). Yield 35 mg, 73%. X-ray-quality crystals of 3 were obtained from CH₂Cl₂/MeOH at room temperature. Anal. Calcd for 3 (C₆₆H₈₂P₄Pt₂): C, 57.05; H, 5.95. Found: C, 57.28; H, 5.44. ¹H NMR (500 MHz, CDCl₃): δ 9.38 (s, 4H, $H_{5.7,12.14}$), 7.91 (dd, J = 3.1, 6.3 Hz, 4H, $H_{1.4.8.11}$), 7.36 $(d, J = 7.5 Hz, 4H, o-C_6H_5), 7.31 (dd, J = 3.1, 6.3 Hz, 4H, H_{2.3,9.10}),$ 7.27-7.24 (m, 4H, m-C₆H₅), 7.16 (t, J = 7.6 Hz, 2H, p-C₆H₅), 2.29-2.25 (m, 24H, PCH₂CH₃), 1.36-1.29 (m, 36H, PCH₂CH₃). ³¹P{¹H} NMR (202.4 MHz, CDCl₃): δ 12.32 (s, ¹*J*_{Pt-P} = 2369 Hz). ESI-MS: m/z 1388.3, [M]⁺.

 $[(Ph_3P)(Et_3P)_2Pt^{\parallel}]_2$ -pentacenyl-6,13-diacetylide-(OTf)₂ (4). To a suspension of 1a (25 mg, 0.017 mmol) in CH2Cl2 was added AgOTf (25 mg, 0.097 mmol) with stirring at room temperature over 0.5 h in the absence of light. The resulting mixture was filtered under argon, and excess triphenylphosphine (100 mg) was added. The solution was stirred for 2 h, and the solvent was then reduced by rotavaporation. The title compound was precipitated by addition of excess Et₂O. Yield: 32 mg, 92%. Slow diffusion of Et₂O into an acetonic solution at room temperature afforded dark green crystals suitable for an X-ray crystallography study. Anal. Calcd for 4 (C88H102F6O6P6Pt2S2): C, 52.59; H, 5.12; S, 3.19. Found: C, 52.23; H, 4.77; S, 3.12. ¹H NMR (500 MHz, CDCl₃): δ 9.24 (s, 4H, H_{5,7,12,14}), 8.03-8.01 (m, 4H, H_{1,4,8,11}), 7.89-7.86 (m, 12H, o-C₆H₅), 7.64-7.63 (m, 18H, m,p-C₆H₅), 7.48-7.46 (m, 4H, H_{2,39,10}), 1.56 (multiplet, 24H, PCH₂CH₃), 1.10-1.07 (m, 36H, PCH₂CH₃). $^{31}P{^{1}H}$ NMR (500 MHz, CDCl₃): δ 11.76 (t, $^{1}J_{Pt-P}$ = 2547 Hz, ${}^{2}J_{P-P} = 22 \text{ Hz}, PPh_{3}), 9.03 \text{ (d, } {}^{1}J_{Pt-P} = 2160 \text{ Hz}, {}^{2}J_{P-P} = 22 \text{ Hz}, PEt_{3}).$ ESI-MS: m/z 855.6, $[M - 2OTf]^{2+}$.

[(C_5H_5N)(Et_3P)₂ Pt^{dI}]₂-pentacenyl-6,13-diacetylide-(OTf)₂ (5). The compound was prepared by following the procedure for 4, except that pyridine was used instead of PPh₃. Yield: 85%. Dark green crystals of 5 were grown by slow diffusion of Et_2O into a CH₂Cl₂ solution at room temperature. Anal. Calcd for 5 ($C_{62}H_{82}F_6N_2O_6P_4Pt_2S_2$): C, 45.31; H, 5.03; N, 1.70; S, 3.90. Found: C, 45.22; H, 5.07; N, 1.66; S, 4.19. ¹H NMR (500 MHz, CDCl₃): δ 9.17 (s, 4H, H_{5,7,12,14}), 8,74 (d, *J* = 5.7 Hz, 4H, *o*-C₅H₅N), 8.07 (t, *J* = 7.6 Hz, 2H, *p*-C₅H₅N), 7.87 (multiplet, 4H, H_{1,48,11}), 7.78–7.75 (m, 4H, *m*-C₅H₅N), 7.35–7.33 (multiplet, 4H, H_{2,39,10}), 1.78 (q, 24H, PCH₂CH₃), 1.26–1.19 (t, 36H, PCH₂CH₃). ³¹P{¹H} NMR (202.4 MHz, CDCl₃): δ 16.56 (s, ¹*J*_{Pt-P} = 2322 Hz). ESI-MS: *m*/*z* 672.1, [M – 2OTf]²⁺.

[($C_6H_3(CH_3)_2NC$)(Et_3P)₂Pt'']₂-pentacenyl-6,13-diacetylide-(ClO_4)₂ (6). To a suspension of 1 (40 mg, 0.028 mmol) in acetonitrile (10 mL) was added 2,6-xylyl isocyanide (20 mg, 0.151 mmol). When it was stirred for 2 h, the suspension turned to a clear green solution. The addition of excess LiClO₄ (100 mg) followed by Et₂O afforded the title product, which was collected and dried. Yield: 25 mg, 55%. Dark green crystals of 6 were grown by slow diffusion of Et₂O into a CH₂Cl₂ solution at room temperature. Anal. Calcd for 6 ($C_{68}H_{90}Cl_2N_2O_8P_4Pt_2$): C, 49.55; H, 5.50; N, 1.70. Found: C, 49.60; H, 5.50; N, 1.75. ¹H NMR (500 MHz, CDCl₃): δ 9.20 (s, 4H, H_{5,7,12,14}), 7.96–7.94 (m, 4H, H_{1,48,11}), 7.44–7.42 (m, 4H, H_{2,3,9,10}), 7.38 (t, 2H, *p*-C₆H₃), 7.27 (d, 4H, *m*-C₆H₃), 2.60 (s, 12H, CH₃), 2.37–2.34 (m, 24H, PCH₂CH₃), 1.41–1.35 (m, 36H, PCH₂CH₃). S¹P{¹</sup>H} NMR (202.4 MHz, CDCl₃): δ 17.11 (s, ¹J_{Pt-P} = 2074 Hz). ESI-MS: *m*/z 724.2, [M – 2CIO₄]²⁺.

X-ray Crystallography. The diffraction experiments were carried out on a Bruker AXS SMART CCD three-circle diffractometer with a sealed tube at 223 K using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The software used was as follows: SMART^{22a} for collecting frames of data, indexing reflections, and determining lattice parameters; SAINT^{22a} for integration of intensity of reflections and scaling; SADABS^{22b} for empirical absorption correction; SHELXTL^{22c} for space group determination, structure solution, and least-squares refinements on $|F|^2$. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions. Crystal data and experimental details are summarized in Table 1

RESULTS AND DISCUSSION

Synthesis and Characterization. The compounds 1a,b were synthesized by Sonogashira coupling of *trans*-Pt^{II}(PR₃)-I₂ (R = Et, Bu) and 6,13-diethynylpentacene, which was generated in situ from desilylation of TIPS-pentacene. 1a was sparingly soluble in common organic solvents, frustrating efforts to obtain single crystals for X-ray diffraction. Nonetheless, ¹H and ³¹P{¹H} NMR, high-resolution ESI-MS, and elemental analysis results confirm the proposed formulation of the compound. Figure 1 shows the nearly identical experimental and simulated cluster peaks for [1a]⁺ (*m*/*z* 1440.0). The analogous complex 1b, bearing the more easily solubilized PBu₃, is soluble in many organic solvents, even hexane.

Complex 2 was obtained from substitution of the iodide ions in 1a by benzenethiolate, and complex 3 was prepared from Sonogashira coupling of 1a and phenylacetylene. Complexes 4 and 5 were easily prepared in good yields from halide abstraction with AgOTf followed by reaction with PPh₃ and pyridine, respectively. Facile substitution of iodides in 1a by 2,6-xylyl isocyanide in CH₃CN followed by anion exchange with LiClO₄ afforded the green complex 6. Compounds 2-6were much more soluble than 1a in solvents such as CH₂Cl₂, CHCl₃, and CH₃CN, making X-ray characterization of the complexes possible.

The ¹H NMR spectra of all the complexes exhibit the same pattern of pentacenyl proton signals, which include one singlet ($H_{5,7,12,14}$) and two doublet of doublets ($H_{1,4,8,11}$ and $H_{2,3,9,10}$), indicating a D_{2h} symmetry of the complexes in solution. Similarly, ³¹P{¹H} NMR spectra of all the complexes except 4 show sharp singlets with ¹⁹⁵Pt satellites. The ¹ J_{Pt-P} coupling constants of 2074–2409 Hz are consistent with a trans orientation of the phosphines.^{15d,23} The spectrum of 4 displays a doublet and a triplet with intensity ratio 2:1, which are ascribable to the ligands PEt₃ and PPh₃, respectively. The magnitude of ² J_{P-P} (22 Hz) is consistent with the cis orientation of the two ligands.^{15c,16,24}

Crystal Structures. Structures of 1b, 2·2CH₂Cl₂, 3, 4.2H2O, 5.CH2Cl2, and 6 are shown in Figures 2-7, and selected bond lengths and angles are given in Table 2. The Pt^{II} ions show a distorted-square-planar geometry with C-Pt-P angles of $80.2(3)-92.33(14)^{\circ}$ and P-Pt-X angles of $87.70(14)-101.89(8)^{\circ}$ (X is the donor atom of the ligand L). The two trialkylphophines are in a trans configuration (P1- $Pt-P2 = 173.11(10)-177.24(3)^{\circ}$, and the Pt-P bond lengths (2.2959(13)-2.321(3) Å) are typical for Pt^{II}-tertiary phosphine compounds.^{23b,25} The Pt ions in 4.2H₂O show more severe deviation from the ideal square-planar geometry due to the steric repulsion between the PEt₃ and PPh₃ ligands, which causes the Et₃P-Pt-PEt₃ linkage to bend toward the pentacenyl ring $(P1-Pt-P2 = 162.48(8)^{\circ})$ and elongation of the Pt–PEt₃ bonds (2.333(2) and 2.346(2) Å). The Pt–PPh₃ bond distance of 2.308 (2) Å falls in the normal range of Pt-PPh₃ bond lengths (2.29-2.37 Å).²⁶ Despite the different electronic properties of L, the Pt-C(acetylide) distances in the

Table 1. Crystal Data for 1b, 2·2CH₂Cl₂, 3, 4·2H₂O, 5·CH₂Cl₂, and 6

	1b	$2 \cdot 2 CH_2 Cl_2$	3	$4 \cdot 2 H_2 O$	$5 \cdot CH_2Cl_2$	6
empirical formula	$C_{74}H_{120}I_2P_4Pt_2$	$C_{64}H_{86}Cl_4P_4Pt_2S_2$	$C_{66}H_{82}P_4Pt_2$	$C_{88}H_{106}F_6O_8P_6Pt_2S_2$	$C_{63}H_{84}Cl_2F_6N_2O_6P_4Pt_2S_2$	$C_{68}H_{90}Cl_2N_2O_8P_4Pt_2$
formula wt	1777.56	1575.31	1389.38	2045.85	1728.4	1648.38
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_{1}/c$	$P\overline{1}$	$P2_1/n$	P2/n	$P\overline{1}$	$P2_{1}/c$
unit cell dimens						
a (Å)	8.9087(12)	8.5325(19)	9.3267(12)	22.021(4)	9.359(5)	18.470(3)
b (Å)	15.686(2)	12.255(3)	10.0902(13)	9.6457(17)	19.357(9)	9.6544(13)
c (Å)	27.615(4)	15.834(4)	32.989(4)	22.317(4)	20.162(10)	39.616(6)
α (deg)	90	95.889(4)	90	90	77.513(9)	90
β (deg)	97.571(4)	95.537(4)	94.049(10)	111.396	85.523(10)	99.540(3)
γ (deg)	90	100.011(4)	90	90	78.643(9)	90
V (Å ³)	3825.4(9)	1610.8(6)	3096.8(7)	4413.6(13)	3494(3)	6966.5(16)
Ζ	2	1	2	2	2	4
calcd density (g cm ⁻³)	1.543	1.624	1.49	1.539	1.643	1.572
abs coeff (mm ⁻¹)	4.581	4.706	4.653	3.388	4.292	4.234
F(000)	1772	786	1388	2060	1720	3304
cryst size (mm ³)	0.90 × 0.12 × 0.06	0.30 × 0.06 × 0.06	0.30 × 0.12 × 0.10	$0.40\times0.26\times0.08$	$0.60\times0.10\times0.04$	$0.60 \times 0.14 \times 0.04$
θ range for data collecn (deg)	1.49-27.49	1.30-25.00	2.11-27.50	1.63-25.00	1.34-27.50	1.12-25.00
index ranges	$-11 \leq h \leq 11$	$-10 \le h \le 10$	$-11 \le h \le 12$	$-26 \le h \le 25$	$-12 \le h \le 12$	$-20 \le h \le 21$
	$-20 \le k \le 19$	$-14 \le k \le 14$	$-13 \le k \le 10$	$-11 \le k \le 11$	$-25 \le k \le 25$	$-11 \leq k \leq 11$
	$-30 \le l \le 35$	$-18 \le l \le 18$	$-42 \leq l \leq 41$	$-26 \le l \le 23$	$-26 \le l \le 26$	$-47 \leq l \leq 44$
no. of rflns collected	26 707	16 877	21 506	25 105	44 567	39 257
no. of indep rflns (R(int))	8775 (0.0397)	5664 (0.0670)	7087 (0.0442)	7758 (0.0607)	15 964 (0.0853)	12 264 (0.0738)
max, min transmissn	0.7706, 0.1044	0.7655, 0.3326	0.6662, 0.5459	0.7733, 0.3443	0.8471, 0.1827	0.8489, 0.1856
no. of data/restraints/params	8775/0/376	5664/0/349	7087/41/348	7758/53/550	15 964/133/821	11 264/603/1025
final R indices ^a $(I > 2\sigma(I))$						
R1	0.0296	0.0494	0.0366	0.0615	0.0684	0.0603
wR2	0.0658	0.0999	0.0845	0.1397	0.1758	0.1396
goodness of fit (GOF) ^b	1.063	1.109	1.078	1.142	1.033	1.02
largest diff peak, hole (e ${\rm \AA}^{-3})$	2.012, -0.569	1.722, -3.826	2.288, -0.748	2.792, -1.063	14.832, -2.657	2.460, -1.402
		π^{2} (π^{4}) 1/2 b	$COP \left[\left(T^{2} \right) \right]$	$\pi 2 \lambda 2 / (\lambda 1 1 / 2)$.1 .

 a R1 = (|| F_{o} | - | F_{c} |)/(| F_{o} |); wR2 = [$w(F_{o}^{2} - F_{c}^{2})/w(F_{o}^{4})$]^{1/2}. b GOF = [$(w(F_{o}^{2} - F_{c}^{2})^{2}/(n - p)$]^{1/2}. For all crystal determinations, the scan type and wavelength of radiation used are ω and 0.710 73 Å, respectively.



Figure 1. (a) ESI-MS cluster peak for $[1a]^+$ and (b) simulated isotopic distribution for $[1a]^+$.

complexes are rather similar (1.984(9)-1.963(9) Å). The Pt–X bond distances are normal.^{23c,27}

In **1b**, $2 \cdot 2CH_2Cl_2$, **3**, and $4 \cdot 2H_2O$, the coordination planes of the two Pt ions are parallel to each other and make a dihedral angles of 89.14, 72.82, 87.45, and 73.12°, respectively, with the central pentacenyl ring. On the other hand, the two coordination planes in $5 \cdot CH_2Cl_2$ and **6** are staggered (dihedral angles 54.82 and 32.91°, respectively) and the dihedral angles

between the planes and the pentacenyl rings are 59.58, 69.21, 70.83, and 78.24 $^{\circ}$, respectively.

The pentacenyl rings of **1b**, $2 \cdot 2 \text{CH}_2 \text{Cl}_2$, and $4 \cdot 2 \text{H}_2 \text{O}$ are widely separated (>6 Å) and are parallel in the crystals. It is noted that some H atoms of the butyl groups (**1b**) and the ethyl groups ($2 \cdot 2 \text{CH}_2 \text{Cl}_2$ and $4 \cdot 2 \text{H}_2 \text{O}$) are close to the pentacenyl rings with calculated H(Bu/Et)–C(pentacenyl ring) distances of 2.644–2.893 Å, which fall within the range of C–H… π hydrogen bonds,²⁸ suggesting the presence of these interactions (Figure 2b).

The pentacenyl rings in the crystals of 3 (Figure 4b) and $5 \cdot CH_2Cl_2$ (Figure 6b) slightly overlap in a head-to-tail fashion, forming staircaselike patterns. The two overlapped rings in $5 \cdot CH_2Cl_2$ are offset along the short axes of the rings. The rings in 3 are uniformly separated by 3.466 Å (perpendicular distance between the mean planes of the rings), but the rings in $5 \cdot CH_2Cl_2$ are alternately separated by 3.477 and 3.422 Å. The distances fall in the range of $\pi - \pi$ interactions.²⁹

The pentacenyl rings in the crystal of **6** form a 2D herringbone pattern (Figure 7b) similar to that of pentacene. Each pentacenyl ring is involved in edge-to-face $C-H\cdots\pi$ interactions with the rings in two adjacent columns. The interacting rings are nearly perpendicular to each other, showing a dihedral angle of 87.95°, which is larger than the corresponding angle (51.78°) in the crystal of pentacene.³⁰ The terminal H₁, H₂, H₈, and H₉ atoms of the pentacenyl ring are







Figure 2. (a) ORTEP plot of **1b** (thermal ellipsoids drawn at the 50% probability level). H atoms are not shown for clarity. Color scheme: Pt, green; P, orange; C, gray; I, purple. (b) Solid-state packing of **1b** showing possible C-H··· π interactions between H atoms (light gray) of butyl groups and the pentacenyl rings (d1 = 2.704 Å; d2 = 2.845 Å; d3 = 2.876 Å; d4 = 2.853 Å; d5 = 2.845 Å; d6 = 2.883 Å).



Figure 3. ORTEP plot of $2 \cdot 2CH_2Cl_2$ (thermal ellipsoids drawn at the 50% probability level). H atoms and solvent molecules are not shown for clarity. Color scheme: Pt, green; P, orange; C, gray; S, yellow.

directed toward the first and second rings of its two adjacent pentacenyl rings. The centroid–centroid distance between the terminal (six-membered) ring of the first molecule and the second (six-membered) ring of the adjacent molecule is 5.146 Å (4.713 Å for pentacene). The distance is typical for edge-to-face interactions between aromatic molecules.³¹



Figure 4. (a) ORTEP plot of **3** (thermal ellipsoids drawn at the 50% probability level). H atoms and disordered ethyl groups are not shown for clarity. Color scheme: Pt, green; P, orange; C, gray. (b) π - π stacking of **3**.



Figure 5. ORTEP plot of $4.2H_2O$ (thermal ellipsoids drawn at the 50% probability level). H atoms, anions, and water molecules are not shown for clarity. Color scheme: Pt, green; P, orange; C, gray.

Absorption and Emission Spectroscopy. Figure 8 shows the absorption spectra of the complexes, and spectral data are summarized in Table 3. Complex 1a is sparingly soluble, and therefore only its solution emission was measured. All the complexes display four absorption bands: a broad intense vibronic band at 500–770 nm (I), a weak and narrow band around 435–444 nm (II), a shoulder at 356–377 nm (III), and a very strong, sharp band at 314–320 nm (IV). The spectra of pentacene and TIPS-pentacene display similar absorptions, but at higher energies. The absorption bands are assigned to ${}^{1}\pi \rightarrow \pi^{*}$ transitions primarily localized in the pentacenyl-6,13-diacetylide ligand. Pentacene belongs to a class of molecules called alternant hydrocarbons, which exhibit intense absorptions arising from four electronic transitions, namely LUMO \leftarrow HOMO (${}^{1}B_{1u} \leftarrow {}^{1}A_{g}$), LUMO \leftarrow HOMO-1 (${}^{1}B_{2u} \leftarrow {}^{1}A_{g}$), and LUMO+1 \leftarrow HOMO-1 (${}^{1}B_{1u} \leftarrow {}^{1}A_{g}$). The second and third transitions lead to the two degenerate ${}^{1}B_{2u}$ excited states, which undergo strong



Figure 6. (a) ORTEP plot of $\mathbf{5} \cdot \text{CH}_2\text{Cl}_2$ (thermal ellipsoids drawn at the 30% probability level). H atoms, anions, and solvent molecules are not shown for clarity. Color scheme: Pt, green; P, orange; C, gray; N, blue. (b) $\pi - \pi$ stacking of $\mathbf{5} \cdot \text{CH}_2\text{Cl}_2$.

configuration interaction to give the high-energy "plus" state ${}^{1}B_{2u}$ and the low-energy "minus" state ${}^{1}B_{2u}$. Although the symmetries of the Pt₂ complexes and pentacene are different, there is still a direct correspondence between the four absorption bands displayed by the complexes and the four electronic transitions of pentacene. Band I in the spectra of the complexes corresponds to the LUMO \leftarrow HOMO $({}^{1}B_{1u} \leftarrow {}^{1}A_{g})$ transition, which is also known as an S_0 (singlet ground state) $\rightarrow S_1$ (the lowest energy singlet excited state) transition. The intense band IV corresponds to the LUMO+1 \leftarrow HOMO-1 (${}^{1}B_{1u} \leftarrow {}^{1}A_{o}$) transition. The shoulder III is attributed to the transition to the "plus" state ${}^1B_{2u}$ + (${}^1B_{2u}$ + \leftarrow 1A_g). The weak absorption II is ascribable to the transition to the "minus" state $({}^{1}B_{2u}^{-} \leftarrow {}^{1}A_{z})$, which is pseudo parity forbidden. The transition is significantly intensified in the spectra of the complexes, indicating that the electronic structure of the pentacenyl ring is significantly perturbed by the Pt ions and the ethynyl groups. Similar intensification of the forbidden ${}^{1}B_{2u}^{-} \leftarrow {}^{1}A_{g}$ transition has been observed in Au^I and Pt^{II} pyrene¹⁷ and anthracene³³ complexes and is taken as evidence for metal perturbation.

Comparing the spectra of the complexes with that of TIPSpentacene shows that replacing the triisopropylsilyl groups with the $[L(R_3P)_2Pt]^{n+}$ ions (R = ethyl, butyl, n = 1, 2) leads to a red shift of the four transitions. While band III is red-shifted only slightly (~250 cm⁻¹), the energies of the bands I, II, and IV are lowered by 450–1200, 480–2000, and 400–1000 cm⁻¹, respectively. The energy of the LUMO \leftarrow HOMO transition (which corresponds to band I of the complexes) of pentacene is lowered by 1540 cm⁻¹ by substitution of triisopropylsilylethynyl groups at its 6- and 13-positions. Our result shows that



Figure 7. (a) ORTEP plot of **6** (thermal ellipsoids drawn at the 30% probability level). H atoms, anions, and disordered xylyl groups are not shown for clarity. Color scheme: Pt, green; P, orange; C, gray; N, blue. (b) Herringbone pattern of the pentacenyl rings of **6**. For clarity, only the rings are shown.

platination and alkynylation collectively red-shifts the transition up to 2740 cm^{-1} (0.34 eV).

Interestingly, the complexes can be divided into two groups on the basis of the energies of their LUMO \leftarrow HOMO transitions. The neutral complexes have similar LUMO \leftarrow HOMO transition energies (λ_{max} 687–696 nm) which are invariably lower than those of the cationic complexes (λ_{max} 662–664 nm). In addition, the neutral complexes show broader bands I. Although the red shift (440–740 cm⁻¹) is small, it is significant, as it clearly indicates that the absorption energy is sensitive to the [L(R₃P)₂Pt]^{*n*+} ions. Notably, while 4–6 do not show any significant absorption beyond 700 nm, the bands I of **1b**, **2**, and **3** extend into the near-IR region.

All the complexes are photoluminescent, and their solution and solid-state emission spectra are shown in Figures 9 and 10, respectively. The fluorescence of **1a**,**b**, **2**, and **3** spans from 650 to 900 nm and that of 4-6 from 630 to 850 nm. The lifetimes and quantum yields of the solution emission are given in Table 3.

The nanosecond lifetimes (2.7-8.9 ns) and small Stokes shifts between the emission and the LUMO \leftarrow HOMO transition suggest the luminescence is LUMO \rightarrow HOMO $(S_1 \rightarrow S_0)$ fluorescence centered in the pentacenyl ring. Quantum yields of the emission range from 0.025 to 0.162. Similar to the case for the absorptions, the fluorescences of the complexes are red-shifted from the fluorescence of TIPSpentacene ($\lambda_{max} = 656 \text{ nm}$) and pentacene ($\lambda_{max} 578 \text{ nm}$) by 430–1470 and 2490–3530 cm⁻¹, respectively. In accord with the energies of the LUMO \leftarrow HOMO transitions, the emissions of **1a,b**, **2**, and **3** ($\lambda_{max} 710-726 \text{ nm}$) are 490– 1040 cm⁻¹ lower than those of **4**–**6** ($\lambda_{max} 675-686 \text{ nm}$). Table 4 shows the percentage of emission intensity at wavelengths shorter and longer than 700 nm.

	1b	$2 \cdot 2 CH_2 Cl_2$	3	$4 \cdot 2 H_2 O$	$5 \cdot CH_2Cl_2$	6
			Bond Distances			
Pt(1)-C(1)	1.971(4)	1.966(8)	1.971(5)	1.975(8)	1.963(9)	1.984(9)
Pt(1)-X	2.6545(3)	2.363(2)	1.990(5)	2.308(2)	2.088(8)	1.928(9)
Pt(1) - P(1)	2.3081(10)	2.321(2)	2.2975(13)	2.333(2)	2.302(3)	2.300(3)
Pt(1) - P(2)	2.3140(10)	2.312(2)	2.2959(13)	2.346(2)	2.321(3)	2.317(2)
			Bond Angles			
C(1)-Pt(1)-X	177.48(10)	177.7(3)	179.1(2)	173.8(2)	177.0(4)	176.9(4)
P(1)-Pt(1)-P(2)	177.24(3)	176.58(8)	176.68(5)	162.48(8)	173.11(10)	174.35(9)
C(1)-Pt(1)-P(1)	90.98(10)	87.4(2)	92.33(14)	80.2(3)	86.5(3)	85.3(3)
X - Pt(1) - P(1)	88.13(3)	92.89(7)	87.70(14)	101.89(8)	91.3(2)	92.6(3)
C(1) - Pt(1) - P(2)	86.92(10)	90.8(2)	87.23(14)	82.5(3)	89.1(3)	89.1(3)
X - Pt(1) - P(2)	93.90(3)	88.97(8)	92.68(14)	95.60(8)	93.2(2)	93.0(3)
C(1)-C(2)-C(6)	177.5(4)	177.9(8)	171.1(5)	175.9(10)	173.7(11)	177.8(10)
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 $^{t}X = donor atom of the auxiliary ligand L; L = I, S, C, P, N, C for 1b and 2-6, respectively.$



Figure 8. UV-vis absorption spectra of 1b (black), 2 (red), 3 (orange), 4 (green), 5 (blue), and 6 (violet) in CH_2Cl_2 at room temperature.

While only 34.2-50.57% of the total fluorescence intensity of 4-6 is at wavelengths longer than 700 nm, the emissions of 1a,b, 2, and 3 lie mainly (77.3-87.3% of total emission intensity) in the near-IR region. Accordingly, the complexes can be regarded as near-IR emitters. Solids of 1a,b and 2 (λ_{max} 768-779 nm) display emissions lower in energy than the corresponding solution emissions. The solid-state luminescences of 1a and 2 are weak, and solids of 3-6 are not emissive.

Given the orbital parentage of the absorption and emission, the energies of the transitions can be used to gauge the HOMO-LUMO gaps. In view of the localization of the excited state in the pentacenyl ring, it is reasonable to assume that the exchange interaction and electron-electron repulsion in the lowest energy singlet excited states of the complexes and in TIPS-pentacene and pentacene are similar. Also, according to the energies of LUMO ← HOMO transitions, the HOMO-LUMO gaps follow the order 1a,b, 2, 3 < 4-6 < TIPSpentacene < pentacene. Recent computational studies¹⁴ showed that the HOMO-LUMO gap in TIPS-pentacene is reduced because of the inductive effect of the sp-hybridized ethynyl substituents, which preferentially stabilize the LUMO more than the HOMO. The reduced HOMO-LUMO gaps in the Pt2 complexes are partly due to the inductive effect of the ethynyl groups. Replacing the triisopropylsilyl groups with the positively charged $[L(Et_3P)_2Pt]^{2+}$ (L = pyridine, PPh₃, 2,6-xylyl isocyanide)

could increase the inductive effect, leading to further decrease of the HOMO-LUMO gaps. The neutral complexes with π -donating anionic ligands L show the largest red shifts and, hence, the smallest HOMO-LUMO gaps. In a recent study, we showed that the absorption and fluorescence of $[I(Et_3P)_2Pt]_2$ -tetracenyl-5,12-diacetylide $(\lambda_{\rm max}$ 572 nm) are lower in energy than those of (Ph₃- PAu^{I} ₂-tetracenyl-5,12-diacetylide (λ_{max} 553 nm).¹⁶ As the Pt^{II} ions are stronger π -donors than the electrophilic Au^I ion, our finding highlights the effect of metal-acene π interactions on the energies of the frontier π and π^* orbitals of the acene. It is possible that the small HOMO-LUMO gaps in 1–3 are due to orbital interactions with $[L(Et_3P)_2Pt]$ $(L = I^-, PhS^-, PhC_2^-)$. Our recent study shows that the HOMO of tetracenyl-5,12-diacetylide is higher in energy than the $5d\pi$ orbitals of the Pt ion in the $[I(Et_3P)_2Pt]$ fragment. Similarly, the $5d\pi$ orbitals of the Pt ions should be lower in energy than the HOMO of the pentacenyl-6,13diacetylide, which is more extensively π -conjugated than the tetracenyl-5,12-diacetylide. The anionic, π -donating L is expected to destabilize the $d\pi$ orbital of the Pt ions, reducing the energy gap between the metal orbitals and the HOMO of pentacenyl-6,13-diacetylide ion (Scheme 2).

According to second-order perturbation theory,³⁴ decreasing the energy gap would increase the extent of metal–ligand orbital interactions, resulting in a more destabilized HOMO and LUMO. Since the $d\pi$ orbitals are closer in energy to the HOMO than to the LUMO, the HOMO should be more destabilized than the LUMO by the π interactions. The overall result is a decrease of the HOMO–LUMO gap (Scheme 2). On the other hand, the Sd π orbitals of the Pt ions in the cationic complexes should be lower in energy than those of the neutral complexes. As the gap between the metal and ligand orbitals increases, the π interactions become weaker and hence the red shifts of the absorption and fluorescence become smaller.

Cyclic voltammograms (CVs) of **3** and **5** show two quasireversible oxidation waves at -0.18 and 0.37 V and at 0.08 and 0.60 V (vs Fc⁺/Fc). The first oxidation of the complexes is cathodically shifted from the corresponding oxidation of TIPSpentacene, which occurs at -0.38 V. It is consistent with the proposed bonding picture where the HOMOs of the complexes, which should be mainly localized in the pentacenyl-6,13-diacetylide, are destabilized by the metal– ligand π interactions. The fact that the first oxidation potential Table 3. Absorption and Emission Spectroscopic Data of the Compounds

	band (nm) (ϵ (10 ⁻⁴ M ⁻¹ cm ⁻¹))							
compd	I	II	III	IV	soln	solid state	emission lifetime $ au_{ m fl}$ (ns)	emission quantum yield Φ_{fl}
la	а	а	а	а	710	779 ⁶	4.0	а
1b	687 (3.20), 632 (1.78), 586 (0.62) (s)	442 (0.25)	364 (1.73) (s), 339 (2.86)	318 (28.67)	713	768	5.0	0.072
2	694 (3.04), 637 (1.73), 589 (0.66) (s)	443 (0.32)	366 (1.97) (s), 339 (3.48)	319 (24.45)	723	778 ^b	3.2	0.025
3	696 (3.32), 639 (1.89), 590 (0.66) (s)	444 (0.36)	377 (2.41)	320 (29.60)	726	с	2.7	0.025
4	664 (3.34), 610 (1.73), 564 (0.59) (s)	435 (0.34), 410 (0.40) (s)	361 (1.33) (s), 331 (3.24)	314 (25.20)	675	с	8.9	0.162
5	666 (2.80), 613 (1.53), 565 (0.54) (s)	436 (0.30), 410 (0.37) (s)	363 (1.45)	315 (26.97)	686	с	6.0	0.079
6	662 (3.80), 609 (2.04), 563 (0.74) (s)	439 (0.44), 413 (0.50), 395 (0.74)	356 (1.70) (s), 341 (3.26) (s)	314 (20.73)	677	с	5.8	0.082
aNat Ja	tomained commutally because of the m	oor colubility of 10	bThe emission in	tonsitus is store		None	-	

"Not determined accurately because of the poor solubility of 1a. "The emission intensity is very weak. "Nonemissive.



Figure 9. Solution emission spectra of the complexes in CH_2Cl_2 at room temperature.



Figure 10. Solid-state emission spectra of 1a (brown), 1b (black), and 2 (orange) at room temperature.

of 3 (-0.18 V) is lower than that of 5 (0.08 V) indicates that the HOMO energy of 3 is higher than that of 5, as suggested by the electronic spectroscopy of the complexes. Complexes 3 and 5 show reduction waves at -1.86 and -1.73 V, respectively, which are lower than the corresponding reduction of TIPS-pentacene (-1.50 V), suggesting that the LUMOs of the complexes are destabilized by the metalligand interactions.

Table 4	. Percentage	of	Emission	Intensity	at	Wavelengths
<700 nr	n and >700 1	ım				

compd	<700 nm (%)	>700 nm (%)
1a	22.7	77.3
1b	18.7	81.3
2	12.2	87.8
3	11.6	88.4
4	65.8	34.2
5	49.3	50.7
6	57.0	43.0

Scheme 2



CONCLUSION

In this study, we demonstrated that the electronic structure of pentacenyl-6,13-diacetylide can be perturbed by Pt^{II} coordination. The extent of perturbation, as reflected by the red shift of the absorption and fluorescence, is sensitive to the electronic properties of the $[L(R_3P)_2Pt]^{n+}$ ions. The π -donating and anionic auxiliary ligands have stronger perturbation than the π -accepting, neutral ligands. The fluorescence of the complexes is mainly based on the pentacenyl ring, and the Pt ions appended with π -donating, anionic ligands can shift the fluorescence to the near-IR region. The combined perturbations of alkynation and platination lowered the LUMO \leftarrow HOMO transition up to 0.34 eV.

ASSOCIATED CONTENT

Supporting Information

CIF files giving crystallographic data for 1b, $2 \cdot 2$ CH₂Cl₂, 3, $4 \cdot 2$ H₂O, $5 \cdot$ CH₂Cl₂, and 6, and figures giving cyclic voltammograms of 3, 5,

and TIPS-pentacene. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: chmyiphk@nus.edu.sg.

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REFERENCES

(1) (a) Escobedo, J. O.; Rusin, O.; Lim, S.; Strongin, R. M. Curr. Opin. Chem. Biol. 2010, 14, 64–70. (b) Qian, G.; Wang, Z. Y. Chem. Asian J. 2010, 5, 1006–1029.

(2) (a) Borek, C.; Hanson, K.; Djurovich, P. I.; Thompson, M. E.; Aznavour, K.; Bau, R.; Sun, Y.; Forrest, S. R.; Brooks, J.; Michalski, L.; Brown, J. Angew. Chem., Int. Ed. 2007, 46, 1109–1112. (b) Won, D.-H.; Toganoh, M.; Terada, Y.; Fukatsu, S.; Uno, H.; Furuta, H. Angew. Chem., Int. Ed. 2008, 47, 5438–5441.

(3) (a) Arunkumar, E.; Forbes, C. C.; Noll, B. C.; Smith, B. D. J. Am. Chem. Soc. 2005, 127, 3288–3289. (b) Arunkumar, E.; Fu, N.; Smith, B. D. Chem. Eur. J. 2006, 12, 4684–4690.

(4) (a) Zhao, W.; Carreira, E. M. Angew. Chem., Int. Ed. 2005, 44, 1677–1679. (b) McDonnell, S. O.; O'Shea, D. F. Org. Lett. 2006, 8, 3493–3496.

(5) (a) Zucchi, G. I.; Maury, O.; Thuéry, P.; Ephritikhine, M. Inorg. Chem. 2008, 47, 10398–10406. (b) Ronson, T. K.; Lazarides, T.; Adams, H.; Pope, S. J. A.; Sykes, D.; Faulkner, S.; Coles, S. J.; Hursthouse, M. B.; Clegg, W.; Harrington, R. W.; Ward, M. D. Chem. Eur. J. 2006, 12, 9299–9313.

(6) (a) Altınoğlu, E. İ.; Adair, J. H. Wiley Interdiscip. Rev.: Nanomed. Nanobiotechnol. 2010, 2, 461–477. (b) Wang, X.-Z.; Wong, W.-Y.; Cheung, K.-Y.; Fung, M.-K.; Djurisic, A. B.; Chan, W.-K. Dalton Trans. 2008, 5484–5494. (c) Wang, X.-Z.; Wang, Q.; Yan, L.; Wong, W.-Y.; Cheung, K.-Y.; Ng, A.; Djurišić, A. B.; Chan, W.-K. Macromol. Rapid Commun. 2010, 31, 861–867.

(7) (a) Pschirer, N. G.; Kohl, C.; Nolde, F.; Qu, J.; Müllen, K. Angew. Chem., Int. Ed. 2006, 45, 1401–1404. (b) Zhou, G. J.; Wong, W. Y.; Ye, C.; Lin, Z. Adv. Funct. Mater. 2007, 17, 963–975. (c) Zhou, G.-J.; Wong, W.-Y. Chem. Soc. Rev. 2011, 40, 2541–2566. (d) Aly, S. M.; Ho, C.-L.; Wong, W.-Y.; Fortin, D.; Harvey, P. D. Macromolecules 2009, 42, 6902–6916. (e) Liu, L.; Wong, W.-Y.; Poon, S.-Y.; Shi, J.-X.; Cheah, K.-W.; Lin, Z. Chem. Mater. 2006, 18, 1369–1378.

(8) Maulding, D. R.; Roberts, B. G. J. Org. Chem. 1969, 34, 1734– 1736.

(9) Perkampus, H.-H. UV-VIS Atlas of Organic Compounds, 2nd ed.; VCH: Weinheim, Germany, 1992.

(10) (a) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. J. Am. Chem. Soc. **1998**, 120, 664–672. (b) Maliakal, A.; Raghavachari, K.; Katz, H.; Chandross, E.; Siegrist, T. Chem. Mater. **2004**, 16, 4980–4986.

(11) Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. J. Am. Chem. Soc. 2000, 122, 12876–12877.

(12) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. J. Am. Chem. Soc. 2001, 123, 9482–9483.

(13) (a) Coppo, P.; Yeates, S. G. Adv. Mater. 2005, 17, 3001–3005.
(b) Griffith, O. L.; Gruhn, N. E.; Anthony, J. E.; Purushothaman, B.; Lichtenberger, D. L. J. Phys. Chem. C 2008, 112, 20518–20524.

(14) Kaur, I.; Jia, W.; Kopreski, R. P.; Selvarasah, S.; Dokmeci, M. R.; Pramanik, C.; McGruer, N. E.; Miller, G. P. J. Am. Chem. Soc. **2008**, 130, 16274–16286.

(15) (a) Partyka, D. V.; Esswein, A. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. Organometallics 2007, 26, 3279–3282. (b) Gao, L.; Peay, M. A.; Partyka, D. V.; Updegraff, J. B.; Teets, T. S.; Esswein, A. J.; Zeller, M.; Hunter, A. D.; Gray, T. G. Organometallics 2009, 28, 5669-5681. (c) Wang, B.-Y.; Karikachery, A. R.; Li, Y.; Singh, A.; Lee, H. B.; Sun, W.; Sharp, P. R. J. Am. Chem. Soc. 2009, 131, 3150-3151. (d) Khan, M. S.; Al-Mandhary, M. R. A.; Al-Suti, M. K.; Al-Battashi, F. R.; Al-Saadi, S.; Ahrens, B.; Bjernemose, J. K.; Mahon, M. F.; Raithby, P. R.; Younus, M.; Chawdhury, N.; Kohler, A.; Marseglia, E. A.; Tedesco, E.; Feeder, N.; Teat, S. J. Dalton Trans. 2004, 2377-2385. (e) Chan, C. K. M.; Tao, C.-H.; Tam, H.-L.; Zhu, N.; Yam, V. W.-W.; Cheah, K.-W. Inorg. Chem. 2009, 48, 2855-2864. (f) Kim, K.-Y.; Liu, S.; Köse, M. E.; Schanze, K. S. Inorg. Chem. 2006, 45, 2509-2519. (g) Wong, W.-Y.; Ho, C.-L. Acc. Chem. Res. 2010, 43, 1246-1256. (h) Wong, W.-Y.; Ho, C.-L. Coord. Chem. Rev. 2006, 250, 2627-2690. (i) Wong, W.-Y. Dalton Trans. 2007, 4495-4510. (j) Wong, W.-Y.; Harvey, P. D. Macromol. Rapid Commun. 2010, 31, 671-713. (k) Wong, W.-Y. Macromol. Chem. Phys. 2008, 209, 14-24. (1) Wong, W.-Y.; Wang, X.-Z.; He, Z.; Djurisic, A. B.; Yip, C.-T.; Cheung, K.-Y.; Wang, H.; Mak, C. S. K.; Chan, W.-K. Nat. Mater. 2007, 6, 521-527.

(16) Nguyen, M.-H.; Yip, J. H. K. Organometallics **2010**, *29*, 2422–2429.

(17) (a) Hu, J.; Yip, J. H. K.; Ma, D.-L.; Wong, K.-Y.; Chung, W.-H. Organometallics **2009**, 28, 51–59. (b) Heng, W. Y.; Hu, J.; Yip, J. H. K. Organometallics **2007**, 26, 6760–6768.

(18) Hannebohn, O.; Klemm, W. Z. Anorg. Allg. Chem. 1936, 229, 225–251.

(19) Rahn, J. A.; Baltusis, L.; Nelson, J. H. Inorg. Chem. 1990, 29, 750-755.

(20) Chen, J.; Subramanian, S.; Parkin, S. R.; Siegler, M.; Gallup, K.; Haughn, C.; Martin, D. C.; Anthony, J. E. *J. Mater. Chem.* **2008**, *18*, 1961–1969.

(21) Isak, S. J.; Eyring, E. M. J. Phys. Chem. 1992, 96, 1738–1742.
(22) (a) SMART & SAINT Software Reference Manuals, version 4.0;
Siemens Energy and Automation, Inc., Analytical Instrumentation: Madison, WI, 1996. (b) Sheldrick, G. M. SADABS: Software for Empirical Absorption Correction; University of Göttingen, Göttingen, Germany, 1996. (c) SHELXTL Reference Manual, version 5.03; Siemens Energy and Automation, Inc., Analytical Instrumentation: Madison, WI, 1996.

(23) (a) Yam, V. W.-W.; Tao, C.-H.; Zhang, L.; Wong, K. M.-C.; Cheung, K.-K. Organometallics 2001, 20, 453–459. (b) Tao, C.-H.; Zhu, N.; Yam, V. W.-W. Chem. Eur. J. 2005, 11, 1647–1657.
(c) Chang, X.; Lee, K.-E.; Il Jeon, S.; Kim, Y.-J.; Lee, H. K.; Lee, S. W. Dalton Trans. 2005, 3722–3731.

(24) Chanda, N.; Sharp, P. R. Organometallics 2007, 26, 3368–3373.
(25) Ghosh, S.; Chakrabarty, R.; Mukherjee, P. S. Inorg. Chem. 2009, 48, 549–556.

(26) (a) Al-Resayes, S. I.; Hitchcock, P. B.; Nixon, J. F.; Mingos, D. M. P. J. Chem. Soc., Chem. Commun. **1985**, 365–366. (b) Stang, P. J.; Kowalski, M. H.; Schiavelli, M. D.; Longford, D. J. Am. Chem. Soc. **1989**, 111, 3347–3356.

(27) (a) Johnson, C. A.; Haley, M. M.; Rather, E.; Han, F.; Weakley, T. J. R. Organometallics **2005**, 24, 1161–1172. (b) Arévalo, A.; Bernès, S.; García, J. J.; Maitlis, P. M. Organometallics **1999**, 18, 1680–1685. (c) Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Schaffner, S.; Shardlow, E. J. Dalton Trans. **2005**, 234–235. (d) Crisp, M. G.; Tiekink, E. R. T.; Rendina, L. M. Inorg. Chem. **2003**, 42, 1057–1063. (28) (a) Nishio, M.; Hirota, M.; Umezawa, Y. The CH/ π interaction: Evidence, Nature, and Consequences; Wiley-VCH: New York, 1998. (b) Nishio, M.; Hirota, M. Tetrahedron **1989**, 45, 7201–7245. (c) Nishio, M.; Umezawa, Y.; Hirota, M.; Takeuchi, Y. Tetrahedron **1995**, 51, 8665–8701. (d) Desiraju, G. R. Acc. Chem. Res. **2002**, 35, 565–573. (e) Desiraju, G. R.; Steiner, T. The Weak Hydrogen Bond: In Structural Chemistry and Biology; Oxford University Press: New York, 1999.

(29) (a) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. Org. Lett. 2002, 4, 15–18. (b) Lehnherr, D.; Murray, A. H.; McDonald, R.; Ferguson, M. J.; Tykwinski, R. R. Chem. Eur. J. 2009, 15, 12580–12584. (c) Roesky, H. W.; Andruh, M. Coord. Chem. Rev. 2003, 236, 91–119. (d) Janiak, C. Dalton Trans. 2000, 3885–3896.

(30) Holmes, D.; Kumaraswamy, S.; Matzger, A. J.; Vollhardt, K. P. C. Chem. Eur. J. **1999**, *5*, 3399–3412.

(31) (a) Jorgensen, W. L.; Severance, D. L. J. Am. Chem. Soc. 1990, 112, 4768–4774. (b) Paliwal, S.; Geib, S.; Wilcox, C. S. J. Am. Chem. Soc. 1994, 116, 4497–4498. (c) McNelis, B. J.; Nathan, L. C.; Clark, C. J. J. Chem. Soc., Dalton Trans. 1999, 11, 1831–1834.

(32) (a) Ham, N. S.; Ruedenberg, K. J. Chem. Phys. 1956, 25, 13-26.
(b) Pariser, R. J. Chem. Phys. 1956, 24, 250-268. (c) Klessinger, M.; Michl, J. Excited States and Photochemistry of Organic Molecules; VCH: Weinheim, Germany, 1995.

(33) Hu, J.; Lin, R.; Yip, J. H. K.; Wong, K.-Y.; Ma, D.-L.; Vittal, J. J. Organometallics 2007, 26, 6533–6543.

(34) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. Orbital Interactions in Chemistry; Wiley-Interscience: New York, 1985.