proposal the photocatalytic activity strongly depends on the electronic nature of the amorphous matrix.[20]

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Synthesis, Electrochemistry, and Spectroscopy of Blue Platinum(II) Polyynes and Diynes**

Muhammed Younus, Anna Köhler, Stephane Cron, Nazia Chawdhury, Muna R. A. Al-Mandhary, Muhammad S. Khan, Jack Lewis, Nicholas J. Long, Richard H. Friend, and Paul R. Raithby*

Conjugated polymers continue to attract great interest because of their potential use as organic semiconductors in optoelectronic devices such as light-emitting diodes,[1] lasers,[2] photocells,[3, 4] and field-effect transistors.[5] Organometallic conjugated polymers such as transition metal σ-acetylide polymers[6] provide information on the photophysical processes that occur in organic conjugated polymers.[7] Organometallic polymers of general formula **A** can be modified by

$[-M(L)_n-C\equiv C-X-C\equiv C-]_\infty$ **A**

(M = Fe, Ru, Os, Ni, Pd, Pt; L = phosphane or arsane, X = aromatic spacer)

changing the metal, the auxiliary ligands, or the spacer.[8, 9] Most metal polyyne polymers characterized so far have large band gaps in the range of 2.4 – 3.2 eV,[8, 10, 11] which compare unfavorably with those of some new conjugated organic polymers (< 1 eV).[12, 13] These organic polymers were designed by using the concept[14] of alternating donor (electron-rich thiophene) and acceptor (electron-deficient thieno[3,4-*b*]pyrazine) units. With the aim of preparing a metal polyyne polymer with a band gap smaller than 2 eV, we synthesized a soluble donor – acceptor polymer in which an *n*-butylphosphane-substituted platinum(II) acetylene group acts as donor, and a thieno[3,4-*b*]pyrazine as acceptor.

The synthesis of the thieno[3,4-*b*]pyrazine ligand and of the platinum(II) polymer is summarized in Scheme 1. The compounds dibromo-5,7-diphenyl-2,3-thieno[3,4-*b*]pyrazine (**2**) and diphenyl-2,3-trimethylsilylethynyl-5,7-thieno[3,4-*b*]pyrazine (**3**) were prepared by literature methods.[15, 16] Treatment of **3** with four equivalents of K_2CO_3 afforded 2,3-ethynyl-5,7-thieno[3,4-*b*]pyrazine **4** as a brownish yellow, air- and light-sensitive solid in 75 % yield. The polymeric and dimeric

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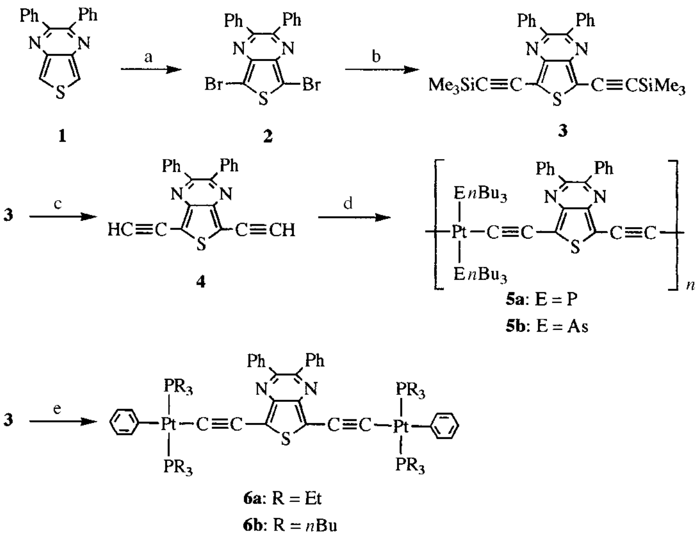

Scheme 1. Synthesis of **4**–**6**: a) *N*-bromosuccinimide, CH$_3$COOH, CHCl$_3$; b) Me$_3$SiC≡CH, CuI, Pd(OOCCH$_3$)$_2$, PPh$_3$, *i*Pr$_2$NH; c) K$_2$CO$_3$ (4 equiv), MeOH; d) *trans*-[PtCl$_2$(P*n*Bu$_3$)$_2$] or *trans*-[PtCl$_2$(As*n*Bu$_3$)$_2$], CuI, *i*Pr$_2$NH; e) e) 1) *n*Bu$_4$NF, THF, 2) *trans*-[PtCl(PR$_3$)$_2$(Ph)] (2 equiv), CuI, Et$_2$NH, CH$_2$Cl$_2$.

complexes of platinum were synthesized by classical condensation reactions between diterminal alkynes and platinum chlorides.[17] The reaction of freshly prepared diyne **4** with one equivalent of *trans*-[PtCl$_2$(P*n*Bu$_3$)$_2$] in the presence of CuI in diisopropylamine at 0 °C gave the deep blue polymer **5a** in 43 % yield. The average molecular weight of the polymer was determined by gel-permeation chromatography (GPC) to be 14006, which corresponds to an average value of $n = 15$. We were unable to prepare pure dimetallic complexes from **4** and two equivalents of *trans*-[PtCl$_2$(PEt$_3$)$_2$], as the reaction gave a mixture of oligomers which could not be separated. Therefore, **4** was treated with two equivalents each of *trans*-[PtCl(PEt$_3$)$_2$(Ph)] and *trans*-[Pt(P*n*Bu$_3$)$_2$Cl(Ph)], in which one coordination site is protected by a phenyl group, in CH$_2$Cl$_2$/Et$_2$NH in the presence of Cu^{I} at 20 °C to afford the pure platinum dimers **6a** and **6b** in about 70 % yield. The spectroscopic and analytical data are in accord with the proposed formulations of the new compounds. The metal complexes are all air-stable and soluble in common organic solvents. The reaction of one equivalent of *trans*-[PtCl$_2$(As*n*Bu$_3$)$_2$] with **4** gave **5b** in 40 % yield. The average molecular weight of this polymer was $M = 17375$ ($n = 17$) according to GPC.

The electrochemical properties of the ligand **3** and of the metal complexes were studied by cyclic voltammetry (Table 1). The ligand showed a reversible reduction wave, as was observed for analogous organic polymers.[12, 13] We attribute this to the reduction of the thieno[3,4-*b*]pyrazine unit. The metal complexes **6a** and **6b** show one quasi-reversible and two irreversible oxidation waves for the stepwise two-electron oxidation at the platinum center [Eq. (1)]. The reference

$$Pt^{2+} \rightarrow Pt^{3+} + e^- \rightarrow Pt^{4+} + 2\,e^- \qquad (1)$$

complex *trans*-[Pt(C≡C-*p*-C$_6$H$_4$C≡CH)(PEt$_3$)$_2$(Ph)] also shows an irreversible oxidation wave (at +0.77 V), and Sato et al. reported an irreversible anodic wave at +0.61 V for *trans*-[Pt(C$_6$H$_4$-*p*-CH$_3$)(C≡C-*p*-C$_6$H$_5$)(PPh$_3$)$_2$].[18]

Table 1. Absorption maxima λ_{max}, extiction coefficients ε, band gaps E_{gap}, and redox potentials of the ligand and platinum complexes.

Compd	λ_{max}[a] [nm] ($\lg\varepsilon$)	E_{gap} [eV][a] (in solid state)	$E_{1/2}$(ox)[b] [V]	$E_{1/2}$(red)[b] [V]
3	457 (3.91)	2.40 (2.36)	–	–1.61
5a	627 (4.11)	1.77 (1.72)	+0.21,[c] +1.03[c]	–
6a	583 (3.94)	1.83 (1.76)	+0.040 +0.67,[c] +0.92[c]	–1.71[c]
6b	585 (3.71)	1.82	+0.003 +0.65,[c] +0.94[c]	–

[a] In CH$_2$Cl$_2$. [b] 0.1 M [*n*Bu$_4$N][BF$_4$] in CH$_2$Cl$_2$, Pt electrode, scan rate 100 mV s^{-1}, Ag wire reference electrode. [c] Irreversible process. All electrode potentials are relative to that of ferrocene in the same system.

The absorption spectra of **2**, **3**, **5a**, and **6a** are shown in Figure 1. The position of band I is lowered significantly (by 0.7 eV) when the metal is introduced—that is, on going from **3** to **5a**—in accordance with our expectations for a donor–acceptor compound.[14] In contrast to similar compounds,[7, 10] there is hardly any further shift on going from the monomer **6a** to the polymer **5a**. Hence, the lowest excited state is confined to a single repeat unit.

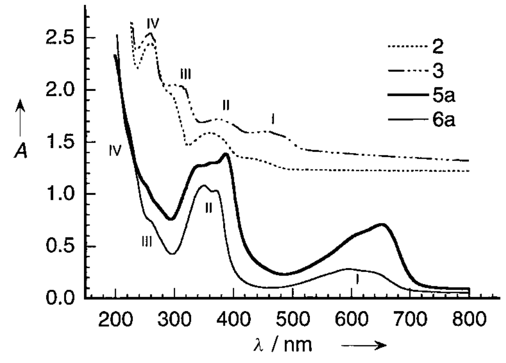

Figure 1. Absorption *A* of **2**, **3**, **5a**, and **6a**. The spectra have been scaled and shifted vertically for comparison and are not corrected for reflection. I–IV denote the different absorption bands.

The low band gap of **5a** allows the measurement of the photocurrent in a sandwich-type diode structure not only for excitation in absorption band I, but also for excitation in absorption bands II, III, and IV. We found that photoconductivity is associated with each of the higher energy absorption bands (Figure 2). In air, a photocurrent quantum yield of up to 1 % at 400 nm is attained, which is unusually high for single-layer sandwich diodes. This UV photoelectric behavior prompted analogous research on conjugated organic polymers.[19]

The photoluminescence spectra of **2**, **3**, and **5a** have very similar shapes, but the energetic position of the emission is

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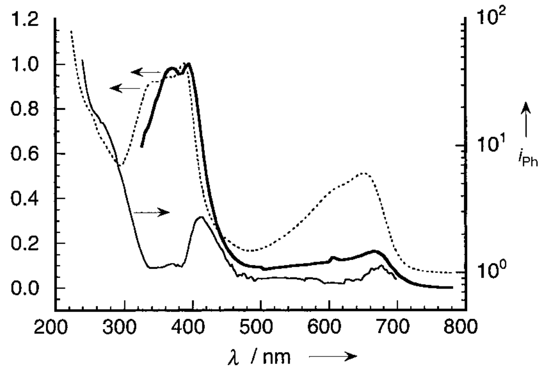

Figure 2. Absorption A of **5a** (dotted line) and photocurrent i_{Ph} (electrons per incident photon, corrected for the absorption of the electrode) of the Al/**5a**/indidum tin oxide photocell (thick line)and the Al/**5a**/Au photocell (thin line).

shifted (Figure 3). The peak at 695 nm in the emission spectrum of **3** disappears in dilute solution and can therefore be attributed to interchain interactions. From the similar form of the emission bands of ligand and polymer, we infer that the emission is mainly due to the π–π* transition of the conjugated ligand, although the energy levels of the orbitals involved are shifted by strong interaction with the metal center.

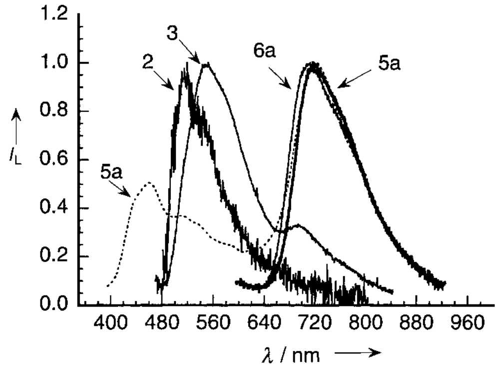

Figure 3. Photoluminescence spectra of **2**, **3**, **5a**, and **6a**, normalized to unity at the emission maxima. The excitation wavelength was 457 nm for **2** and **3**, 514 nm for **5a** (thick solid line) and **6a**, and 334–365 nm for **5a** (dotted line, smoothed data).

The low energy level of **5a** allows excitation in absorption band II. An additional high-energy emission at 460 nm is observed (Figure 3). Emission from higher excited states is unusual for most molecules, but well known for azulene and its derivatives.[20] For azulene, this is attributed to the large energy gap of about 1.5 eV between the S_2 and S_1 excited states.[20] Polymer **5a** also has a large S_2–S_1 gap of 1.3 eV and contains a similarly extended conjugated chromophore unit in the bridging ligand.

The low-energy emission of **5a** and **6a** at 715 nm is atypical for polymers of structure **A**. Polymers and monomers with other spacers X typically show a fine structure in the emission spectrum that is already evident at 20 °C[21] and particularly pronounced at low temperatures.[8–11, 22] In **5a** and **6a**, the only remnant of such a structure is very weak shoulder around 775 nm. Compounds with structure **A** also typically exhibit a strong emission from a triplet excited state due to strong spin–orbit coupling induced by the metal center.[9–11, 21] Such a triplet emission was not observed here.

Experimental Section

5a: To a solution of *trans*-[$PtCl_2(PnBu_3)_2$] (0.134 g, 2 mmol) in diisopropylamine (60 mL) at 0 °C were added CuI (3 mg) and freshly prepared **4** (0.67 g, 0.2 mmol). The solution was stirred for 3 h at 0 °C and then allowed to warm to 20 °C. Afterwards, it was stirred for a further 2 h at 20 °C. The color of the solution gradually changed from yellow to deep blue. The solvent was removed. The blue solid was dissolved in dichloromethane and passed through a short silica column first with dichloromethane and then with dichloromethane/ether (1/1). The first fraction (eluted with dichloromethane) was a mixture of polymer, oligomers, and platinum starting material which could not be separated. The second fraction was a solution of pure polymer. After removal of the solvent and washing with dry methanol, the blue polymer was obtained in 43 % yield. Complex **5b** was prepared analogously from **4** and *trans*-[$PtCl_2(AsBu_3)_2$].

6a: To a solution of **3** (0.096 g, 0.2 mmol) in dichloromethane (10 mL) was added a 1 M solution of nBu_4NF (0.4 mL, 0.4 mmol) in THF. The reaction mixture was stirred for 2 h. Desilylation of the acetylene was confirmed by IR spectroscopy and TLC (silica gel). To this solution were added diethylamine (10 mL), *trans*-[$PtCl(PEt_3)_2(Ph)$] (0.217 g, 0.4 mmol), and CuI (3 mg). The reaction mixture immediately changed from yellow to violet. It was stirred for another 4 h, in which time the color changed from violet to blue. The solvent was then removed, and the residue was purified by chromatography on a silica gel column with dichloromethane/hexane (2/1). The complex was obtained as blue solid (0.165 g, 61 %) after washing with methanol.

6b was prepared by same the procedure as **6a** by using *trans*-[$PtCl(PnBu_3)_2(Ph)$]. The product was obtained as a blue oil which took months to crystallize.

Selected spectroscopic data. **3:** FAB-MS: m/z: 480.2 [M^+] (calcd 480.1); IR (CH_2Cl_2): $\tilde{\nu} = 2138\ cm^{-1}$ (C≡C); ^1H NMR ($CDCl_3$, 250 Hz): $\delta = 0.31$ (s, 18 H, $(CH_3)_3Si$). **4:** FAB-MS: m/z: 333 [M^+] (calcd 336); IR (CH_2Cl_2): $\tilde{\nu} = 2098\ cm^{-1}$ (C≡C), 3298 cm^{-1} (≡CH); ^1H NMR ($CDCl_3$, 250 Hz): $\delta = 3.8$ (s, 2 H, CCH). **5a:** IR (CH_2Cl_2): $\tilde{\nu} = 2077\ cm^{-1}$(C≡C); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 250 Hz): $\delta = -137.8$ (s, PBu_3), $J_{Pt,P} = 2340$ Hz; elemental analysis calcd for $C_{46}H_{64}N_2P_2SPt$: C 59.16, H 6.91; found: C 58.65, H 6.85 %. **5b**: IR (CH_2Cl_2): $\tilde{\nu} = 2077\ cm^{-1}$ (C≡C); elemental analysis calcd for $C_{46}H_{64}N_2As_2SPt$: C 54.06, H 6.31; found: C 56.15, H 6.25. **6a:** FAB-MS: m/z: 1351.8 [M^+] (calcd 1351); IR (CH_2Cl_2): $\tilde{\nu}$ 2074 cm^{-1} (C≡C); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 250 Hz): $\delta = -131.13$ (s, PBu_3), $J_{Pt,P} = 2661$ Hz; elemental analysis calcd for $C_{58}H_{80}N_2P_4SPt_2$: C 51.55, H 5.92; found: C 51.68, H 5.44; **6b:** FAB-MS: m/z: 1483.5 [M^+] (calcd 1483.8); IR (CH_2Cl_2): $\tilde{\nu} = 2084\ cm^{-1}$ (C≡C); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 250 Hz) $\delta = -139.28$ (s, PBu_3), $J_{Pt,P} = 2659$ Hz; elemental analysis calcd for $C_{82}H_{128}N_2P_4SPt_2$: C, 58.36, H, 7.59; found: C 58.50, H 7.62.

Films for optical measurements were spin-coated or drop-cast from solution onto quartz substrates. Film thicknesses were typically 100–200 nm. Optical absorption was measured with a Perkin-Elmer λ-9 spectrometer. Excitation for the photoluminescence measurements was provided by the 457 nm, 514 nm or UV (334–365 nm) lines of an Ar^+ laser. The samples were measured under nitrogen atmosphere. Photocurrent measurements were performed in air with zero external electric field applied on sandwich-type Al/**5a**/indium tin oxide (ITO) and Al/**5a**/Au photocells with excitation through the ITO or semitransparent Au electrode. Excitation was provided by a 100-W tungsten lamp or a 150-W xenon arc lamp, respectively, dispersed by appropriate monochromators. The spectra are corrected for the spectral curve of the illuminating system and for the absorption of the ITO or Au electrode.

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Unprecedented Encapsulation of Carbonyl Guest with Designer Lewis Acid Receptor[**]

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Physical inclusion of small molecules can be commonly effected with zeolites, cyclodextrins, and synthetic macrocycles as host molecules.[1–6] The self-assembly of cavity-forming smaller subunits serves as another strategy to encapsulate guest molecules.[7] We report here a new encapsulation of guest substrates with a bowl-shaped Lewis acid host, aluminum tris(2,6-diphenylphenoxide) (ATPH),[8] based on the Lewis acid–base complex formation. The resulting Lewis acid capsules persist over timescales that are sufficient to enable chemical processes to take place within them. Therefore, they serve a double function, as substrate protector and accelerator, in selective organic transformations (Figure 1).

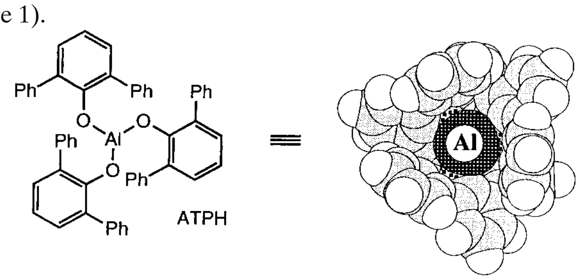

Figure 1. Space-filling model of aluminum tris(2,6-diphenylphenoxide) (ATPH) with an appropriate bowl-shaped cavity for guest molecules.

The Lewis acid receptor ATPH and its congeners self-assemble with a dicarbonyl guest molecule in organic solvents to form a dimeric capsule. The X-ray crystal structure of such a complex with 1,4-dimethylpiperazine-2,5-dione as a model guest is shown in Figure 2.[9, 10] Intermolecular coordinative

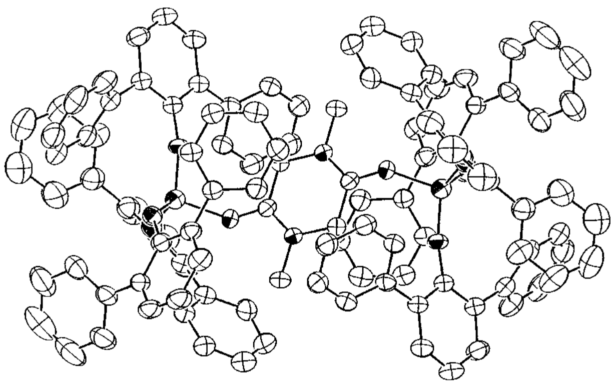

Figure 2. ORTEP diagram of the molecular capsule of ATPH and 1,4-dimethylpiperazine-2,5-dione through coordinative bonding. The solvent molecules (CH_2Cl_2) and all hydrogen atoms are omitted for clarity.

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